Impact of Low Temperature Electrical Resistance Heating on Subsurface Flow and Mass Transport

by

Magdalena Maria Krol

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Civil Engineering
University of Toronto

Copyright © 2011 by Magdalena Maria Krol
Abstract

Impact of Low Temperature Electrical Resistance Heating on Subsurface Flow and Mass Transport

Magdalena Maria Krol
Doctor of Philosophy
Graduate Department of Civil Engineering
University of Toronto
2011

This thesis examined the effect of sub-boiling temperatures on subsurface flow and mass transport, as a result of electrical resistance heating (ERH). Low temperature ERH was simulated using a newly developed two-dimensional, electro-thermal, flow and transport model (ETM). To capture the non-isothermal processes in the subsurface during low temperature ERH, the ETM included temperature dependent equations for density, viscosity, and electrical conductivity. The model was validated with laboratory experiments in which voltage distribution, instantaneous power, temperature, and tracer transport were measured. Both the tracer experiments and the simulation results indicated that flow and contaminant movement could be significantly impacted by low temperature ERH due to temperature induced buoyant flow.

In the first part of the thesis, the ETM was used to study the onset of buoyant flow in the subsurface and its effect on contaminant transport. Buoyant flow was predicted to occur when the ratio between the Rayleigh and thermal Peclet numbers (buoyancy ratio), was greater than 1. The buoyancy ratio was expressed in terms of subsurface temperature, thermal expansion coefficient and hydraulic gradient, thus facilitating its application to subsurface thermal activities. The effect of buoyant flow on contaminant transport was found to be dependent on the buoyancy ratio and Rayleigh number.

The second part of the thesis examined the effect of soil heterogeneity, electrical conductivity and applied groundwater flux on energy and mass transport. The impact of
these factors was evaluated using the ANOVA analysis. To examine soil heterogeneity effects, random permeability fields for two aquifers with varying levels of heterogeneity were generated. Higher soil electrical conductivity values increased the power dissipated and resulted in shorter heating times and quicker onset of buoyant flow. Consequently, electrical conductivity had a statistically significant effect on the subsurface energy distribution. The applied groundwater flux had a strong effect on heat and mass transport with lower velocities resulting in upward plume movement due to buoyancy effects. In addition, buoyant flow was observed to dominate over flow through high permeability zones.

The last chapter of the thesis investigated the formation and movement of discrete gas bubbles during ERH by combining ETM with a macroscopic invasion percolation (MIP) model. The model simulated soils with different permeabilities and entry pressures at various operating temperatures and groundwater velocities. It was observed that discrete bubble formation occurred in all soils, with upward mobility being limited by lower temperatures and higher entry pressures. By including the MIP model, the resulting aqueous concentrations were significantly different from results obtained with a conventional advective-dispersive model, especially in high permeability soils. This was due to bubbles moving to cooler areas, collapsing, and contaminating previously clean zones. This cooling effect also let to possible non aqueous phase liquid (NAPL) formation.

The results of this thesis demonstrated that sub-boiling temperatures affect subsurface flow and mass transport, especially when temperature-induced buoyant flow occurred. Although this study focused on ERH applications, the results may be applicable to other subsurface thermal activities such as geothermal heating.
Dedication

To my mother who introduced me to the world of research, and to my father who showed me the beauty of mathematics. I would not have embarked, or finished, this journey without their constant support and encouragement.
Acknowledgements

I have had the good fortune to have a supervisor who is not only an esteemed researcher but also a considerate and kind individual. Dr. Brent Sleep has provided me with continual support, feedback, and guidance; his help is truly appreciated.

I would also like to thank Dr. Richard Johnson, from Oregon Health and Science University, for providing the necessary experimental data for this research. Dr. Johnson has also been extremely helpful in providing feedback on all aspects of this thesis.

Dr. Kevin Mumford, from Queen’s University, provided advice and insight into Chapter 5 while my committee members, Dr. Chris Kennedy, Dr. Bryan Karney, and Dr. Giovanni Grasselli, offered great recommendations and feedback throughout the entire process. I am very thankful for their help and support.

Over the course of my stay at the University of Toronto, I have had the pleasure of sharing an office with many wonderful people. These students have made the everyday memorable and for their friendship I am grateful: Adwoa Cobbina, Shannon Joseph, Brenna Enright, Jonathan Hunt, Pulin Mondal, Jessica Hernandez, Caitlin Sykes, Lesley Herstein, Daley Mikalson, Erica Pensini, Bruce Xu, and Alex Charpentier (the honorary GB418 member). A special thank you goes to Amalia Kokkinaki who provided invaluable insight, statistical clarifications, and much needed coffee breaks.

I would not have been able to finish this project without the help of my family. I am forever indebted to my mother, who would hop on a bus to tend to our kids during exams or looming deadlines, and to my father for being patient while I got frustrated with electrical theory. I would also like to thank my parents-in-law for their continual encouragement and support; and my children, Stefan and Amelia, for bringing balance to my life and for reminding me of what is really important.

Lastly, a huge thank you goes to my husband Martin, who offered encouragement during times of frustration, acted as a single parent during thesis writing, and provided emergency MATLAB and Latex help. I am truly lucky to have had his support and company throughout my studies.
Preface

This thesis has been prepared as four separate journal papers. Chapters 2 and 5 have been submitted to academic journals and are co-authored. The original contributions made by each author are listed below:

Chapter 2

Title: Impact of low temperature electrical resistance heating on subsurface flow and transport
Authors: Magdalena M. Krol, Brent E. Sleep and Richard L. Johnson
Submitted to: Water Resources Research

The two-dimensional electro-thermal numerical model was developed by M. M. Krol. The small and large tank experiments were conducted at the Oregon Health and Science University by R. L. Johnson. Fitting of the experimental data was conducted by M. M. Krol. Modelling of tracer tests using MT3DMS was done by B. E. Sleep with velocity fields generated by M. M. Krol using the electro-thermal model. Interpretations of the results was performed by M. M. Krol with consultation with B. E. Sleep and R. L Johnson. The text was written by M. M. Krol and edited by B. E. Sleep and R. L. Johnson.

Chapter 5

Title: Modeling discrete gas bubble formation and mobilization during subsurface heating of contaminated zones
Authors: Magdalena M. Krol, Kevin G. Mumford, Brent E. Sleep and Richard L. Johnson
Submitted to: Advances in Water Resources

The two-dimensional electro-thermal numerical model was augmented with a macroscopic invasion percolation model (MIP) by M. M. Krol. The original MIP model was developed by K. G. Mumford and modified for non isothermal conditions by M. M. Krol in consultation with B. E. Sleep and K. G. Mumford. The numerical simulations were performed by M. M. Krol. Interpretations of the results was performed by M. M. Krol with consultation with B. E. Sleep and K. G. Mumford. The text was written by M. M. Krol and edited by B. E. Sleep, K. G. Mumford and R. L. Johnson.
## Contents

1 Introduction ................................................................................. 1
   1.1 Problem Scope ................................................................. 1
   1.2 Low Temperature Electrical Resistance Heating .................... 2
   1.3 Approach ........................................................................ 3
   1.4 Research Objectives .......................................................... 4
   1.5 Thesis Overview ................................................................. 5

2 Low Temperature ERH and Subsurface Flow and Transport ......... 7
   2.1 Introduction .................................................................... 8
   2.2 Theory ........................................................................... 10
      2.2.1 Temperature Dependent Properties .............................. 11
   2.3 Materials and Methods ........................................................ 13
      2.3.1 Small Tank Experiment .............................................. 13
      2.3.2 Large Tank Experiment ............................................. 14
      2.3.3 Numerical Approach ............................................... 15
   2.4 Results and Discussion ....................................................... 17
      2.4.1 Voltage and Power .................................................... 17
      2.4.2 Temperature ............................................................ 18
      2.4.3 Tracer Study ............................................................ 19
   2.5 Conclusions/Implications ..................................................... 22

3 Impacts of Subsurface Heating on Buoyant Flow and Contaminant Transport as Characterized by Dimensionless Numbers .... 23
   3.1 Introduction .................................................................... 24
   3.2 Electro-Thermal Model ........................................................ 25
   3.3 Dimensionless Numbers ..................................................... 26
3.4 Simulation Description .................................................. 30
3.5 Results and Discussion .................................................. 32
  3.5.1 Buoyancy Ratio ..................................................... 32
  3.5.2 Effect of Buoyancy on Contaminant Transport ................. 34
3.6 Conclusions and Implications ......................................... 36

4 Influence of Soil Heterogeneity on Energy and Mass Transport 38
  4.1 Introduction .......................................................... 38
  4.2 Electro-Thermal Model ............................................... 41
  4.3 Statistical Approach ................................................ 41
    4.3.1 Factors Considered ............................................ 41
    4.3.2 Parameters of Heat and Mass Transport ...................... 42
    4.3.3 Analysis of Variance .......................................... 44
  4.4 Simulation Description .............................................. 46
  4.5 Simulation Results .................................................. 47
    4.5.1 Variance of Soil Permeability ................................ 47
    4.5.2 One-Factor ANOVA .............................................. 49
    4.5.3 Two-Factor ANOVA ............................................. 54
  4.6 Discussion ........................................................... 57
    4.6.1 Effect of Soil Heterogeneity on Mass and Heat Distribution.. 57
    4.6.2 Effect of Electrical Conductivity on Mass and Heat Distribution. 58
    4.6.3 Effect of Applied Groundwater Flux on Mass and Heat Distribution 59
  4.7 Conclusions/Implications .......................................... 61

5 Discrete Gas Bubble Formation and Mobilization during ERH 62
  5.1 Introduction ........................................................ 62
  5.2 Conceptual Model ................................................... 64
    5.2.1 ETM - MIP Model ............................................... 65
    5.2.2 Equilibrium Equations ........................................ 65
    5.2.3 Macroscopic Invasion Percolation Model .................... 67
  5.3 Simulation Description .............................................. 71
  5.4 Simulation Results ................................................ 73
    5.4.1 Case 1 - Simulation of #25 Ottawa Sand .................... 74
    5.4.2 Case 2 - Simulation of #50 Ottawa Sand .................... 75
5.4.3 Case 3 - Simulation of #75 Ottawa Sand ........................................... 78
5.5 Discussion ........................................................................................................ 81
  5.5.1 Entry Pressure .............................................................................................. 81
  5.5.2 Groundwater Velocity .................................................................................. 82
  5.5.3 Solubility Limit and Mass Removal ............................................................... 83
5.6 Conclusions/Implications .................................................................................. 87

6 Conclusions and Recommendations ..................................................................... 88
  6.1 Overall Conclusions ........................................................................................ 88
  6.2 Contributions ................................................................................................... 90
  6.3 Future Work ...................................................................................................... 91

A ERH Background Theory ...................................................................................... 106
  A.1 ERH Process and Governing Equations ............................................................ 106
  A.2 Power Calculations .......................................................................................... 110
    A.2.1 Method 1: Time Stepping ............................................................................ 111
    A.2.2 Method 2: Complex Numbers .................................................................... 112
    A.2.3 Method 3: RMS Values .............................................................................. 113

B Model Validation .................................................................................................. 115
  B.1 One Dimensional Voltage and Power Measurements ....................................... 115
  B.2 One Dimensional Heat Measurements ................................................................ 116

C Model Flowcharts .................................................................................................. 120
List of Figures

2.1 Schematic drawing of the small tank (cross section) ........................................ 14
2.2 Schematic drawing of the large tank (cross section) ........................................ 14
2.3 Voltage distribution in large tank: (a) initial experimental voltage; (b) initial predicted voltage; (c) final experimental voltage; (d) final predicted voltage .......................................................... 18
2.4 Experimental and predicted power for: (a) large tank (b) small tank ................. 19
2.5 Comparison of experimental and predicted temperature distributions in the small tank (red circles indicate electrode positions): (a) experiment, 1.5 hours; (b) model, 1.5 hours (c) experiment, 3 hours; (d) model, 3 hours 20
2.6 Small tank experimental tracer results for: (a) isothermal model, 1.5 hours (b) isothermal model, 3 hours (c) experiment, 1.5 hours; (d) model, 1.5 hours; (e) experiment, 3 hours; (f) model, 3 hours (the colour bar corresponds to modelled tracer results) ............................................. 21
3.1 Representation of the System being Modelled .................................................... 27
3.2 Initial TCE aqueous concentration (mg/L) in a vertical cross-section of the subsurface; red circles represent electrodes ............................................................... 31
3.3 Temperature contours and streamlines (shown in purple) for different $Ra/Pe$ ratios. Maximum temperatures: (a) 20.3°C (b) 22.2°C (c) 37.3°C (d) 70°C 33
3.4 Velocity through the middle ($z = 15$) of the simulated domain (case e) ............ 33
3.5 Concentration contours and streamlines (shown in purple) for all cases, 200 days after heating to 80°C; the value in brackets corresponds to $Ra/Pe$ 35
4.1 Temperature contours and energy parameters used to quantify the movement and spread of the energy plume; mass parameters are calculated similarly. .......................................................... 43
4.2 Initial TCE aqueous concentration (mg/L) in a vertical slice of the subsurface; red circles represent electrodes

4.3 Estimate of variance for the centre or energy of the Borden Aquifer

4.4 Aquifer permeability distributions and corresponding streamlines

4.5 Concentration contours for Borden aquifer for different soil permeability realizations after 50 days of heating to 80°C; Case 4; Red circles represent electrode locations

4.6 Concentration contours for Swiss aquifer for different soil permeability realizations after 50 days of heating to 80°C; Case 4; Red circles represent electrode locations

4.7 Effect of electrical conductivity (x-axis) on (a) energy spread in X-direction (b) mass spread in X-direction (c) energy spread in Z-direction (d) mass spread in Z-direction (e) centre of energy in X-direction; (f) centre of mass in X-direction (g) centre of energy in Z-direction; (h) centre of mass in Z-direction; after 10 days of heating

4.8 Effect of applied groundwater flux (x-axis) on: (a) energy spread in X-direction (b) mass spread in X-direction (c) energy spread in Z-direction (d) mass spread in Z-direction (e) centre of energy in X-direction; (f) centre of mass in X-direction (g) centre of energy in Z-direction; (h) centre of mass in Z-direction

4.9 Maximum concentration after 10 days of heating with changing: (a) electrical conductivity (b) applied flux

4.10 Mean values of: (a) maximum concentration with changing groundwater flux (b) centre of energy in the Z direction with changing groundwater flux

4.11 Permeability contours and streamlines for Swiss aquifer (a) before heating (b) after 10 days of heating; case 4

5.1 Gas clusters before and after (a) expansion (b) mobilization and (c) fragmentation (hatched squares represent gas occupied grid blocks while white squares are fully water saturated blocks); adapted from Wagner et al. (1997)

5.2 Initial aqueous concentration (mg/L) in a vertical slice of the subsurface; red circles represent electrodes
5.3 Temperature distribution for #25 Ottawa sand after 30 minutes of heating (red circles represent electrodes). Temperature distribution in #50 and #75 Ottawa sands were similar. The hatched area in (a) represents the “heated zone”.

5.4 Gas saturations for different sands at 70°C, 80°C and 90°C, after approximately 9 min of heating.

5.5 Gas saturation in #25 Ottawa sand at different times during heating. Maximum subsurface temperatures are indicated in brackets.

5.6 Concentration contours for different sands at 70°C, 80°C and 90°C, after 30 minutes of heating (last contour represents the maximum contaminant level (MCL) for 1,1,1 TCA (0.2 mg/L)).

5.7 Concentration contours for different sands at 70°C, 80°C and 90°C, after 30 minutes of heating, gas phase not modelled (last contour represents MCL for 1,1,1 TCA (0.2 mg/L)).

5.8 Maximum gas bubble elevation at different temperature and groundwater velocities (elevation is measured from the top of the domain, representing the ground surface).

5.9 Concentration contours for the different sands at 70°C, 80°C and 90°C, after 30 minutes of heating, low groundwater velocity (last contour represents MCL for 1,1,1 TCA (0.2 mg/L)). Possible NAPL formation is seen in the 90°C scenario in (b) and (c), where the concentrations are above 1330 mg/L.

5.10 Mass outside the source zone ($M_o$ = initial mass = 0.0218 mol).

A.1 Typical Three Electrode ERH Layout.

A.2 Voltage Distribution with Time at Three Electrodes.

B.1 Geometry of Example Problem.

B.2 Approximation of Example Problem.

B.3 Comparison of Simulated and Analytical Voltage Distribution for 1D Voltage Example.

B.4 Comparison of Simulated and Analytical Power Distribution for 1D Voltage Example.

B.5 Comparison of a Plug Heat Example using the Electro-Thermal Model and the Ogata Banks Solution.
C.1 ETM Modules .................................................. 121
C.2 Electro-thermal model flowchart ............................. 122
C.3 Combined electro-thermal model and the macroscopic invasion percolation model flowchart (** see Figure C.4) ......................... 123
C.4 Macroscopic invasion percolation model flowchart (** see Figure C.3) .......... 124
## List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Properties of 2D Tanks and Simulation Parameters</td>
<td>17</td>
</tr>
<tr>
<td>3.1</td>
<td>Simulated Cases</td>
<td>31</td>
</tr>
<tr>
<td>3.2</td>
<td>Initial Properties</td>
<td>31</td>
</tr>
<tr>
<td>3.3</td>
<td>Dimensionless Numbers and Buoyancy Ratios of the Simulated Cases</td>
<td>36</td>
</tr>
<tr>
<td>4.1</td>
<td>Aquifer Properties and Simulation Parameters</td>
<td>47</td>
</tr>
<tr>
<td>4.2</td>
<td>Simulated Cases</td>
<td>47</td>
</tr>
<tr>
<td>4.3</td>
<td>P-values and Trends for One-factor ANOVA (at 10 days)</td>
<td>49</td>
</tr>
<tr>
<td>4.4</td>
<td>P-values for Two-factor ANOVA (at 10 days)</td>
<td>56</td>
</tr>
<tr>
<td>5.1</td>
<td>Simulation Scenarios</td>
<td>72</td>
</tr>
<tr>
<td>5.2</td>
<td>System Initial Conditions and Properties of 1,1,1 TCA</td>
<td>73</td>
</tr>
<tr>
<td>A.1</td>
<td>Temperature Dependent Properties</td>
<td>107</td>
</tr>
<tr>
<td>A.2</td>
<td>Governing Equation in the Electrical Model</td>
<td>108</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Problem Scope

A third of the world’s fresh water supply comes from groundwater found in aquifers (Statistics Canada, 2003). Groundwater recharges lakes, wetlands, and streams, and is an important source of water for agricultural and industrial activities. In Canada, nearly ten million people obtain their drinking water from aquifers and rely on groundwater for all their household needs (Government of Canada, 1995). Since aquifers are recharged by surface water, as well as through ground infiltration, any surface or subsurface contamination - from industrial spills, landfills, or agricultural activities - has the potential to reach aquifers and impact groundwater quality. If groundwater becomes contaminated, different remedial technologies can be employed to restore it to acceptable levels.

Traditional groundwater remediation technologies include: pump and treat methods, air sparging, soil vapour extraction (SVE), and surfactant flushing. In the 1990s, in-situ thermal treatments were identified as potential methods for cleaning up sites contaminated with organic pollutants (Buettner & Daily, 1995; U.S. EPA, 1997). Thermal technologies include steam or hot water injection, thermal conduction heating, radio frequency heating (RFH), and electrical resistance heating (ERH). All these technologies increase the subsurface temperature, resulting in an increase in contaminant volatility. Unlike steam or hot water injection, ERH, RFH and thermal conduction heating can heat up the soil regardless of its stratigraphy. Additionally, RFH and ERH are the only thermal technologies that can heat specific targeted locations. Lastly, ERH is less expensive to operate than RFH and can be used in both saturated and unsaturated soils (Davis, 1997). On account of these advantages, ERH is the most widely used thermal

1.2 Low Temperature Electrical Resistance Heating

ERH was originally developed in the 1970s to enhance subsurface oil recovery (McGee & Vermeulen, 2007; Buettner & Daily, 1995). In the 1990s, the Lawrence Livermore National Laboratory tested ERH as a potential remediation technology. Since then, ERH has been used at numerous contaminated sites, including those contaminated with non aqueous phase liquids (NAPL) (Buettner et al., 1992).

ERH is performed using 3 phase or 6 phase heating where a series of electrodes are placed in the soil in a hexagonal or triangular pattern and connected to an AC voltage source. The current generated between the electrodes is conducted through the subsurface and the resistance to the current is dissipated as heat (U.S. EPA, 1997; Vermeulen & McGee, 2000). The increase in temperature volatilizes the contaminants and generates steam which strips the contaminants from the subsurface (Davis, 1998; Beyke & Fleming, 2005). The resulting vapour, water and NAPL (if present) is collected through extraction wells and treated by conventional methods such as carbon adsorption, air stripping, or condensation (U.S. EPA, 2004).

In a typical ERH application, the aqueous phase within the soil is brought to its boiling point and the primary mass removal mechanism is volatilization and/or steam distillation. Hence, significant infrastructure is needed to manage and treat the fluids, and to deliver the needed power to increase the subsurface temperatures to boiling. High temperatures can also adversely impact secondary remediation techniques, such as bioremediation. Consequently, operating ERH at sub-boiling temperatures has been suggested as an alternative to traditional ERH applications.

Low temperature ERH, operated between 50°C and 90°C, would require less power and infrastructure and may also promote degradation due to increased microbial activity (Friis et al., 2007; Costanza & Pennell, 2007; Rossman et al., 2006; U.S. EPA, 2004; Sleep & McClure, 2001a,b). In addition, since boiling of immiscible mixtures occurs at temperatures below the boiling point of either water or the organic compound, low temperature ERH may still result in contaminant volatilization. However, unlike typical ERH applications, low temperature heating would be dominated by advection and dispersion processes rather than volatilization. Therefore, the effect of temperature on these transport processes must be considered in order to optimize remedial efforts.
1.3 Approach

The aim of this thesis is to examine the effect of low temperatures on subsurface flow and contaminant mass transport. Temperatures below water boiling levels (between 50°C and 90°C) are investigated to evaluate the feasibility of low temperature ERH. The results of this investigation can also be applied to ERH pre-heat and cool-down stages, geothermal heating, and other remedial activities such as hot water injection. The subsurface temperature during all these activities will be below water boiling levels.

To investigate the impact of low temperatures on flow and mass transport, several factors were investigated, including: buoyant flow; variable subsurface properties such as permeability, electrical conductivity and groundwater velocity; and discrete bubble formation.

**Buoyancy:** Increased subsurface temperatures decrease water density and viscosity resulting in fast, buoyant flow throughout the heated zone. Buoyancy effects are usually unimportant for typical ERH applications since volatilization is the main mass removal process. However, at sub-boiling temperatures, buoyant flow could either help or hinder remedial efforts.

Buoyancy effects have been well documented in briny or coastal aquifers. In these studies, buoyant flow occurred as a result of changes in groundwater solute concentration (Langevin & Guo, 2006; Konz et al., 2009). Convective water flow has also been observed in geothermal heating and hot water injection applications in high permeability soils (Diersch & Kolditz, 2002; Molson et al., 1992). These studies found that the movement of the thermal plume was influenced by the induced buoyancy. Research in the areas of heat transfer and fluid dynamics showed that the onset of buoyancy in porous media was dependent on the Rayleigh and thermal Peclet numbers, with smaller groundwater velocities resulting in more buoyant, convective groundwater movement (Prasad et al., 1988; Lai & Kulacki, 1991; Lai et al., 1990; Prasad & Kulacki, 1984). No studies have been conducted to examine buoyancy effects on groundwater movement and contaminant transport during thermal remediation activities.

**Heterogeneity:** Increased soil heterogeneity has been reported to cause plume spreading and changes in mass distribution (Dekker & Abriola, 2000; Sudicky et al., 1983; Kueper et al., 1989; Sleep & Sykes, 1993b; She & Sleep, 1999; Schincariol et al., 1997).
Similarly, the effect of soil heterogeneity on heat transfer was found to impact the size and movement of the heat plume, effect the heat transfer rate, and cause channeling of heat (Nield & Kuznetsov, 2000; Bridger & Allen, 2010; Buscheck et al., 1983; Hidalgo et al., 2009; Chen et al., 2002). Other variable subsurface properties that impact flow and heat transport include soil electrical conductivity and inlet groundwater velocity. Studies examining the effect of electrical conductivity on subsurface heating, observed that clay layers heated faster due to higher electrical conductivity values (Carrigan & Nitao, 2000; Butler & Knight, 1998). While no studies have examined the effect of groundwater velocity on mass transport during subsurface heating, groundwater velocity can impact the strength of buoyant flow, directly affecting mass distribution.

**Discrete Gas Formation:** Formation of discrete gas bubbles in the subsurface occurs if the total gas pressure overcomes the atmospheric or in-situ pressure. Since both the water vapour pressure and partial pressures of the contaminants contribute to the total gas pressure, the temperature required for gas formation can be below water boiling levels. Hence, the operation of ERH at low temperatures may result in the formation of discrete gas bubbles. If gas bubbles form, expand and mobilize above the heated zone, they can collapse upon reaching cooler temperatures and transfer gas phase mass into the aqueous phase. The formation and movement of gas bubbles above NAPL plumes were observed by Roy & Smith (2007); Mumford et al. (2008, 2009b,a) and Mumford et al. (2010). Gas clusters in contact with NAPL pools, expanded due to the partitioning of NAPL compound to the gas phase, then fragmented and mobilized (Roy & Smith, 2007). Mumford et al. (2010) showed that this discontinuous gas phase led to aqueous concentrations of NAPL constituent downgradient and above the source zone, due to partitioning of mass from the gas to aqueous phase. These concentrations were higher than expected using conventional models for NAPL dissolution. Studies by Roy & Smith (2007); Mumford et al. (2008, 2009b,a) and Mumford et al. (2010) suggest that bubble formation in heated contaminated zones is not only probable but can have a significant impact on subsurface aqueous concentration.

### 1.4 Research Objectives

In this thesis, the impact of low temperature ERH on subsurface contamination was examined. To achieve this goal, the following research objectives were developed:
1. Test the hypothesis that subsurface flow and mass transport is affected by low temperature ERH. This objective was addressed by developing a finite difference, electro-thermal model (ETM) capable of simulating subsurface heating by ERH, as well as temperature dependent fluid flow and mass transport (Chapter 2).

2. Determine the conditions for buoyant flow and its effects on contaminant transport. This objective was addressed by simulating scenarios where soils with different permeabilities and Darcy velocities were heated with ERH. Criteria were developed using Rayleigh and Peclet numbers to determine the onset of buoyant flow and its impact on contaminant transport (Chapter 3).

3. Determine the effect of soil heterogeneity on energy and mass distribution during low temperature heating. This objective was addressed by generating random fields of permeabilities for aquifers with varying levels of heterogeneity and performing statistical analyses. The effect of different electrical conductivities and groundwater flux values were also examined (Chapter 4).

4. Investigate if low temperature heating can produce a discontinuous gas phase and how this affects subsurface mass transport. This objective was addressed by modifying the ETM model to include a macroscopic invasion percolation model and simulating gas bubble expansion and mobilization (Chapter 5).

1.5 Thesis Overview

This thesis consists of four papers prepared for submission to academic journals which address the research objectives stated above. Each chapter includes an introduction and background section, and therefore background material on ERH and the electro-thermal model is repeated in Chapters 2-5. References to thesis chapters have been added, as appropriate.

Chapter 2 describes the developed 2D heat and transport model, including background theory, temperature dependent subsurface properties and the applied numerical approach. Model validation experiments performed at the Oregon Health and Science University are also described. The experimental results for voltage, power consumption, temperature distribution, and mass transport, along with the predicted values by the model, are presented. This chapter has been submitted to Water Resources Research.
Chapter 3 describes the simulations performed using the 2D model to study the effect of buoyant flow on contaminant transport. A relationship between temperature change and groundwater gradient is introduced that describes the onset of buoyant flow given site specific conditions. Criteria indicating the occurrence of buoyant flow and its impact on contaminant transport are described. This chapter has been submitted to *Ground Water*.

Chapter 4 addresses the impact of soil heterogeneity, groundwater flux and soil electrical conductivity on heat and mass distribution. The statistical analyses performed using random realizations of permeability for two aquifers are described. The outcome of one and two-factor ANOVA tests which assessed the significance of soil heterogeneity, inlet groundwater velocity, and soil electrical conductivity on mass and heat parameters are given. The factors that have a significant effect on heat and mass transport are discussed. This chapter will be submitted to *Journal of Contaminant Hydrology*.

Chapter 5 details the macroscopic invasion percolation (MIP) module which was incorporated into the 2D electro-thermal model. The formation, expansion and mobilization of discrete bubbles formed under low temperature subsurface heating are described. The effect of bubble formation on mass distribution under different soil and temperature conditions is discussed. This chapter was submitted to *Advances in Water Resources*.

Chapter 6 presents the overall conclusions, contributions, and recommendations for future work.

Appendix A includes a more detailed description of the governing equations of the ETM model. Appendix B describes the comparison of a one-dimensional model output with an analytical solution for power and voltage, and verifies the energy portion of the model with an Ogata-Banks solution. A schematic illustration of the model is given in Appendix C.
Chapter 2

Low Temperature ERH and Subsurface Flow and Transport

Abstract

Electrical resistance heating (ERH) is a remediation technology that produces subsurface heating by generating an electrical current between emplaced electrodes. Typically, ERH is applied to heat the subsurface to boiling temperatures, leading to volatilization of water and organics, allowing for the recovery of volatilized organics by vacuum extraction. In some applications it may be advantageous to limit ERH temperature to sub-boiling levels in order to reduce energy consumption and avoid uncontrolled vapour migration. At sub-boiling temperatures, decreases in water density and viscosity may have a significant effect on the flow field and contaminant transport and removal. To investigate these effects, a fully coupled, two-dimensional finite difference electro-thermal flow and transport model was developed. The model simulates fully-coupled electrical current flow, temperature dependent fluid flow and mass transport. The model incorporates temperature dependent equations for density, viscosity, diffusion coefficient and soil electrical conductivity, capturing the non isothermal processes dominant in the subsurface during the sub-boiling phase of thermal remediation. The model was validated with laboratory scale experiments in which voltage distribution, instantaneous power, temperature, and tracer transport were measured. The tracer experiments and modelling results indicated that temperature induced buoyant flow and contaminant movement could be significant when applying ERH in the subsurface.
2.1 Introduction

Electrical resistance heating (ERH) was developed by the petroleum industry to enhance subsurface oil recovery (Buettner & Daily, 1995). It was first tested as a potential remediation technology by the Lawrence Livermore National Laboratory and has since been used at numerous contaminated sites, including those contaminated with non-aqueous phase liquids (NAPLs). ERH has several advantages over other thermal methods: it can operate at temperatures below the boiling point of water; it can be applied in saturated conditions; it can deliver heat to a specific targeted location; and it is less limited by stratigraphy since it is not dependent on fluid injection (Davis, 1997; U.S. EPA, 2004; Buettner & Daily, 1995; Lawrence Livermore National Laboratory, 1994).

ERH is typically applied using an array of electrodes placed in the soil in a hexagonal or triangular pattern and connected to a three or six phase AC voltage source. Current flow between electrodes results in subsurface heating. The increase in temperature, increases the vapour pressures, solubility, and diffusion coefficients of the contaminants, and electrical conductivity of water, while lowering viscosity, density, and sorption coefficients (Looney & Falta, 2000; Boulding & Ginn, 2004).

Typical ERH applications for NAPL removal raise the subsurface temperature to the boiling point of the water-NAPL immiscible mixture. In this case, the primary mass removal is through volatilization and/or steam distillation where the contaminant vapours and fluids are collected and treated on-site (Davis, 1998; Beyke & Fleming, 2005). Therefore, ERH requires significant infrastructure to both manage and treat the fluids, as well as to deliver the needed power to increase the subsurface temperatures to the boiling point. In addition, the high temperatures can result in unfavorable conditions for secondary remediation techniques, such as bioremediation.

Operating ERH at sub-boiling temperatures may address these issues. Lower temperatures require less power and less infrastructure. Heating to lower temperatures may also enhance microbial activity or promote abiotic degradation, further enhancing remediation (Friis et al., 2007; Costanza & Pennell, 2007; Rossman et al., 2006; U.S. EPA, 2004). In addition, low temperature ERH may still take advantage of less aggressive stripping since boiling of immiscible mixtures occurs at a temperature below the boiling point of either water or the organic compound; sometimes referred to as the heteroazeotropic boiling point, as it relates to immiscible liquids (Kiva et al., 2003). This boiling point is the temperature required to bring the total vapor pressures of the mixture to atmo-
spheric, or in situ pressure, and is less than the boiling point of water or of the individual compounds.

To date, ERH literature has focused on high temperature applications (Hiebert et al., 1989, 1986; McGee & Vermeulen, 2007; Vinsome et al., 1994; Carrigan & Nitao, 2000; Buettner & Daily, 1995). In most of these studies there was no consideration of water flow (Hiebert et al., 1986; McGee & Vermeulen, 2007; Vinsome et al., 1994) and only the temperature dependence of the organic phase viscosity was included. Carrigan & Nitao (2000) and Hiebert et al. (1989) considered fluid transport while modelling ERH heating, but dependent properties such as fluid density or viscosity were not examined and buoyancy effects were ignored in part because mass removal in these cases was through volatilization. However, mass removal and transport at low temperatures will be dominated by advection, dispersion, desorption and biological/chemical reactions. All these mechanisms are temperature dependent, therefore understanding the effect of temperature on these processes is necessary to optimize remedial efforts.

Buoyancy effects have been well documented in briny or coastal aquifers by Langevin & Guo (2006) and Konz et al. (2009), where buoyancy effects are due to changes in groundwater solute concentration. In addition, Diersch & Kolditz (2002) examined the effect of variable density due to geothermal heating, where convective water flow was seen in regions of high permeability. Density effects were also examined by Molson et al. (1992) who developed a finite element model for energy transport after hot water injection into a shallow unconfined aquifer. Temperature dependent density and viscosity of water were considered in this study and the movement of the thermal plume was influenced by the induced buoyancy.

Few studies have looked at buoyancy effects on groundwater movement as it pertains to ERH and contaminant remediation. O’Carroll & Sleep (2007, 2009) examined the effect of temperature on interfacial tension and viscosity during hot water flushing, showing that heat can have a significant impact on contaminant removal. However, changes in groundwater hydraulics and contaminant transport due to buoyant flow were not examined.

This chapter presents a two dimensional (2D) electro-thermal model for low temperature ERH that simulates fully coupled electrical current flow, heat transport, water flow, and solute transport. This study explores the effect of low temperature heating on subsurface hydraulics and solute transport in the context of soil and groundwater remediation. The model incorporates several temperature dependent parameters including...
density, viscosity, electrical conductivity, and diffusion coefficient. The model is validated with two 2D lab scale experiments, predicting power consumption, voltage, temperature distribution, and mass transport through the system.

2.2 Theory

Modelling of ERH is based on Ohm’s Law which relates the current density \( J \), to the electric potential \( V \) and electrical conductivity of the medium \( \sigma \). Electromagnetic effects are neglected since ERH is operated at low frequencies (60 Hz) resulting in quasi-static electric fields. Therefore currents associated with time varying magnetic fields are considered negligible (Hiebert, 1987).

Ohm’s Law states:

\[
\vec{J} = -\sigma \nabla V
\]  

(2.1)

Using conservation of electric charge and allowing for a spatially variable electrical conductivity, due to temperature dependence, Equation (2.1) becomes:

\[
\nabla \cdot (\sigma \nabla V) = Q
\]  

(2.2)

where \( Q \) represents sinks and sources of electric charge, and is non-zero only at the electrodes. Since ERH uses alternating current, the electrode potential is a function of time resulting in a phase-shifted voltage distribution:

\[
V = V_o \cos(\omega t + \varphi)
\]  

(2.3)

where \( V_o \) is the voltage amplitude, \( \omega \) is the angular frequency, and \( \varphi \) is the phase angle. The power dissipated can be calculated by either averaging the value through a power cycle, treating the voltage as a phasor quantity, or separating the electrode voltages into separate, single-phase solutions as described by Carrigan & Nitao (2000). The electro-thermal model in this study uses phasors to calculate the voltage distribution, as described by Hiebert \textit{et al.} (1986, 1989) and McGee & Vermeulen (2007):

\[
V = V_1 \cos(\omega t) + V_2 \sin(\omega t) = V_1 + jV_2
\]  

(2.4)

where \( V_1 \) and \( V_2 \) correspond to the real and imaginary roots of the voltage (rms), respec-
The power dissipation in the subsurface \((U)\) is determined using Equation 2.5 and used in the energy equation (Eq. 2.6) to obtain the subsurface temperature distribution.

\[
U = \sigma |\nabla V|^2
\] (2.5)

\[
\frac{\partial}{\partial t} \left[ \rho_w \phi c_w T + (1 - \phi) \rho_b c T \right] + c_w \rho_w \nabla \cdot [\bar{q} T] - K_H \nabla^2 T - U = 0
\] (2.6)

where \(T\) is the temperature, \(\rho_w\) is the density of water, \(\phi\) is soil porosity, \(\rho_b\) is the bulk density of the soil, \(c\) is the heat capacity of the soil, \(c_w\) is the heat capacity of water, \(\bar{q}\) is the Darcy velocity vector, and \(K_H\) is the bulk thermal conductivity.

Mass transport in the system is calculated taking into account advection and dispersion (Sleep & Sykes, 1993a):

\[
\frac{\partial}{\partial t} \left[ \rho_w \phi C \right] + \nabla \cdot [\rho_w C \bar{q}] + \nabla \cdot \left[ \phi J_D^D \right] = 0
\] (2.7)

where \(C\) is the mass fraction of the contaminant and \(J^D\) is the dispersive flux vector.

Since fluid density changes with temperature, the Darcy velocity is written in terms of an equivalent freshwater head \((h_f)\), which is defined as (Frind, 1982):

\[
h_f = \frac{P}{\rho_f g} + z
\] (2.8)

where \(\rho_f\) is the freshwater density (taken to be the density at ambient temperature), while \(\rho\) is the density of the fluid at the current temperature. This leads to a form of Darcy’s Law for systems with varying densities:

\[
\bar{q} = -\frac{k g \rho_f}{\mu} \left[ \nabla h_f + \rho_r \nabla z \right]
\] (2.9)

where \(\rho_r\) is the density coefficient \((\rho - \rho_f) / \rho_f\), \(k\) is the soil permeability and \(\mu\) is the water viscosity. Similar procedures have been used by others when modelling density driven flow in briny aquifers (Langevin & Guo, 2006), deep aquifer systems (Bachu, 1995), and gas transport (Sleep & Sykes, 1989).

### 2.2.1 Temperature Dependent Properties

Several parameters in Equations (2.1) to (2.9) are temperature dependent, therefore appropriate relationships are included in the electro-thermal model. Electrical conduction

...
in clean sands is largely due to ionic conduction through the bulk pore fluid (Sen et al., 1988; Butler & Knight, 1998; Sen & Goode, 1992; Shang & Rowe, 2003; Friedman, 2005) and can be described using Archie’s Law (Archie, 1942), while less permeable soils need to take into account the presence of clay particles (Butler & Knight, 1998; Sen et al., 1988; Waxman & Smits, 1968). For both types of soils, the electrical conductivity of the subsurface depends on the fluid electrical conductivity ($\sigma_w$), which is temperature dependent, as described by Arps (1953):

$$\sigma_{w2} = \sigma_{w1} \frac{T_2 + 21.5}{T_1 + 21.5}$$

(2.10)

where $\sigma_{w1}$ corresponds to a water electrical conductivity at a reference temperature $T_1$.

Liquid viscosity decreases with increased temperature. There are many approximations to this relationship including the Andrade equation (Poling et al., 2001) and the Lewis-Squires method (Poling et al., 2001). In this study, the relationship described by the Van Velzen, Cardozo and Langenkamp Method (Reid et al., 1977) is used:

$$\log(\mu) = \beta_\mu \left[ \frac{1}{T} + \frac{1}{\tau_o} \right]$$

(2.11)

where $\beta_\mu$ and $\tau_o$ are the viscosity temperature dependence parameters (Munson, 2002).

Liquid densities depend on pressure and temperature. As the temperature increases, the density of the fluid decreases and can be approximated using polynomial interpolation functions (Yang & Edwards, 2000) or using the following linear relationship (Gebhart et al., 1988):

$$\rho = \rho_0 [1 + \alpha(P - P_0)] [1 + \beta(T - T_0)]$$

(2.12)

where $\rho$ is the liquid density, $\rho_0$ is the reference density at a reference temperature $T_0$ and reference pressure $P_0$, $T$ is the temperature, $P$ is the pressure, $\alpha$ is the pressure coefficient, and $\beta$ is the thermal expansion coefficient. In the electro-thermal model, the pressure differences were assumed negligible.

The aqueous molecular diffusion coefficient was calculated from a ratio of viscosities as follows (Reid et al., 1977):

$$\frac{D_d}{(D_d)^{ref}} = \left( \frac{\mu_w}{\mu_{w,ref}} \right)^{-1.14}$$

(2.13)
where $\mu_{w}^{ref}$ is the reference water viscosity and $D_{d}^{ref}$ is the reference diffusion coefficient, both taken at the ambient temperature.

## 2.3 Materials and Methods

### 2.3.1 Small Tank Experiment

To study transport processes in the subsurface during heating, an experiment was conducted in a small (60 cm long, 45 cm tall and 1 cm thick, Figure 2.1) polycarbonate tank at the Oregon Health & Science University (OHSU) using single phase ERH. The experiment focused on the movement of groundwater during subsurface heating. The tank was packed with 0.5 mm glass beads with a hydraulic conductivity of approximately 0.3 cm/s. Groundwater was injected at a rate of 5 cm$^3$/min using a multi-channel peristaltic pump with five injection and 5 extraction wells. The tank included two columns of 6 electrodes. The first column was connected to a 120 V AC power source while the other six electrodes were attached to neutral. To increase the electrical conductivity of the system, a 2 g/L sodium sulfate solution was used as groundwater. The temperature data were collected through 48 thermocouples that surrounded the heated zone. Temperature and AC current measurements were recorded using Labview® and a Measurement Computing® data acquisition board. The same system was used to control temperature during the experiment. Four of the thermocouples, located 2-3 cm from the electrodes, were used to maintain temperature at the target value. Before the start of the experiment, the tank was fully water saturated.

A preliminary isothermal experiment using Rhodamine WT was conducted in the small tank to serve as a comparison to the non isothermal experiments. In the second experiment, the temperature was increased initially to 30°C and maintained for 36 minutes, after which the temperature was increased to 50°C. To examine the hydraulics of the heated system, Rhodamine WT was injected at a rate of 0.03 cm$^3$/min into 5 injection ports once the temperature reached 50°C, approximately 2 hours after the start of the experiment. The tracer was injected for 140 minutes. Images of the tracer were captured using a Nikon D90 camera interfaced to a computer, for time-lapse image capture. During the experiment the ambient temperature remained relatively constant at 21.2 ± 1.2°C. The experiment lasted 8 hours and 45 minutes. The photographs were post-processed with Labview® to highlight distribution of the tracer.
### 2.3.2 Large Tank Experiment

A second experiment was conducted in a large tank that was 1.2 m tall by 2.4 m long and 0.15 m thick (Figure 2.2). The tank walls were made of polycarbonate, and the tank was filled with medium silica sand at the top with 0.3 m of a mixture of sand and illite clay at the bottom. Groundwater was injected into a fully-screened well at the inlet end of the tank using a constant-rate ceramic-piston pump and a constant-head reservoir was used at the effluent end. Darcy velocity was maintained at $8.7 \times 10^{-5}$ m/s and the injected water had a concentration of 1.2 g/L of sodium sulfate. Temperature and voltage were monitored at 70 locations using a data acquisition and control system similar to that used in the small tank. Nine electrodes were placed in the clay layer and the two outer columns were connected to a 110 V AC power source while the three center electrodes were connected to the neutral lead. Once again, temperature was controlled by monitoring thermocouples located close to the electrodes.
2.3.3 Numerical Approach

The electro-thermal model equations were discretized using block-centered implicit finite differences. At the beginning of each time step the voltage distribution was calculated using Equation (2.2), with electrode voltages applied as source terms and electrical conductivities calculated using temperatures from the previous time step. The boundaries were assumed to be insulated with respect to current flow. Following calculation of the electric field, the power dissipation was calculated using Equation (2.5). The groundwater flow equation given by Equation (2.9) was then solved for hydraulic head and Darcy velocity, with temperature dependent fluid density and viscosity calculated using temperatures from the previous time step.

As the heat and flow equations are coupled through the temperature dependence of water properties, an iterative approach was used. Given the Darcy velocities and heat transfer coefficients, the heat equation (2.6), was solved for temperature. The solution of the water flow and heat transport equations was then repeated iteratively, using the updated values of temperature dependent (viscosity, density) parameters from the current time step (implicit formulation) to calculate new fluid properties. This was performed until an absolute convergence criteria of $1 \times 10^{-6}$ for temperature was achieved. The obtained Darcy velocities and temperatures were then used to calculate mass transfer coefficients (dispersion coefficient) and the mass transport equation (2.7) was solved for solute mass fractions. Parameters that changed spatially were averaged between grid blocks, using the harmonic mean value. These parameters included the hydraulic conductivity, electrical conductivity and thermal conductivity. The model was capable of applying upstream or midpoint weighting methods for the solution of the advective-dispersive equation.

The heat transport boundary conditions for simulating the tank experiments were zero flux (Type II) for the top and bottom of the system, while a known energy flux was specified at the inlet. Since all experiments were performed in uninsulated polycarbonate tanks, there were heat losses across the tank walls. These were modelled by calculating the amount of energy required to heat the polycarbonate walls as well as the heat loss through an air buffer zone outside the tank. At each node, a heat sink term was added to account for the energy required to heat the wall:

$$U_{wall} = \frac{2c_w(T^t - T^{t-1})}{t}$$  \hspace{1cm} (2.14)
where \( c_w \) is the volumetric heat capacity of the wall, and \( T^t \) and \( T^{t-1} \) are the wall temperatures at time steps \( t \) and \( t - 1 \).

The heat loss term for the conduction across the air layer was calculated using:

\[
U_{\text{air}} = \frac{2K_{\text{Hair}}(T^t - T_{\text{ref}})}{d \cdot \Delta y}
\]  

(2.15)

where \( d \) is the air buffer layer thickness, \( T_{\text{ref}} \) is the ambient temperature outside the tank, \( \Delta y \) is the thickness of the tank, and \( K_{\text{Hair}} \) is the thermal conductivity of air. The air buffer layer thickness was changed until the pearson product correlation coefficient (PMCC) during the heating portion of the experiment was maximized and the temperature distribution was comparable to the experimental data. This resulted in an air buffer thickness of 2 mm. The same heat loss terms were used for both the large and small tank simulations. Both loss terms were multiplied by a factor of two to account for the two sides of the tank and the losses at the top and bottom of the tank were considered negligible.

The boundary conditions for flow and mass transport in both the large and small tanks were zero flux for the top and bottom of the system. The injection and extraction wells in the small tank were modelled as sources and sinks, respectfully, while the large tank assumed a constant flow inlet and constant head outlet boundary condition. The tracer injection wells in the small tank were modelled as sources. The linear equations for the discretized current, groundwater flow, heat transport, and mass transport were evaluated using the backslash (\) operation in MATLAB which uses appropriate algorithms depending on the structure of the matrix.

For temperatures, upstream weighting was used, defined by:

\[
T_{\text{in}} = T_i \quad \text{for} \quad h_f > h_{i+1} \quad (q_x \text{ is positive})
\]

\[
T_{\text{in}} = T_{i+1} \quad \text{for} \quad h_f < h_{i+1} \quad (q_x \text{ is negative})
\]  

(2.16)

To simulate the solid state relay, which turned the power on and off in order to maintain the tank temperature at a desired set point, a temperature check at the thermocouple locations was incorporated into the model. Once the temperature at the thermocouples reached the set point, the power was switched off and turned back on when the temperature dropped down below the set point temperature. During each time step an energy and mass balance was performed on the system to ensure mass and energy conservation.
The electro-thermal model was verified using a 1D Ogata-Banks solution for advective and dispersive transport (Ogata, 1970). In addition, the power and voltage distributions were compared to an analytical one-dimensional solution similar to Hiebert (1987). There was excellent agreement between the analytical solutions and the model, giving a PMCC of 1 for both voltage and power. To further validate the model, the power consumption, temperature, fluid velocity, and mass movement in the 2D tanks were simulated and are given in the following sections. The tank properties as well as model parameters are given in Table 2.1. There was no sorption of Rhodamine WT onto the glass beads.

Table 2.1: Properties of 2D Tanks and Simulation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Small Tank</th>
<th>Large Tank</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_w$</td>
<td>Water Electrical Conductivity (S/m)</td>
<td>0.24</td>
<td>0.12</td>
</tr>
<tr>
<td>$K_{Hb}$</td>
<td>Medium Thermal Conductivity (W/mK)$^a$</td>
<td>0.9</td>
<td>3, 0.8</td>
</tr>
<tr>
<td>$K_{Hair}$</td>
<td>Air Thermal Conductivity (W/mK)$^b$</td>
<td>0.026</td>
<td>0.026</td>
</tr>
<tr>
<td>$c_w$</td>
<td>Wall Volumetric Heat Capacity (J/Cm$^3$)$^c$</td>
<td>$1 \times 10^6$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>$n$</td>
<td>Porosity (-)</td>
<td>0.4</td>
<td>0.3</td>
</tr>
<tr>
<td>$k$</td>
<td>Permeability $\times 10^{-10}$(m$^2$)</td>
<td>4</td>
<td>0.14, 0.00014</td>
</tr>
<tr>
<td>$K_x/K_z$</td>
<td>Anisotropy Ratio (-)</td>
<td>0.7</td>
<td>1</td>
</tr>
<tr>
<td>$\Delta y$</td>
<td>Tank Thickness (m)</td>
<td>0.018</td>
<td>0.15</td>
</tr>
<tr>
<td>$dx, dz$</td>
<td>Discretization (m)</td>
<td>0.002</td>
<td>0.02</td>
</tr>
</tbody>
</table>

2.4 Results and Discussion

2.4.1 Voltage and Power

The large tank was used to assess the capability of the model to simulate voltage distribution in a 2D system with different soil layers. Voltage in the large tank was measured at the start of the experiment and when the experiment reached steady state temperature. The experimental voltage distribution is presented in Figures 2.3(a) and 2.3(c). The largest difference between the initial and final voltage is seen at the bottom of the tank, where higher clay electrical conductivity values led to higher voltage values. This also resulted in higher temperatures in the clay zone. The results of the modelled initial and final voltage contours are presented in Figures 2.3(b) and 2.3(d). The model predicted the experimental voltage with good accuracy and, similar to the experiment, also
predicted an increase in the final voltages in the clay zone.

Figure 2.3: Voltage distribution in large tank: (a) initial experimental voltage; (b) initial predicted voltage; (c) final experimental voltage; (d) final predicted voltage

The experimental and predicted power for the large and small tanks with time is presented in Figures 2.4(a) and 2.4(b), respectively. Overall, the electro-thermal model simulations showed good agreement with the experimental power. However, the peak power in the small tank, when 30°C and 50°C was reached was slightly underestimated by the model, as well as the time to reach these temperatures. In addition, the heat losses in the first part of the experiment were slightly overestimated by the model. Once the temperature reached 50°C, higher heat losses were observed due to the higher temperature differences between the tank and outside temperatures. At the end of the experiment, the predicted power for the small tank was similar to the experimental observations (46 W compared to 47 W) and the total energy predicted for the entire experiment was 866 kJ, compared to the actual 888 kJ supplied by the electrodes, which corresponds to a 2% error. The difference in total electrical energy input over the course of the large tank experiment was calculated to be 8%.

2.4.2 Temperature

Figure 2.5 shows the predicted and experimental temperature distribution of the small tank 1.5 and 3 hours after start of tracer injection (this corresponds to 3.5 and 5 hours of
Figure 2.4: Experimental and predicted power for: (a) large tank (b) small tank heating). The simulated temperatures in the heated zone showed good correspondence with the experimental results. The largest deviation between observed and simulated temperatures was seen in the upper part of the tank, where the model underestimated the temperatures by approximately 9°C. The temperatures simulated near the electrodes were approximately 12°C higher than the cut off temperature of 50°C which was expected since the thermocouples that served the temperature control, were not located at the electrodes.

2.4.3 Tracer Study

The isothermal case was simulated and the model results shown in Figures 2.6(a) and 2.6(b) were in excellent agreement with the experimental data (not shown). The non isothermal tracer movements at 1.5 and 3 hours after tracer injection are presented in Figures 2.6(c) and 2.6(e), respectively. In both figures, the temperature around the electrodes was approximately 50°C. A distinctly different flow pattern from the isothermal
Figure 2.5: Comparison of experimental and predicted temperature distributions in the small tank (red circles indicate electrode positions): (a) experiment, 1.5 hours; (b) model, 1.5 hours (c) experiment, 3 hours; (d) model, 3 hours

case was observed, with strong buoyant flow throughout the heated region. In both figures, the top most tracer plume moved more slowly than the rest of the plumes due to a convective zone which developed in the region above the electrodes.

Tracer movement was simulated for 1.5 and 3 hours after tracer injection and is presented in Figures 2.6(d) and 2.6(f), respectively. Originally, the small tank was modeled using isotropic hydraulic conductivities and low dispersion coefficients. This resulted in large dispersion within the heated zone and distinct tracer “fingers” were not visible. To address this issue, several techniques were tried. A midpoint weighing scheme was implemented and smaller vertical discretization was used to decrease numerical dispersion. This resulted in no significant improvement in the tracer profile. Subsequently, zero hydrodynamic dispersion as well as an anisotropy ratio of 0.7 for hydraulic conductivity was implemented. This resulted in more distinct tracer profiles for the 1.5 hour scenario but the 3 hour tracer profile still showed smearing, especially in the upper tracer plumes. These results suggested that the smearing was not a result of hydrodynamic dispersion
but rather numerical, even at small grid discretization.

Since the resulting groundwater flow in the heated section was diagonal to the finite difference grid, grid orientation effects associated with upstream weighting of the advection terms were determined to be causing the excessive spreading of the tracer plumes.
Consequently, the velocities obtained by the electro-thermal model were exported into a modified version of MT3DMS (Zheng & Wang, 1999). The ULTIMATE scheme (a total variation diminishing (TVD) method) was used and resulted in distinct tracer plumes for both time scenarios. A dispersivity of 0.1 mm was used in the longitudinal and transverse directions.

The model also captured slower and more dispersed tracer movement downgradient of the upper tracer injection point. The buoyant flow in the heated zone developed due to the difference in density of 1.3%. In addition, a decrease in viscosity of 40%, as well as the change in density, resulted in increased velocities within the heated zone on the order of $5.2 \times 10^{-5} \text{ m/s}$, almost 5 times faster than the isothermal velocity.

### 2.5 Conclusions/Implications

An experimental and numerical modelling study was undertaken to examine the effect of low temperature heating on subsurface hydraulics and solute transport. The experiments consisted of two 2D tanks that were heated to 50°C using single phase ERH. A 2D finite difference model was developed to simulate the power, temperature, water flow, and solute transport in the tanks during heating. The model used several temperature dependent properties including water density, viscosity, molecular diffusion, and electrical conductivity. The model successfully predicted the power, voltage and temperature profiles of the tanks. With the use of a higher order weighting of the transport advection terms, the tracer profiles were also accurately reproduced.

Low temperature subsurface heating may provide an advantage over traditional thermal remediation technologies. However, even at relatively low temperatures, localized changes in water density and viscosity can significantly impact groundwater hydraulics. This study showed that heating the subsurface to 50°C resulted in significant changes in velocity (both in direction and magnitude), leading to a considerably different mass distribution than in an isothermal scenario. The results suggest that low temperature heating of contaminated zones can have a large impact on remediation efforts and therefore inclusion of temperature dependent properties in modelling of such systems is important.
Chapter 3

Impacts of Subsurface Heating on Buoyant Flow and Contaminant Transport as Characterized by Dimensionless Numbers

Abstract
The occurrence of subsurface buoyant flow during thermal remediation was investigated using a two dimensional electro-thermal model. The model incorporated electrical current flow associated with electrical resistance heating, energy and mass transport, and density dependent water flow. The model was used to simulate the heating of sixteen subsurface scenarios with different applied groundwater flux values and soil permeabilities. Consistent with other studies, the model predicted the occurrence of buoyant flow when the ratio between the Rayleigh and thermal Peclet numbers (buoyancy ratio), was greater than 1. The effects of buoyant flow on contaminant transport were also examined. The modelled scenarios were grouped into three categories based on the occurrence of buoyant flow and its effect on contaminant transport, as compared to isothermal conditions. Contaminant distribution, in scenarios with buoyancy ratios above 1 and Rayleigh numbers greater than 60, was significantly affected by buoyant flow after 200 days of heating to 80°C. Contaminant transport was not significantly affected when Rayleigh numbers were below 0.6, even with high buoyancy ratios.
3.1 Introduction

Thermal remediation technologies, such as electrical resistance heating (ERH), raise subsurface temperatures to aid in contaminant removal. The resulting temperature increase can produce buoyant groundwater flow which may significantly affect subsurface mass distribution as shown in Chapter 2. Understanding the subsurface conditions that lead to buoyant flow, as well as, the effect of buoyant flow on contaminant transport, can aid in the design and application of subsurface thermal technologies.

Subsurface water and heat movement can be categorized into three types of flow: natural or buoyant flow, forced flow, and mixed flow. Natural or buoyant flow is driven by a temperature or density gradient without external groundwater flow and is often referred to as density-driven flow. This type of flow is characterized by a circular movement of water. Forced flow is the movement of water and heat resulting from a hydraulic gradient and therefore can also be referred to as advective flow. If both processes are occurring, the term mixed flow is used (Haajizadeh & Tien, 1984).

Natural flow has been studied extensively in the fields of fluid dynamics and heat transfer (Lapwood, 1948; Prats, 1966; Straus & Schubert, 1977; Prasad & Kulacki, 1984; Ingham & Pop, 1987; Fusegi et al., 1992; Das & Sahoo, 1999; Simmons et al., 2001; Mealey & Merkin, 2009; Nield et al., 2010). These studies determined that the strength of natural flow was dependent on the Rayleigh number. For a system heated from below, the onset of natural flow occurred at a Rayleigh number of $4\pi^2$.

Mixed flow literature has largely focused on bottom heated boundary conditions to describe geothermal phenomena such as volcanic debris or storage of nuclear wastes (Prasad et al., 1988). Since mixed flow includes advective flow through the porous media, buoyancy was not only affected by the Rayleigh number ($Ra$) but also by the Peclet number ($Pe$) for heat transfer (Prasad et al., 1988; Lai et al., 1990; Prasad & Kulacki, 1984). The transition from natural to mixed flow resulted from either a decrease in $Ra$ or an increase in $Pe$. If natural flow dominated, a multicellular and circular flow resulted near the heat source (Prasad et al., 1988; Lai & Kulacki, 1991). Alternatively, if $Pe$ was above 10 and $Ra$ was below 10 ($Ra/Pe < 1$), little or no natural flow was observed and the streamlines were dominated by forced flow (Prasad et al., 1988).

Similar results were found experimentally. Lai & Kulacki (1991) observed that low groundwater flux values in a tank filled with porous media and heated from below, resulted in streamlines that were symmetrical about the heat source, and therefore rep-
resentative of natural flow. As the velocity increased, the resulting flow and temperature fields were quite different from natural flow since the effect of forced flow became dominant and the symmetrical streamlines associated with natural flow disappeared (Lai & Kulacki, 1991).

Various studies have also been conducted on mixed flow with multiple heat sources (Lai et al., 1990), heated spheres (Andrew et al., 2003) and line sources (Kurdyumov & Linan, 2001). In addition, others have investigated buoyancy effects as a result of variable aquifer densities, either from CO₂ injection (Farajzadeh et al., 2007), salt intrusion (Dentz et al., 2006), or contamination (Schincariol et al., 1994, 1997). Mixed flow can also occur during subsurface thermal remediation, however no studies have examined this phenomenon nor the effects of mixed flow on mass transport.

The effect of mixed flow on contaminant transport during thermal remediation by electrical resistance heating (ERH) is investigated in this chapter. The spread of contaminants is examined with different subsurface and temperature conditions to determine which parameters has the greatest impact on subsurface mass transport.

### 3.2 Electro-Thermal Model

ERH is applied to the subsurface using 3 or 6 phase heating where a series of electrodes are placed in the soil and connected to an AC voltage source (U.S. EPA, 1997; Vermeulen & McGee, 2000). The flow of current between electrodes results in subsurface heating and the increase in temperature facilitates the removal of contaminants (Looney & Falta, 2000; Boulding & Ginn, 2004).

The 2D ETM described in Chapter 2 was used to simulate subsurface heating during ERH, as well as contaminant flow and transport. To obtain the power generated by ERH, the current continuity equation was solved using phasor quantities for voltage to account for the AC voltage used by ERH (Hiebert et al., 1986, 1989; McGee & Vermeulen, 2007). The power dissipation \( U \) in the subsurface was determined using:

\[
U = \sigma | \nabla V |^2
\]  

where \( V \) is the voltage and \( \sigma \) is the bulk electrical conductivity. The power dissipated
by ERH was then used in the energy transport equation:

\[
\frac{\partial}{\partial t} \left[ \rho_w \phi c_w T + (1 - \phi) \rho_b c T \right] + c_w \rho_w \nabla \cdot [\vec{q} T] - K_H \nabla^2 T - U = 0 \tag{3.2}
\]

where \( T \) is the temperature, \( \rho_w \) is the density of water, \( \phi \) is soil porosity, \( \rho_b \) is the bulk density of the soil, \( c \) is the heat capacity of the soil, \( c_w \) is the heat capacity of water, \( \vec{q} \) is the Darcy velocity vector, and \( K_H \) is the bulk thermal conductivity.

The flow of groundwater was modelled using the Darcy equation, taking into account changes in density and viscosity with temperature.

\[
q = -\frac{k}{\mu} \left( \nabla P + \rho_w g \nabla z \right) \tag{3.3}
\]

where \( k \) is the soil permeability, \( g \) is gravitational acceleration, \( P \) is the pressure, \( z \) is the elevation, and \( \mu \) is the water viscosity. An iterative approach was employed to calculate water flow and energy transport since the equations are coupled through the temperature dependence of water properties. A convergence criteria of \( 1 \times 10^{-6} \) for temperature was used and the obtained Darcy velocities were applied to the mass transfer equation:

\[
\frac{\partial}{\partial t} \left[ \rho_w \phi C \right] + \nabla \cdot [\rho_w C \vec{q}] + \nabla \cdot \left[ \phi J^D \right] = 0 \tag{3.4}
\]

where \( C \) is the mass fraction of the contaminant and \( J^D \) is the dispersive flux vector.

ETM used finite differences to discretize the current, mass, flow, and energy equations spatially and temporally, using a backwards difference, block-centered approach. The model used a fully implicit scheme for temporal discretization of these equations and included several temperature dependent properties such as water density and viscosity, and soil electrical conductivity. These properties were averaged between grid blocks using the harmonic mean value.

### 3.3 Dimensionless Numbers

To examine the effect of temperature and subsurface conditions on contaminant transport, a 2D system filled with a saturated, homogeneous porous medium was considered (Figure 3.1). In order to make the equations non-dimensional, the following parameters
(denoted by *) were defined:

\[ x^* = \frac{x}{L} \]
\[ z^* = \frac{z}{L} \]
\[ t^* = \frac{t}{t_o} = \frac{q_{in}t}{L} \]  \hspace{2cm} (3.5)

where \( L = L_x \), \( q_{in} \) is the inlet Darcy velocity, \( x \) and \( z \) are the distances in the horizontal and vertical direction, respectively, \( t_o \) is the tank residence time, and \( t \) is the time. Additionally, \( U_{max} \) was defined as the maximum rate of heating of the subsurface and the dimensionless temperature quantity was defined as follows:

\[ U_{max}t_o = (pc)_{comb}(T_{max} - T_{ref}) = (pc)_{comb}\Delta T \]
\[ \therefore \Delta T = \frac{U_{max}t_o}{(pc)_{comb}} \]  \hspace{2cm} (3.6)

\[ T^* = \frac{T}{\Delta T} \]  \hspace{2cm} (3.7)

Stream functions were used to non-dimensionalize the groundwater velocities:
CHAPTER 3. BUOYANT FLOW

\[ q_x^* = \frac{q_x}{q_{in}} = -\frac{\partial \psi}{\partial z^*} \]
\[ q_z^* = \frac{q_z}{q_{in}} = \frac{\partial \psi}{\partial x^*} \]  

(3.8)

Using these definitions, the steady state form of the energy equation (Eq. 3.2) was made non-dimensional, following a similar approach used by Prasad et al. (1988) and Prasad & Kulacki (1984).

\[
\begin{align*}
\left[ \frac{\partial}{\partial x^*} \left( q_x^* q_{in} T^* \Delta T \right) + \frac{\partial}{\partial z^*} \left( q_z^* q_{in} T^* \Delta T \right) \right] & = \frac{K_H}{L^2} \left[ \frac{\partial^2 T^*}{\partial x^*^2} + \frac{\partial^2 T^*}{\partial z^*^2} \right] + U \\
\left[ \frac{\partial \psi}{\partial x^*} \frac{\partial T^*}{\partial z^*} - \frac{\partial \psi}{\partial z^*} \frac{\partial T^*}{\partial x^*} \right] & = \frac{K_H}{L^2} \left[ \frac{\partial^2 T^*}{\partial x^*^2} + \frac{\partial^2 T^*}{\partial z^*^2} \right] + U \\
\frac{\partial \psi}{\partial x^*} \frac{\partial T^*}{\partial z^*} - \frac{\partial \psi}{\partial z^*} \frac{\partial T^*}{\partial x^*} & = \frac{K_H}{c_p \rho w q_{in} L} \left[ \frac{\partial^2 T^*}{\partial x^*^2} + \frac{\partial^2 T^*}{\partial z^*^2} \right] + \frac{UL}{c_p \rho w q_{in} \Delta T} 
\end{align*}
\]

(3.9)

To simplify the equations further, the thermal Peclet (Pe) number and Rayleigh number (Ra) were used (Lai et al., 1990; Mealey & Merkin, 2009; Prasad & Kulacki, 1984). Pe is defined as the ratio between advective and diffusive heat movement while Ra is the ratio between buoyancy forces and thermal diffusivity (Mealey & Merkin, 2009; Prasad & Kulacki, 1984).

\[
P_e = \frac{q_{in} L}{\alpha} \]  
\[
Ra = \frac{g \beta k \Delta T L}{\nu \alpha} \]  

(3.10)  

(3.11)

where \( \beta \) is the coefficient of thermal expansion, \( \nu \) is the kinematic viscosity, and \( \alpha \) is the thermal diffusivity coefficient equal to \( K_H/\rho_w c_p \). Equation 3.9 becomes:

\[
\frac{\partial \psi}{\partial x^*} \frac{\partial T^*}{\partial z^*} - \frac{\partial \psi}{\partial z^*} \frac{\partial T^*}{\partial x^*} = \frac{1}{Pe} \left[ \frac{\partial^2 T^*}{\partial x^*^2} + \frac{\partial^2 T^*}{\partial z^*^2} \right] + \frac{UL}{c_p \rho w q_{in} \Delta T} 
\]

(3.12)
The heat generation term \((U)\) can be simplified using the maximum rate of heating (Eq. 3.6) and the definition of \(t_o\) (Eq. 3.5):

\[
\frac{\partial \psi}{\partial x^*} \frac{\partial T^*}{\partial z^*} - \frac{\partial \psi}{\partial z^*} \frac{\partial T^*}{\partial x^*} = \frac{1}{Pe} \left[ \frac{\partial^2 T^*}{\partial x^{*2}} + \frac{\partial^2 T^*}{\partial z^{*2}} \right] + \frac{U (c \rho)_{comb}}{U_{max} c_p \rho_w} \tag{3.13}
\]

The ratio between the heat generated and maximum heat term can be expressed as \(U^*\) and the ratio between the heat capacities as:

\[
\Gamma = \frac{(c \rho)_{comb}}{c_p \rho_w} \tag{3.14}
\]

leading to the final non-dimensional equation:

\[
\frac{\partial \psi}{\partial x^*} \frac{\partial T^*}{\partial z^*} - \frac{\partial \psi}{\partial z^*} \frac{\partial T^*}{\partial x^*} = \frac{1}{Pe} \left[ \frac{\partial^2 T^*}{\partial x^{*2}} + \frac{\partial^2 T^*}{\partial z^{*2}} \right] + U^* \Gamma \tag{3.15}
\]

The Darcy flow equation was also made non-dimensional, using the stream functions:

\[
\mu k q_x + \frac{\partial P}{\partial x} = 0
\]

\[
\frac{\mu}{k} q_{x in} + \frac{1}{L} \frac{\partial P}{\partial x^*} = 0
\]

\[
-\frac{\partial \psi}{\partial z^*} \frac{\mu}{k} q_{in} + \frac{1}{L} \frac{\partial P}{\partial x^*} = 0
\]

\[
-\frac{\partial^2 \psi}{\partial z^{*2}} \frac{\mu}{k} q_{in} + \frac{1}{L} \frac{\partial P}{\partial x^*} = 0 \tag{3.16}
\]

\[
\mu k q_z + \rho g + \frac{\partial P}{\partial z} = 0
\]

\[
\frac{\mu}{k} q_{z in} + \rho g + \frac{1}{L} \frac{\partial P}{\partial z^*} = 0
\]

\[
\frac{\partial \psi}{\partial x^*} \frac{\mu}{k} q_{in} + \rho g + \frac{1}{L} \frac{\partial P}{\partial z^*} = 0
\]

\[
\frac{\partial^2 \psi}{\partial x^{*2}} \frac{\mu}{k} q_{in} + g \frac{\partial \rho}{\partial x^*} + \frac{1}{L} \frac{\partial P}{\partial x^* \partial z^*} = 0 \tag{3.17}
\]

Combining Equation 3.16 and 3.17 resulted in:

\[
\frac{\partial^2 \psi}{\partial x^{*2}} q_{in} + \frac{\partial^2 \psi}{\partial z^{*2}} q_{in} + \frac{k q \partial \rho}{\mu \partial x^*} = 0 \tag{3.18}
\]
Using $Ra$ and Equation 3.19 for water density change with temperature, Equation 3.18 was derived in terms of $Ra$ and $Pe$ numbers.

$$\rho_w = \rho_0[1 + \beta(T - T_0)] \quad (3.19)$$

where $\beta$ is the thermal expansion coefficient, $\rho_0$ is the reference water density, and $T_{ref}$ is the reference temperature.

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{k g}{\mu q_{in}} \frac{\partial \rho}{\partial x^*}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{k g \beta \rho_0 \Delta T}{\mu q_{in}} \frac{\partial T^*}{\partial x^*}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{Ra}{Pe} \frac{\partial T^*}{\partial x^*} \quad (3.20)$$

The buoyancy ratio, defined as $Ra/Pe$, was further simplified:

$$\frac{Ra}{Pe} = \frac{k g \beta \rho_0 \Delta T}{\mu q_{in}} = \frac{\beta \Delta T}{i} \quad (3.21)$$

where $i$ is the gradient ($i = q_{in}/K$, and $K$ is the hydraulic conductivity of the soil, $K = \rho_0 g k / \mu$). In this form, the buoyancy ratio relates temperature induced buoyant forces to advective forces and can be used as an indication of subsurface buoyant flow.

### 3.4 Simulation Description

The ETM model was used to simulate ERH on a vertical slice of a homogeneous aquifer, presented in Figure 3.1. The top and bottom boundaries were assumed to have zero heat and mass flux. A specified flux boundary was used on the left side of the domain where a known flux ($q_{in}$) was specified, while a constant head boundary was used on the right side. All voltage boundary conditions were set to zero flux and the velocity at all inlet boundaries was taken to be at the reference temperature ($20^\circ$C). ERH was modelled using two rows of electrodes spaced 4 m apart, with an applied voltage of 120 V. Sixteen cases were simulated using different permeability and applied groundwater flux values, and heated to $80^\circ$C. The cases are summarized in Table 3.1. A concentration of 100 mg/L of trichloroethylene (TCE) was assumed in the centre of the electrodes, as seen in Figure 3.2. The initial properties for the simulations are given in Table 3.2.
Figure 3.2: Initial TCE aqueous concentration (mg/L) in a vertical cross-section of the subsurface; red circles represent electrodes.

<table>
<thead>
<tr>
<th>Table 3.1: Simulated Cases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>c</td>
</tr>
<tr>
<td>d</td>
</tr>
<tr>
<td>e</td>
</tr>
<tr>
<td>f</td>
</tr>
<tr>
<td>g</td>
</tr>
<tr>
<td>h</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3.2: Initial Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma$</td>
</tr>
<tr>
<td>$K_H$</td>
</tr>
<tr>
<td>$C_o$</td>
</tr>
<tr>
<td>$D_o$</td>
</tr>
<tr>
<td>$\phi$</td>
</tr>
<tr>
<td>$L_x$</td>
</tr>
<tr>
<td>$L_z$</td>
</tr>
</tbody>
</table>

3.5 Results and Discussion

The results of the simulations were examined to determine the effect of buoyancy ratio on flow hydraulics and contaminant transport.

3.5.1 Buoyancy Ratio

Figure 3.3 presents the same case (case e) at four different temperatures. Higher temperatures correspond to higher $Ra$ numbers and therefore the buoyancy ratio for the four scenarios increased with temperature. When the $Ra/Pe$ ratio was equal to one, little buoyant flow was observed (Figure 3.3(a)). In this case forced flow was dominant and the resulting streamlines were relatively horizontal. At higher temperatures and higher buoyancy ratios, the effect of natural flow increased, resulting in stronger buoyant flow and groundwater started being directed through the heated zone (Figure 3.3(b)). As the $Ra/Pe$ ratio became large, circular flow appeared on both sides of the electrodes and all the flow was directed through the heated zone (Figure 3.3(c)). At $Ra/Pe = 500$ the resulting streamlines were fairly symmetrical, corresponding to those of natural flow, and indicating that the effect of incoming groundwater was negligible (Figure 3.3(d)).

The recirculation zones which appeared as the $Ra/Pe$ ratio increased have also been observed in cases where porous media were heated from below (Prasad & Kulacki, 1984; Lai et al., 1990; Lai & Kulacki, 1991). In addition, as observed by Prasad et al. (1988), the contribution of natural flow was small when $Ra/Pe < 1$.

Figure 3.3 examined the same case at different temperatures, therefore only $Ra$ was changing. However, since groundwater velocity is dependent on the fluid viscosity and density which are temperature dependent, as temperature rose, groundwater velocity through the heated zone increased. Figure 3.4 presents the velocity through the middle of the simulated domain for the different $Ra/Pe$ ratios shown in Figure 3.3. When $Ra/Pe = 500$, the velocity through the heated zone was over two orders of magnitude higher than the applied groundwater flux. Therefore, although the $Pe$ number was the same for all the simulations in Figure 3.3, since it is defined in terms of applied groundwater flux, the velocity within the heated zone varied with $Ra$. 
Figure 3.3: Temperature contours and streamlines (shown in purple) for different $Ra/Pe$ ratios. Maximum temperatures: (a) 20.3°C (b) 22.2°C (c) 37.3°C (d) 70°C

Figure 3.4: Velocity through the middle ($z = 15$) of the simulated domain (case e)
3.5.2 Effect of Buoyancy on Contaminant Transport

As discussed in Chapter 2, buoyant flow can significantly change the resulting contaminant distribution. However, the degree of buoyant flow which results in a change in mass distribution is unknown. To address this issue, the contaminant distributions of the sixteen cases were examined after 200 days of heating to 80°C, and are presented in Figure 3.5. Except for case a, b, c, d, and h where steady state was reached before 200 days, the buoyancy ratio was the same for each column in Figure 3.5, and therefore so were the resulting streamlines. The concentration contours for the sixteen cases varied as did the extent of buoyant flow. The greatest contaminant movement was seen in the first row and for case d, all the contaminated mass moved out of the simulated area by 200 days.

The results of the sixteen cases in Figure 3.5 were grouped into three categories: Forced flow only - no buoyancy seen (Category 1); mixed flow and minimal effect on contaminant distribution (Category 2); mixed flow and significant effect on contaminant distribution (Category 3). Contaminant distribution was considered to be significantly affected by buoyant flow if the concentration above the initial mass location (z = 13 m) was above 1 mg/L, since if isothermal conditions existed, contaminant transport would be strictly horizontal. Table 3.3 presents the sixteen cases grouped into the three categories and the corresponding Pe, Ra numbers, and buoyancy ratios.

Category 1 occurred when Ra/Pe < 1 while Category 2 and 3 occurred when Ra/Pe ≥ 1, which is consistent with results of Prasad et al. (1988) for localized heating from below. However, a second criterion had to be used when mass distribution was affected by buoyant flow since cases with the same buoyancy ratio were categorized into different groups. An example of this is given by case g and k (Figures 3.5(g) and 3.5(k), respectively). Both cases had the same buoyancy ratio (and streamlines) but different resulting concentration contours.

Since mass transport is dominated by advection, and changes in Pe are due to changes in applied groundwater flux (all other thermal coefficients are the same), Pe was considered as a criterion to evaluate the impact of buoyant flow on mass distribution. However, cases k and e were classified into different categories, yet they had the same Pe number (same q_w). Therefore, Pe was not correlated to mass transport through heated zones.

As discussed previously, velocities within the heated zone increase with Ra (Figure 3.4). Category 3 had much higher values of Ra than Category 2, reflecting the increased contribution of natural flow and increased velocities through the heated zone. Therefore,
Figure 3.5. Concentration contours and streamlines (shown in purple) for all cases, 200 days after heating to 80°C, the value in brackets corresponds to $Ra/Pe$. 

(a) Case a (81)  
(b) Case b (7.5)  
(c) Case c (0.1)  
(d) Case d (0.001)  
(e) Case e (750)  
(f) Case f (75)  
(g) Case g (7.5)  
(h) Case h (0.2)  
(i) Case i (0.75)  
(j) Case j (7.5)  
(k) Case k (7.5)  
(l) Case l (7.5)  
(m) Case m (750)  
(n) Case n (7.5)  
(p) Case p (0.75)  
(q) Case q (7.5)
Table 3.3: Dimensionless Numbers and Buoyancy Ratios of the Simulated Cases

<table>
<thead>
<tr>
<th>Category</th>
<th>Pe</th>
<th>Ra</th>
<th>Ra/Pe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Category 1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>800</td>
<td>94</td>
<td>0.1</td>
</tr>
<tr>
<td>d</td>
<td>8000</td>
<td>10</td>
<td>0.001</td>
</tr>
<tr>
<td>h</td>
<td>80</td>
<td>16</td>
<td>0.2</td>
</tr>
<tr>
<td>l</td>
<td>0.8</td>
<td>0.6</td>
<td>0.75</td>
</tr>
<tr>
<td>p</td>
<td>0.008</td>
<td>0.006</td>
<td>0.75</td>
</tr>
<tr>
<td>Category 2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>0.0008</td>
<td>0.6</td>
<td>750</td>
</tr>
<tr>
<td>j</td>
<td>0.008</td>
<td>0.6</td>
<td>75</td>
</tr>
<tr>
<td>k</td>
<td>0.08</td>
<td>0.6</td>
<td>7.5</td>
</tr>
<tr>
<td>m</td>
<td>0.000008</td>
<td>0.006</td>
<td>750</td>
</tr>
<tr>
<td>n</td>
<td>0.00008</td>
<td>0.006</td>
<td>75</td>
</tr>
<tr>
<td>o</td>
<td>0.0008</td>
<td>0.006</td>
<td>7.5</td>
</tr>
<tr>
<td>Category 3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8</td>
<td>650</td>
<td>81</td>
</tr>
<tr>
<td>b</td>
<td>80</td>
<td>570</td>
<td>7.5</td>
</tr>
<tr>
<td>e</td>
<td>0.08</td>
<td>60</td>
<td>750</td>
</tr>
<tr>
<td>f</td>
<td>0.8</td>
<td>60</td>
<td>75</td>
</tr>
<tr>
<td>g</td>
<td>8</td>
<td>60</td>
<td>7.5</td>
</tr>
</tbody>
</table>

the second criterion to distinguish Category 2 from 3 was taken to be $Ra$. Using Table 3.3, the criterion for Category 2 was determined to be $Ra/Pe \geq 1$ and $Ra \leq 0.6$, while Category 3 occurred when $Ra/Pe \geq 1$ and $Ra \geq 60$.

To examine how these categories apply to experimental results, the small tank conditions from Chapter 2 were examined. The $Ra$ number for the small tank experiment at 50°C was calculated to be 167 while the buoyancy ratio was 7. These values put the small tank experiment into Category 3. The results of the small tank experiment showed significant temperature induced buoyant flow resulting in a change in tracer movement (Figure 2.6), confirming that the experiment falls into Category 3.

### 3.6 Conclusions and Implications

Subsurface heating with no external groundwater flow results in streamlines representative of natural, or buoyancy-driven, flow. If external flow is introduced to the system, the streamline symmetry is altered. Depending on the strength of the applied groundwater flux as well as the subsurface conditions and temperature, the resulting streamlines can
either mimic natural flow, appear to have no buoyant flow at all (forced flow), or lie somewhere in between the two extremes (mixed flow). The buoyancy ratio \((Ra/Pe)\) can indicate the effect of external flow on a heated system.

The results of this study found that if the buoyancy ratio is under 1, the contribution of forced flow increased and less buoyant flow was observed. Alternatively, if the \(Ra/Pe\) ratio increased, natural flow started dominating the effect of the applied groundwater flux was minimized. Additionally, the effect of buoyant flow on contaminant transport could be grouped into three categories in terms of \(Ra\) numbers and the \(Ra/Pe\) ratio. \(Ra/Pe\) ratios below unity produced no significant buoyant flow and heating produced no significant effect on contaminant transport. For systems heated to 80°C for 200 days, \(Ra/Pe\) ratios above unity and \(Ra\) numbers below 0.6 produced significant buoyant flow, but buoyant flow had little effect on contaminant transport. \(Ra/Pe\) ratios above unity and \(Ra\) values greater than 60 produced significant buoyant flow which had a significant effect on contaminant transport.

Thermal remediation activities could result in subsurface buoyant flow leading to unexpected movement of contaminants. This could be especially significant during the pre-heat stage or at the edge of the heated zone where full remediation activities are not occurring, but the temperature is high enough to result in buoyant flow. Establishing what subsurface and temperature conditions lead to buoyant flow that significantly affects contaminant distribution may aid in choosing proper monitoring locations to ensure contaminants are not migrating off site. In addition, buoyant flow could aid in remediating sites with low temperature ERH. If the permeability and hydraulic gradient of a site is known, the buoyancy ratio and the \(Ra\) number could be used to determine the operating temperatures that would result in buoyant flow that would impact contaminant transport.
Chapter 4

Influence of Soil Heterogeneity on Energy and Mass Transport

Abstract
A two-dimensional electro-thermal model was used to simulate the operation of electrical resistance heating at a site contaminated with trichloroethylene. The effects of soil heterogeneity, electrical conductivity and applied groundwater flux were examined in two aquifers with varying levels of heterogeneity. One-factor and two-factor ANOVA analyses were performed to assess the impact of these factors on heat and mass transport. Higher soil electrical conductivity values increased the power dissipated and resulted in shorter heating times and quicker onset of buoyant flow. Consequently, electrical conductivity had a significant effect on the subsurface temperature distribution in both aquifers. Applied flux values had a strong effect on heat and mass transport with lower fluxes resulting in upward plume movement due to buoyancy effects. In addition, when buoyant flow was present, groundwater flow which would under isothermal conditions preferentially flow through high permeability zones, was directed upwards, overriding the effect of permeability. The effect of groundwater flux was found to be dependent on soil heterogeneity.

4.1 Introduction

Thermal technologies, such as electrical resistance heating (ERH) have been used to remediate soil and groundwater at numerous contaminated sites (Powell et al., 2007). ERH heats the subsurface by passing an electrical current between electrodes placed in
the soil. The resistance of the soil and groundwater to the current, dissipates heat, which aids in the removal of subsurface contaminants (U.S. EPA, 1997; Vermeulen & McGee, 2000; Looney & Falta, 2000; Boulding & Ginn, 2004). Although ERH has been used as a remedial technology for several decades, the impact of variable soil properties on ERH operation is not well understood. Examining these effects could enhance the performance of ERH, as well as, other thermal technologies. Subsurface properties which exhibit a certain amount of variability and could affect ERH performance, include soil electrical conductivity, thermal conductivity, soil permeability, groundwater velocity, and soil heat capacity.

The power dissipated by ERH is directly proportional to the subsurface electrical conductivity (EC). Electrical conduction through sandy soils occurs mainly through the pore water. Therefore EC in sands is dependent on soil porosity, saturation, as well as pore water EC which varies with ion concentration (salinity) and temperature (Sen et al., 1988). The presence of clay in the subsurface increases EC since clays tend to have higher residual water saturations and current can also be conducted along the clay surfaces (Butler & Knight, 1998). EC of sands can vary by several orders of magnitude (reported values range from 0.001 to 1 S/m) depending on the composition of the pore water (McNeill, 1980; Sen & Goode, 1992; Waxman & Smits, 1968; Buettner & Daily, 1995). Clays exhibit a smaller range of EC values (0.01 to 1 S/m) and are typically more conductive than sands (McNeill, 1980; Sen & Goode, 1992; Butler & Knight, 1998). Studies on the effect of EC on subsurface heating were conducted by Carrigan & Nitao (2000) who developed a three-dimensional model to simulated ERH in a layered soil. Highest temperatures were observed in the clay layer where the electrodes were placed. Butler & Knight (1998) conducted a study on the effect of clay content on subsurface steam flooding and observed that the presence of clay increased the conductivity of the steam zone. These studies show that soils with higher EC values will heat preferentially, however, the effect of different EC values on heat and mass transport has not been thoroughly investigated.

In order to limit the amount of cooling from incoming water, groundwater control is often implemented during ERH (U.S. Army Corps of Engineers, 2009). However, limiting groundwater can result in higher buoyant flow, influencing mass movement (Chapter 3). Buoyant forces may dominate over heterogeneity effects as observed by Buscheck et al. (1983) where buoyant flow in a layered aquifer was found to be the governing transport mechanism, larger than preferential flow through a permeable layer. In addition, similarly
to Dekker & Abriola (2000) who observed that a higher degree of variance in hydraulic conductivity obscured the effect of rate of contaminant spill, heterogeneity can also mask the effect of inlet velocity on mass and energy distributions.

The effect of thermal conductivity and heat capacity on heat transport was found to have little influence on the thermal plume size in a sand and gravel aquifer (Bridger, 2006; Bridger & Allen, 2010). Convection, rather than conduction, was observed to be the dominant heat transfer mechanism.

Numerous studies have been conducted on the effect of soil permeability on energy transport. Nield & Kuznetsov (2000) examined the effect of layered soils, with different permeabilities and thermal conductivities, on heat transfer rate. Heterogeneity was also found to be a significant factor influencing thermal plume movement in aquifer thermal energy storage systems (Bridger & Allen, 2010; Buscheck et al., 1983). Bridger & Allen (2010) examined the effect of soil layering on subsurface heat transport where heat simulations were performed in a sand and gravel aquifer used for aquifer thermal energy storage. Thermal plumes moved along more permeable zones and soil heterogeneity led to early thermal breakthroughs, affecting system performance.

Permeability variations were also reported to increase lateral spread as well as the width of a heat plume from a groundwater heat exchanger (Hidalgo et al., 2009), while large correlation lengths led to channeling of flow (Chen et al., 2002).

Heterogeneity effects on mass transport have been reported to increase mixing of aqueous mass, leading to plume spreading (Dekker & Abriola, 2000; Sudicky et al., 1983; Kueper et al., 1989; Sleep & Sykes, 1993b; Schincariol et al., 1997). Additionally, when significant heterogeneity was present, aqueous plumes had a considerably different distribution than in homogeneous aquifers (Sudicky et al., 1983).

These studies demonstrate that soil EC, groundwater velocities and soil heterogeneity can impact subsurface heat and mass distributions. However, no quantitative study has been conducted to assess which property significantly effects the distribution and movement of thermal and solute plumes. An electro-thermal model was used in this study to simulate a site heated by ERH. The effect of soil heterogeneity was examined by generating random realizations of soil permeability for two aquifers with varying levels of heterogeneity. Statistical methods were applied to look at the sensitivity of heat and mass distribution in the two soils. The effect of soil EC and applied groundwater flux on the movement and spread of heat and aqueous mass was also examined, as well as, the interaction between these parameters and soil heterogeneity.
4.2 Electro-Thermal Model

A two dimensional electro-thermal model (ETM) was used in this study to simulate ERH, and to model contaminant flow and transport. The model included several temperature dependent properties, such as EC, water density and viscosity, and accurately modelled advective-dispersive flow under temperature-induced buoyant flow. The ETM used finite differences to discretize the current, mass, flow, and energy equations spatially and temporally, using a backwards difference, block-centered approach. Temporal discretization of these equations was performed using a fully implicit scheme. The ETM is fully described in Chapter 2.

4.3 Statistical Approach

To quantify the effect of heterogeneity on heat and mass transport in the subsurface, two aquifers with different soil permeability distributions were considered: the Borden aquifer, and a Swiss sand and gravel aquifer located in the northeastern part of Switzerland (Jussel et al., 1994). The two aquifers had similar mean values and distributions of permeability but the variance of permeability was higher for the Swiss aquifer. Both aquifers were simulated with different initial bulk electrical conductivities and applied groundwater fluxes. The three factors: variance of permeability, EC, and groundwater flux; are described in Section 4.3.1. To quantify the model output, several parameters that characterize heat and solute plume distribution were used and are described in Section 4.3.2. The analysis of variance (ANOVA) method was used to asses the impact on heat and mass transport and is described in Section 4.3.3.

4.3.1 Factors Considered

The effect of permeability heterogeneity on fluid flow and transport has been well established in the literature (Dekker & Abriola, 2000; Sudicky, 1986; Hoeksema & Kitanidis, 1985). The distribution of permeability has been described by a normal or exponential distribution (for ln(k)) (Sudicky, 1986; Woodbury & Sudicky, 1991). Permeability also has a strong spatial correlation structure due to the manner that soil layers were deposited, leading to larger correlation lengths in the horizontal rather than vertical direction (Dekker & Abriola, 2000).
The power dissipated by ERH is directly dependent on the bulk electrical conductivity \( (\sigma_b) \). EC is dependent on the saturation \( (S_w) \), pore water EC \( (\sigma_w) \) and porosity \( (\phi) \) as described by Archie’s law (Archie, 1942):

\[
\sigma_b = \phi^m S_w^n \sigma_w \tag{4.1}
\]

where \( m \) is the cementation exponent ranging from 1.3 to 1.5 for clean sands and \( n \) is the saturation coefficient, typically taken to be 2 (Butler & Knight, 1998). Pore water EC changes with temperature and salinity (Sen & Goode, 1992). Therefore, bulk EC can vary depending on the soil type as well as the subsurface conditions. Although many studies have shown that electrical conductivity can vary substantially (Waxman & Smits, 1968; Sen et al., 1988; Henry, 1997; Butler & Knight, 1998; McNeill, 1980), the effect of electrical conductivity on energy and mass transport during ERH is not fully understood. In addition, operators of ERH have claimed that ERH will preferentially heat more conductive soil such as silts and clays (Beyke, 2006) but a quantitative analysis of the effect of EC on heat and mass transport has not been performed.

Groundwater velocities can vary extensively depending on the porous medium. Although it is expected that groundwater velocity will impact heat and mass transport, different applied groundwater fluxes were considered in this study to examine if higher variance in soil permeability will obscure the effect of groundwater velocities. In addition, the onset of buoyant flow will depend on the buoyancy ratio (Chapter 3) which is affected by the groundwater velocity. Therefore, by examining variable velocities, the effect of buoyant flow on mass and energy transport is also investigated.

### 4.3.2 Parameters of Heat and Mass Transport

For each aquifer, random fields of permeability were generated using the Field Generator in PMWIN (Processing Modflow 5.3) which uses Mejia’s algorithm (Frenzel, 1995; Mejia & Rodriguez-Iturbe, 1974). By generating numerous permeability realizations and examining how the heat and mass distribution changes, a view of the “average” heating and mass transport behaviour was examined. To interpret the model output and quantify the movement and shape of heat and mass distributions, several heat and mass parameters were used. These parameters were based on the investigations by Dekker & Abriola
Figure 4.1: Temperature contours and energy parameters used to quantify the movement and spread of the energy plume; mass parameters are calculated similarly.

(2000) and modified for this study. The horizontal centre of energy was calculated by:

\[ x_{ce} = \frac{1}{E} \int x \, de \]  

(4.2)

where \( E \) is the total energy of the system, \( x \) is the distance in the x direction, and \( de \) is the incremental portion of energy. The vertical centre of energy was calculated similarly in the z direction. The spreading of heat was measured using the radius of gyration:

\[ x_{spread}^e = \sqrt{\frac{I_z^e}{E}} \]  

(4.3)

where \( I_z^e \) is the second moment of energy about the z-axis and is defined as:

\[ I_z^e = \int x^2 \, de \]  

(4.4)

where \( x \) is the distance from the z-axis. The spread of energy in the z direction was also calculated, using Eq. 4.4 but using the second moment of energy about the x-axis. These parameters are presented in Figure 4.1.

To quantify the shape and movement of the mass distribution, similar parameters
were used. The horizontal centre of mass was calculated using:

\[ x_{cm} = \frac{1}{M} \int x \, dm \]  \hspace{1cm} (4.5)

where \( M \) is the total mass of the system, \( x \) is the distance in the x direction, and \( dm \) is the incremental portion of mass. The spreading of mass was measured similarly to the energy, where the radius of gyration for mass was defined as:

\[ x_{spread}^{m} = \sqrt{\frac{I_z^m}{M}} \]  \hspace{1cm} (4.6)

where \( I_z^m \) is the second moment of mass about the z axis and is defined as:

\[ I_z^m = \int x^2 \, dm \]  \hspace{1cm} (4.7)

where \( x \) is the distance from the z-axis. The vertical mass parameters were similarly calculated.

The last parameter that was used to examine the effect of heterogeneity on mass distribution was the maximum concentration in the subsurface at the time of the analysis.

### 4.3.3 Analysis of Variance

The analysis of variance (ANOVA) is a statistical method that allows for the impact of a factor to be examined (Montgomery & Runger, 2007). The one-factor analysis of variance (ANOVA) is based on a linear statistical model as given by:

\[ y_{ij} = \mu + \tau_i + \varepsilon_{ij} \]  \hspace{1cm} (4.8)

where \( y_{ij} \) is the value of the random variable at \( j \)th observation under \( i \)th factor, \( \mu \) is the overall mean, \( \tau_i \) is the factor effect, and \( \varepsilon_{ij} \) is the random error component (Montgomery & Runger, 2007). The analysis assumes that the observations are obtained in a random order.

In this study, the electrical conductivity, applied groundwater flux, or permeability are the factors (\( \tau \)), while the parameters used to quantify the change in mass or heat distribution are the random variable values (\( y \)).
To quantify the effect of a factor, the null hypothesis \((H)\) was used:

\[
H_0 : \tau_1 = \tau_2 = \cdots = \tau_1 = 0 \\
H_1 : \tau_i \neq 0 \text{ for at least one } i
\]

To test the null hypothesis, the F-test was performed and was given in terms of the P-value which is the measure of the probability of the null hypothesis being true. A significance level of 0.05 was used.

The one factor ANOVA generated P-values for both Borden and Swiss aquifer separately and did not take into account the differences in variance of the two permeability distributions. This can lead to the masking or obstruction of the effect of heterogeneity. To directly examine the effect of the different variances of soil permeability, a two-factorial ANOVA analysis was performed.

A two-factor analysis examines more than one factor of interest. The advantage of performing a two-factorial analysis is that it directly examines the effect of both factors as well as the interaction of the two factors. The two-factor ANOVA is based on the following statistical model:

\[
y_{ijk} = \mu + \tau_i + \beta_j + (\tau \beta)_{ij} + \varepsilon_{ijk} \quad (4.9)
\]

where \(y_{ijk}\) is the value of the random variable at \(ij\)th observation under \(k\)th replicate, \(\mu\) is the overall mean, \(\tau_i\) is the effect of factor A, \(\beta\) is the effect of factor B, \((\tau \beta)\) is the effect of interaction between A and B and \(\varepsilon_{ij}\) is the random error component (Montgomery & Runger, 2007). The hypothesis tested is that there is no effect on the mean response by changing factor A, no effect for changing factor B, and no effect for AB interaction. The results are also given in terms of the P-value, and because there are three effects being tested, three P-values are calculated. When two factors are considered interaction between the factors can occur, signifying that the effect of one factor on a parameter will be different at different levels of the other factor. If large interaction between factors is present, it can mask the importance of main effects (Montgomery & Runger, 2007).

In this study, the change in EC or applied flux was examined along with variable soil permeability. Therefore the two factors considered for the two-factor ANOVA were: EC and variance in permeability; or groundwater flux and variance in permeability.
4.4 Simulation Description

The ETM model was used to simulate ERH in a vertical slice of an aquifer, presented in Figure 4.2. The top and bottom heat and mass boundary conditions were assumed to be zero flux. A constant flow boundary condition was used on the left side of the domain where a known flux \( q_{in} \) was specified at a reference temperature (20°C), while a constant head boundary was used on the right hand side. All voltage boundary conditions were set to zero flux. ERH was modelled using three electrodes spaced at a radius of 4 m, with an applied voltage of 400 V. An initial concentration of 1000 mg/L of trichloroethylene (TCE) was specified in the centre of the heated zone (Figure 4.2). The model simulated 50 days of heating to 80°C but the statistical analysis was performed after 10 days of heating in order to ensure the entire mass and energy plumes were within the simulated domain.

To examine the effect of soil heterogeneity on heat and mass transport, two aquifers with different degrees of heterogeneity were modelled. The Borden aquifer was used as a base scenario using properties obtained from Dekker & Abriola (2000), presented in Table 4.1. The Borden aquifer was selected as the base case because it is a well characterized and relatively homogeneous aquifer (Dekker & Abriola, 2000; Sudicky, 1986). The Swiss aquifer was more heterogeneous but had similar mean permeability and correlation lengths as the Borden aquifer (Dekker & Abriola, 2000; Jussel et al., 1994). However, the variance of permeability was higher in the Swiss aquifer, resulting in higher contrast in permeability. The simulations were modelled using the layout shown in Figure 4.2. Realizations of permeability were generated using the Field Generator in Modflow (Processing Modflow 5.3) which used the vertical and horizontal correlation lengths, as well as, the log mean value and log standard deviation of permeability as the input values. The aquifer properties are shown in Table 4.1. One hundred realizations were generated for each aquifer and 20 realizations were chosen randomly for the analysis. The estimate of variance was calculated for different parameters and convergence of variance was observed to occur within 20 realizations, as shown in Figure 4.3.

To examine the effect of EC and groundwater velocity on heat and mass transport, five different cases were examined. Each case had either a different specified bulk electrical conductivity or applied flux. The lowest EC value corresponded to a typical sand EC, while the largest value represented a more silty soil. Alternatively, the higher EC value could correspond to a briny sandy aquifer. The range for applied flux values were chosen
Table 4.1: Aquifer Properties and Simulation Parameters

<table>
<thead>
<tr>
<th></th>
<th>Borden Aquifer</th>
<th>Swiss Aquifer</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \phi )</td>
<td>Porosity (−)(^a)</td>
<td>0.34</td>
</tr>
<tr>
<td>( k )</td>
<td>Average permeability ((m^2))(^b),(^c)</td>
<td>(1.1 \times 10^{-11})</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>Variance (log(k)) (−)(^b),(^c)</td>
<td>0.2130</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Mean (log(k)) (−)(^b),(^c)</td>
<td>-11.01</td>
</tr>
<tr>
<td>( x )</td>
<td>Horizontal correlation length (m)(^b)</td>
<td>5.1</td>
</tr>
<tr>
<td>( z )</td>
<td>Vertical correlation length (m)(^b)</td>
<td>0.21</td>
</tr>
<tr>
<td>( K_x )</td>
<td>Initial hydraulic conductivity (m/s)(^b),(^c)</td>
<td>(1.1 \times 10^{-4})</td>
</tr>
<tr>
<td>( dx ), ( dz )</td>
<td>Grid discretization (m)</td>
<td>0.5, 0.5</td>
</tr>
<tr>
<td>( q_{in} )</td>
<td>Applied Groundwater Flux (m/s)(^e)</td>
<td>(1 \times 10^{-6}), (2 \times 10^{-6}), (3 \times 10^{-7})</td>
</tr>
<tr>
<td>( \sigma_b )</td>
<td>Bulk electrical conductivity (S/m)(^f)</td>
<td>0.02, 0.1, 0.2</td>
</tr>
<tr>
<td>( C_0 )</td>
<td>Initial TCE concentration (mg/L)</td>
<td>1000</td>
</tr>
</tbody>
</table>

Sources: \(^a\)Sudicky (1986) \(^b\)Woodbury & Sudicky (1991) \(^c\)Jussel et al. (1994) \(^d\)Brown et al. (1994) \(^e\)Sudicky et al. (1983) \(^f\)Waxman & Smits (1968)

Table 4.2: Simulated Cases

<table>
<thead>
<tr>
<th>Case</th>
<th>Applied flux ((q_{in})) (m/s)</th>
<th>Soil EC ((\sigma_b)) (S/m)</th>
<th>Time to reach 80°C (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1 \times 10^{-6})</td>
<td>0.218</td>
<td>2.8</td>
</tr>
<tr>
<td>2</td>
<td>(2 \times 10^{-6})</td>
<td>0.1</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>(1 \times 10^{-6})</td>
<td>0.1</td>
<td>6.8</td>
</tr>
<tr>
<td>4</td>
<td>(3 \times 10^{-7})</td>
<td>0.1</td>
<td>6.8</td>
</tr>
<tr>
<td>5</td>
<td>(1 \times 10^{-6})</td>
<td>0.02</td>
<td>8.3</td>
</tr>
</tbody>
</table>

corresponding to velocities reported in the Borden aquifer (Sudicky et al., 1983). Both EC and flux values were initially homogeneous but changed spatially as the subsurface temperature increased. The cases are summarized in Table 4.2.

4.5 Simulation Results

4.5.1 Variance of Soil Permeability

The Swiss aquifer was modelled with the same mean permeability, correlation length, porosity, and electrical and thermal properties as the Borden aquifer but with a higher variance in permeability, resulting in larger contrasts in the permeability fields. Figure 4.4 presents a single realization of permeability for both aquifers as well as the resulting
Figure 4.2: Initial TCE aqueous concentration (mg/L) in a vertical slice of the subsurface; red circles represent electrodes.

Figure 4.3: Estimate of variance for the centre or energy of the Borden Aquifer.
Table 4.3: P-values and Trends for One-factor ANOVA (at 10 days)

<table>
<thead>
<tr>
<th></th>
<th>Electrical Conductivity</th>
<th>Applied Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Borden Aquifer</td>
<td>Swiss Aquifer</td>
</tr>
<tr>
<td></td>
<td>P-value    Trend</td>
<td>P-value    Trend</td>
</tr>
<tr>
<td>Energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x-spread</td>
<td>1.23e-02 +</td>
<td>5.21e-02 +</td>
</tr>
<tr>
<td>z-spread</td>
<td>5.10e-03 −</td>
<td>1.19e-01 +</td>
</tr>
<tr>
<td>x-centre</td>
<td>1.00e-02 +</td>
<td>4.13e-02 +</td>
</tr>
<tr>
<td>z-centre</td>
<td>4.31e-03 −</td>
<td>5.77e-02 +</td>
</tr>
<tr>
<td>Mass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x-spread</td>
<td>3.32e-01</td>
<td>5.31e-01</td>
</tr>
<tr>
<td>z-spread</td>
<td>1.28e-01</td>
<td>1.74e-02 −</td>
</tr>
<tr>
<td>x-centre</td>
<td>3.53e-01</td>
<td>5.69e-01</td>
</tr>
<tr>
<td>z-centre</td>
<td>1.22e-01</td>
<td>1.61e-02 −</td>
</tr>
<tr>
<td>Conc.</td>
<td>7.69e-02</td>
<td>6.81e-01</td>
</tr>
</tbody>
</table>

Note: (+) indicates an increasing trend with increasing EC or $q_{in}$ values; (-) indicates a decreasing trend with increasing EC or $q_{in}$ values; shaded values indicate P-values below 0.05.

streamlines. Greater variability in the permeability contours was observed in the Swiss aquifer leading to more tortuous streamlines.

Differences in variance of permeability fields also resulted in noticeably different mass distributions in the Borden and Swiss aquifers. Four realizations of mass distribution after 50 days of heating are shown in Figures 4.5 and 4.6 for both aquifers (case 4: $q_{in} = 3 \times 10^{-7}$ and $EC = 0.1$).

### 4.5.2 One-Factor ANOVA

The one-factor ANOVA was conducted on each aquifer by varying EC or applied flux values. To examine the effect of EC, case 1, 3 and 5 were simulated for 20 permeability realizations (Table 4.2). These cases had different initial EC values but the same applied flux ($1 \times 10^{-6} \text{ m/s}$). The ANOVA analysis was conducted using EC as the varying factor and P-values were obtained for all heat and mass parameters for both aquifers. The P-values are presented in Table 4.3 and Figure 4.7 presents the box plots for the different parameters. The median is shown by the central mark on the box plots, the upper and lower quartiles are given by the edges of the box and the whiskers of the box plots represent the tails of the distribution.
Figure 4.4: Aquifer permeability distributions and corresponding streamlines
Figure 4.5: Concentration contours for Borden aquifer for different soil permeability realizations after 50 days of heating to 80°C; Case 4; Red circles represent electrode locations.
Figure 4.6: Concentration contours for Swiss aquifer for different soil permeability realizations after 50 days of heating to 80°C; Case 4; Red circles represent electrode locations.
Figure 4.7: Effect of electrical conductivity (x-axis) on (a) energy spread in X-direction (b) mass spread in X-direction (c) energy spread in Z-direction (d) mass spread in Z-direction (e) centre of energy in X-direction; (f) centre of mass in X-direction (g) centre of energy in Z-direction; (h) centre of mass in Z-direction; after 10 days of heating.
The P-values calculated with the one-factor ANOVA, indicated that EC had a significant effect on the energy distribution of the Borden aquifer and on the horizontal centre of energy and vertical distribution of mass for the Swiss aquifer (Table 4.3). The vertical depth was measured from the ground surface, therefore a decrease in the centre of mass or energy values indicated that the energy or solute plume was located closer to the surface. Figures 4.7(g) and 4.7(h) showed that as EC increased, the resulting energy and solute plumes moved upwards. Although the one-factor ANOVA did not show a significant effect of EC on energy distribution in the Swiss aquifer, the box plots displayed clear trends with changing EC values (Figures 4.7(a), 4.7(c), and 4.7(g)). Therefore, the effect of EC was obscured by the increased variability of the permeability of the Swiss aquifer.

The one-factor ANOVA was also performed on the effect of groundwater flux on energy and mass parameters. The same procedure was undertaken as with EC but cases 2, 3 and 4 were used (Table 4.2) and initial EC values were the same for each case (0.1 S/m). Figure 4.8 presents the box plots for the different energy and mass parameters and the corresponding P-values are presented in Table 4.3. Groundwater flux had a significant effect on almost all the mass and energy parameters except for the vertical energy spread and vertical centre of energy of the Borden aquifer.

Figure 4.9 presents the box plots for maximum concentration with changing EC and flux values. Increased flux values resulted in a decrease in maximum concentration after 10 days of heating. The P-value for the effect of groundwater flux on concentration was very low indicating that this factor has a significant impact on concentrations. An increase in EC values caused a slight downward trend in concentrations (Figure 4.9(a)) but the corresponding P-value was above 0.05 and therefore this trend was not statistically significant.

4.5.3 Two-Factor ANOVA

Since the one-factor ANOVA did not consider the different permeabilities of the two aquifers and some masking of effects was observed, the two-factor ANOVA was performed. The two-factor ANOVA can assess both the effect of soil heterogeneity as well as another factor (EC or flux) on heat and mass transport, and examine the interaction between soil heterogeneity and the varying factor. The P-values for the two factor ANOVA analysis are presented in Table 4.4. Similarly to the one-factor ANOVA, any P-value below 0.05
Figure 4.8: Effect of applied groundwater flux (x-axis) on: (a) energy spread in X-direction (b) mass spread in X-direction (c) energy spread in Z-direction (d) mass spread in Z-direction (e) centre of energy in X-direction; (f) centre of mass in X-direction (g) centre of energy in Z-direction; (h) centre of mass in Z-direction;
Figure 4.9: Maximum concentration after 10 days of heating with changing: (a) electrical conductivity (b) applied flux;

<table>
<thead>
<tr>
<th>Table 4.4: P-values for Two-factor ANOVA (at 10 days)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrical Conductivity</strong></td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td><strong>Energy</strong></td>
</tr>
<tr>
<td>k Effect</td>
</tr>
<tr>
<td>x-spread</td>
</tr>
<tr>
<td>z-spread</td>
</tr>
<tr>
<td>x-centre</td>
</tr>
<tr>
<td>z-centre</td>
</tr>
<tr>
<td><strong>Mass</strong></td>
</tr>
<tr>
<td>x-spread</td>
</tr>
<tr>
<td>z-spread</td>
</tr>
<tr>
<td>x-centre</td>
</tr>
<tr>
<td>z-centre</td>
</tr>
<tr>
<td><strong>Conc.</strong></td>
</tr>
</tbody>
</table>

Note: Shaded values indicate P-values below 0.05 indicated that the factor had a statistically significant effect on that parameter.

The two-factor ANOVA analysis revealed several results that differed from the one-factor analysis. The one-factor ANOVA showed no effect of EC on most energy parameters in the Swiss aquifer although the box plots showed clear trends. The two-factor ANOVA resulted in P-values of less than 0.05 for all energy parameters with changing EC. This indicates that the increased variance of soil permeability in the Swiss aquifer obscured the effect of EC on the energy distribution. No masking effect was observed for groundwater fluxes.

The P-values corresponding to the effect of applied fluxes were substantially lower than for EC, indicating that groundwater flux has a greater effect on the mass and
energy parameters. However, interaction between flux values and soil heterogeneity was found to be significant for many of the parameters.

When more than one factor is considered simultaneously, interaction between the two factors can exist. Significant interaction P-values indicate that the effect of one factor depends on the level of the second factor (Montgomery & Runger, 2007). In this study, significant interaction was observed between soil heterogeneity and groundwater flux while the interaction between soil heterogeneity and EC was not significant. This implies that the effect of EC on the heat and mass parameters was the main effect and it does not depend on the level of soil heterogeneity. The same cannot be claimed for groundwater flux values.

To examine the interaction between groundwater flux and soil heterogeneity, two-factor interaction plots for both aquifers are presented in Figure 4.10. The interaction plot between inlet velocity and soil heterogeneity on maximum concentration is shown in Figure 4.10(a). The mean values of maximum concentration were plotted with changing flux values for both aquifer and showed a visible decreasing trend of maximum concentrations with increased fluxes. The lines were nearly parallel indicating no interaction between the factors. Therefore the effect of applied flux on maximum concentration is the same, regardless of soil heterogeneity. The calculated P-values in Table 4.4 confirmed that both heterogeneity and applied flux significantly affect the maximum subsurface concentration.

Interaction between applied flux and heterogeneity on vertical centre of energy is shown in Figure 4.10(b). In this case, the effect of groundwater flux differs for the two aquifers and the lines are not parallel. This indicates that the effect of applied flux on the vertical centre of energy depends on the level of soil heterogeneity and unless the soil heterogeneity is known, the resulting trend cannot be specified.

4.6 Discussion

4.6.1 Effect of Soil Heterogeneity on Mass and Heat Distribution

The effect of increased variance in soil permeability is shown in Figures 4.7 and 4.8. For most cases, the Swiss aquifer exhibited a trend similar to that of the Borden aquifer, but the higher variance in permeability distribution obscured some of the effects. The mask-
Figure 4.10: Mean values of: (a) maximum concentration with changing groundwater flux (b) centre of energy in the Z direction with changing groundwater flux.

An effect was seen with changing EC values but not with applied flux values, indicating that the increased soil variability can obscure the effect of EC. The two-factor ANOVA indicated that the variance in permeability had an effect on all mass parameters with changing fluxes. This was also seen in Figure 4.8, where the spread of parameters in the Swiss aquifer was much higher than in the Borden aquifer.

4.6.2 Effect of Electrical Conductivity on Mass and Heat Distribution

The box plots showing the effect of EC on mass and heat parameters are presented in Figure 4.7. A clear decrease in vertical centre of mass and energy values was observed with increased EC values, indicating an upward movement in energy and solute plumes. Since EC has a direct impact on ERH power, higher EC values resulted in an increased rate of subsurface heating. Increased temperatures led to more buoyant flow, resulting in greater vertical movement of the energy and solute plumes. The ANOVA analyses confirmed that EC significantly impacted the energy distribution as well as the vertical distribution of mass (Table 4.3). Since all the cases were simulated up to 80°C, the final temperature was the same and therefore the buoyancy ratio was similar after 10 days of heating. The difference in parameter values between case 1, 3 and 5 can be attributed to the rate of heating as a result of the different EC values. Higher EC values resulted in faster subsurface heating and quicker onset of buoyant flow. This led to higher vertical centre of energy and mass values, as seen in Figure 4.7(g) and 4.7(h). The time required to bring the subsurface to 80°C was examined for the three cases and is presented in Table 4.2. Case 1, with the highest EC value, reached 80°C more than 5 hours faster.
than case 5, which had the lowest EC value.

Aqueous concentration was found not to be significantly impacted by the value of EC, indicating that it is only the location of the solute plume, not the distribution of mass that is affected by EC (the spread of mass is not sensitive to changes in EC).

Lastly, the two-factor ANOVA results showed that there is no interaction between the EC and the levels of heterogeneity examined. Therefore the effect of EC on mass and energy transport does not depend on subsurface heterogeneity, and these trends would be observed in soils with different variance in permeability (within the levels examined).

### 4.6.3 Effect of Applied Groundwater Flux on Mass and Heat Distribution

The applied flux significantly impacted most mass and energy parameters. The P-values were found to be much lower than for EC effects, indicating that energy and mass parameters were strongly influenced by the flux values. The ANOVA analyses also showed that in almost all the cases, the effect of groundwater flux was dependent on heterogeneity (interaction P-values were below the 0.05 significance level).

Groundwater flux affected all mass parameters and horizontal energy parameters. As flux decreased, more buoyant flow was observed and the solute plume moved upwards, as indicated in Figure 4.8(h). Buoyant flow was also observed to override heterogeneity effects, similarly to what was reported by Buscheck et al. (1983). Figure 4.11 presents the same permeability realization for the Swiss aquifer before and after heating to 10 days. In the isothermal case, flow was preferentially directed through the high permeability zones. However as buoyant flow became established, the majority of the flow was directed upwards and not through higher permeability zones. This effect may have led to the high interaction observed between heterogeneity and applied flux values.

Lastly, the aqueous concentrations were found to be influenced by the applied flux, with higher flux values resulting in lower concentrations. No interaction was found between the two factors, indicating that the trend of decreasing concentrations as fluxes increased, would be observed under any variance of soil permeability.
Figure 4.11: Permeability contours and streamlines for Swiss aquifer (a) before heating (b) after 10 days of heating; case 4
4.7 Conclusions/Implications

This study examined the effect of soil heterogeneity on energy and mass transport during ERH operation using a 2D electro-thermal model. Numerous simulations were performed on random realizations of permeability for two aquifers with varying levels of heterogeneity. The effect of applied groundwater flux and electrical conductivity on energy and mass distributions were also examined. The one-factor and two-factor ANOVA analyses were employed to establish the significance of changing flux or EC values, with varying levels of soil permeability.

The simulations showed that an increase in EC had a significant effect on the energy distribution resulting in an increased upward movement due to faster heating times and quicker onset of buoyant flow. The effect of EC was also found to be independent of the levels of heterogeneity examined.

Applied flux values had a strong effect on the mass and energy distribution. Lower fluxes resulted in more buoyant flow and therefore greater upward plume movement. Buoyant flow was also observed to dominate over preferential flow through more permeable zones. In addition, the effect of flux was found to be dependent on soil heterogeneity and therefore the impact of flux could not be predicted without knowing the level of soil heterogeneity.

The results from this study suggest that the factor most critical in predicting the distribution and movement of the energy plume is the electrical conductivity of soil, while the solute plume is highly impacted by applied flux values. Since the effect of flux is dependent on the level of heterogeneity, and heterogeneity obscured the effect of EC, the two-factor ANOVA was better suited for the analysis of these factors. Lastly, the application of this study can be extended beyond ERH, and applied to any other thermal technology or application. Knowing the effects of heterogeneity, EC, and applied flux values on energy and mass distribution, can aid in the design of thermal remediation systems and identify potential operational problems.
Chapter 5

Discrete Gas Bubble Formation and Mobilization during ERH

Abstract
During thermal remediation the increase in subsurface temperature can lead to bubble formation and mobilization. In order to investigate the effect of gas formation on resulting aqueous concentrations, a 2D finite difference flow and mass transport model was developed which incorporates a macroscopic invasion percolation (MIP) model to simulate bubble expansion and movement. The model was used to simulate three soil scenarios with different permeabilities and entry pressures at various operating temperatures and groundwater velocities. It was observed that discrete bubble formation occurred in all three soils, upward mobility being limited by lower temperatures and higher entry pressures. Bubble mobilization resulted in a different aqueous mass distribution than if no discrete gas formation was modelled, especially at higher temperatures. This was a result of bubbles moving upwards to cooler areas, then collapsing, and contaminating previously clean zones. The cooling effect also led to the accumulation of mass resulting in concentrations over the solubility limit of the contaminant, which was not predicted using conventional advective-dispersive models.

5.1 Introduction
Discrete gas bubble formation in the subsurface has been observed as a result of microbial activity (Ye et al., 2009; Amos et al., 2005; Beckwith & Baird, 2001; Soares, 2000; Blicher-Mathiesen et al., 1998), water table oscillations (Ronen et al., 1989; Williams &
Oostrom, 2000), and application of direct gas injection and permanganate injection for subsurface remediation (Fry et al., 1997; Schroth et al., 2001). Originally, these bubbles were considered to be immobile. However, recent studies have shown that trapped bubbles are not necessarily static. For example, the formation and movement of gas bubbles above non-aqueous phase liquid (NAPL) sources have been studied by Roy & Smith (2007); Mumford et al. (2008, 2009b, a) and Mumford et al. (2010). Roy & Smith (2007) found that gas clusters in contact with NAPL pools, would expand due to the partitioning of NAPL compound to the gas phase, then fragment and mobilize upward. Mumford et al. (2010) showed that this discontinuous gas phase can lead to aqueous concentrations of NAPL constituent downgradient and above the source zone due to partitioning of mass from the gas to aqueous phase. These concentrations were higher than expected using conventional models for NAPL dissolution. Mumford et al. (2010) also used a mass transport and macroscopic invasion percolation (MIP) model to investigate the transient behaviour of the resulting aqueous concentrations due to the presence of a discontinuous gas phase. Amos & Mayer (2006) investigated the formation, expansion and contraction of gas bubbles trapped by water table rise or due to methanogenesis in a contaminated aquifer using a reactive model. It was shown that including bubble formation in the model allowed for a more accurate prediction of the rate and extent of methanogenesis as well as the resulting aqueous concentration.

Recently there has been an interest in combining thermal remediation technologies, such as electrical resistance heating (ERH), with other remediation methods such as bioremediation (Friis et al., 2006; Truex et al., 2007). It has been suggested that operating ERH at lower operating temperatures (below 100°C) could decrease operating costs while still reaching desired cleanup levels. These levels would be achieved with increased biodegradation rates (Beyke et al., 2009) and less aggressive stripping, since operating ERH at lower temperatures can still result in gas formation due to heteroazeotropic boiling (Kiva et al., 2003). However, the formation of a discrete gas phase could create a concern for remediation technology operators. Without the widespread creation of a gas phase at water-boiling temperatures, any gas mobilized within the heated (i.e. treatment) zone must pass through a water saturated zone before being captured by a near-surface vapor extraction system. Thus, gas bubbles that expand and mobilize above a heated zone could collapse and transfer gas-phase mass back into the aqueous phase. While this can increase mass transfer from source zones, if not addressed, it can lead to increased concentrations in previously uncontaminated groundwater. In addition,
unlike isothermal conditions, bubble formation due to subsurface heating can occur under completely saturated conditions (with no trapped gas phase in the vicinity of the contaminated source zone) and with only dissolved contaminants in the groundwater (no separate phase present). Lastly, the formation of a discrete gas phase is not only a concern for low temperature heating but also during the pre-heat remediation phase and at the edge of the heated zone where temperatures are lower than pure water boiling temperatures.

Since thermal technologies such as ERH are typically operated at $100^\circ$C, the effect of lower temperatures on gas generation has typically been ignored. This paper continues the work of Mumford et al. (2010) by combining a MIP model with the electro-thermal, flow and transport model described in Chapter 2, to examine the behaviour of a discontinuous gas phase under non isothermal conditions. This paper examines the effects of various temperatures, different entry pressures as well as groundwater velocities on the formation, expansion, and mobilization of discrete bubbles.

### 5.2 Conceptual Model

The simulations presented in this paper were completed by combining a two dimensional (2D) electro-thermal model (ETM) and a MIP model. The ETM portion of the model calculated temperature and mass distribution upon heating of the subsurface using ERH. Chapter 2 gives a detailed description of the model which includes several temperature dependent properties, such as electrical conductivity, water density and viscosity, and accurately models advective-dispersive flow under temperature-induced buoyant flow. The MIP technique is based on the model of Mumford et al. (2010) and modified for non isothermal conditions. Therefore, the model applied the same assumptions as Mumford et al. (2010), included here, as well as those related to a heated subsurface: (1) local equilibrium between the aqueous and gas phases (2) aqueous flow is not significantly affected by local changes in gas saturation (3) gas phase expansion occurs as a quasi-static displacement and gas movement occurs during the MIP step only; no advection or diffusion of the gas phase in the ETM mass transport step (4) gas phase mobilization occurs much faster than expansion or dissolution, such that mass transfer between gas and aqueous phase during a mobilization (MIP) step is negligible (5) thermal equilibrium exists between water and gas phases.
5.2.1 ETM - MIP Model

The ETM model used finite differences to discretize the current, mass, flow and energy equations spatially and temporally, using a backwards difference, block-centered approach. The model used a fully implicit method for the temporal discretization of the current, energy, flow and mass transport equations. Since the heat and flow equations were coupled through temperature dependence of water properties, an iterative approach was used to calculate both the temperature and velocities in the system. Parameters that changed spatially were averaged between grid blocks, using the harmonic mean value. These parameters included the hydraulic conductivity, water density, and electrical conductivity.

The ETM-MIP model assumed that aqueous transport, gas phase formation, expansion and movement occurred within the same time step. Each time step was divided into four distinct modules: electrical; thermal and flow; mass transport; gas movement.

During the electrical module, the voltage and heat generated during ERH was calculated and used in the thermal and flow module to calculate the temperature distribution and velocity fields. Also within the thermal and flow module, all the temperature dependent variables were calculated. These included the Henry’s coefficient, water vapour pressure, water density and viscosity, and hydraulic conductivities. Lastly, new gas saturations were obtained through equilibrium calculations which were in turn used to calculate new total pressures and aqueous phase concentrations. These concentrations were used in the mass transport module, where the aqueous mass was transported according to the advection-dispersion equation.

The gas movement module identified gas clusters and determined whether the bubbles mobilized or expanded using a MIP algorithm, as described by Mumford et al. (2010). Equilibrium calculations were performed after each mass transport and gas movement step.

5.2.2 Equilibrium Equations

Equilibrium between aqueous and gas phase for one organic specie was established using Henry’s law, Dalton’s law and Ideal Gas Law, as follows:
\[ C_g = x_g \frac{P_{\text{tot}}}{RT} \quad (5.1) \]
\[ C_w = \frac{C_g}{K} \quad (5.2) \]
\[ P = C_w H \quad (5.3) \]
\[ S_g + S_w = 1 \quad (5.4) \]
\[ \sum x_g = 1 \quad (5.5) \]
\[ \sum x_w = 1 \quad (5.6) \]
\[ P_{\text{tot}}^g = \sum P = P_c + P_w \quad (5.7) \]

where the subscripts \( g \) and \( w \) refer to gas or water phase, respectively; \( C \) is the concentration of the organic specie; \( x \) is the molar fraction; \( P_{\text{tot}}^g \) total gas pressure; \( P \) is the partial pressure; \( T \) is the subsurface temperature; \( R \) is the ideal gas constant; \( K \) is the partitioning coefficient of organic specie; \( H \) is the Henry’s coefficient of organic specie; \( S \) is saturation; \( P_w \) is the water pressure; and \( P_c \) is the capillary pressure.

For a two species system (water and one dissolved organic specie), the total gas pressure consisted of the water vapour pressure \( (P_w^v) \) and the partial pressure of the organic specie, which was written in terms of the Henry’s coefficient (Eq. 5.3):

\[
P_{\text{tot}}^g = P_w^v + C_w H = P_c + P_w \\
C_w H = P_c + P_w - P_w^v \quad (5.8)
\]

Using these relationships, the total organic mass \( (M) \) in the system was calculated as follows:

\[
M = M_g + M_w \\
M = C_g S_g \phi + C_w (1 - S_g) \phi \\
M = K C_w S_g \phi + C_w (1 - S_g) \phi \quad (5.9)
\]

where \( \phi \) is the porosity. Equations (5.8) and (5.9) were combined, resulting in:

\[
M = K \left( \frac{P_w + P_c - P_w^v}{H} \right) S_g \phi + \left( \frac{P_w + P_c - P_w^v}{H} \right) (1 - S_g) \phi \quad (5.10)
\]
where, the capillary pressure is a function of gas saturation as described by the Brooks-Corey relationship:

\[
P_c = \left( \frac{1 - S_g - S_{wr}}{1 - S_{wr}} \right)^{-\lambda} P_d
\] (5.11)

\(S_{wr}\) is the residual water saturation, \(\lambda\) is the pore size distribution index and \(P_d\) is the displacement pressure. Whereas these values are all soil properties and do not change with time, \(H\), \(K\), and \(P_{w}^v\) are temperature dependent and were calculated at each time step.

### 5.2.3 Macroscopic Invasion Percolation Model

The MIP model is a modified form of the invasion percolation (IP) technique which has been used extensively to model fluid displacement processes in the subsurface (Glass & Yarrington, 2003; Kueper & McWhorter, 1992; Glass et al., 2001). IP and MIP techniques use invasion and drainage thresholds to control the fluid movement, however whereas IP represents the porous medium by a network of sites and bonds, MIP models the domain with sites only. In addition, MIP differs from IP because the sites represent a sub-region of the medium (as opposed to an individual pore) and they can be occupied by multiple fluids (Kueper & McWhorter, 1992). Similar to Mumford et al. (2010), this study used the capillary pressure - saturation relationship (Eq. 5.11), to model the occurrence of two fluids (water and gas) within one site.

A gas bubble formed once the average gas pressure overcame the confining pressure. However, the gas movement module which used the MIP algorithm, within the combined ETM/MIP model, was called upon only once the gas saturation exceeded the critical gas saturation (\(S_{gcr}\)). This value, taken to be 0.3 (Mumford et al., 2010), represented the gas saturation that a block needed to reach in order for the gas in one block to be connected to the gas in an adjacent block. Any grid block with a gas saturation over \(S_{gcr}\) could be included in a multi-block cluster and able to mobilize, fragment, or expand. In addition, any newly occupied block was assigned a gas saturation equal to \(S_{gcr}\).

To calculate the gas saturation, each block in the domain was assigned an entry pressure (\(P^e\)), a terminal pressure (\(P^t\)), and a displacement pressure (\(P_d\)). A variable distribution of displacement pressures was obtained using a cumulative distribution function based on the Young-Laplace equation (described in Section 5.3). Entry pressures
were calculated using Eq. (5.11), applying the obtained displacement pressures and setting the water saturation to \((1 - S_{gcr})\). The ratio between terminal pressure and entry pressure was taken to be 0.57 throughout the domain (Mumford et al., 2009b; Gerhard & Kueper, 2003). Thresholds for drainage \((P^{te})\) and for imbibition \((P^{tt})\) were defined as follows:

\[
P^{te} = P^e + P_w
\]
\[
P^{tt} = P^t + P_w
\]

Gas saturations were obtained using Eq. 5.10. If any block resulted in a gas saturation exceeding \(S_{gcr}\), the gas movement module was called upon. Any blocks with gas saturations at or above \(S_{gcr}\) were tagged. Using the MATLAB image processing toolbox, any connected tagged blocks were identified as part of the same cluster. In searching for connections, only blocks sharing faces were considered (coordination number of 4). Each cluster was looked at individually and assessed for expansion or mobilization, following the rules outlined by Glass et al. (2001) and Li & Yortsos (1995).

The three processes are shown in Figure 5.1, where the hatched squares represent gas-occupied blocks while white squares are fully water saturated grid blocks. In order for a gas cluster to expand into an adjoining block (Figure 5.1(a)), the average gas pressure in a cluster \((P_{ave}^{1,2})\) had to be greater than the drainage threshold of the adjacent block \((P^{te}_3)\) (subscripts refer to block numbers).

For mobilization (Figure 5.1(b)), the minimum drainage threshold of a block located next to a gas cluster \((P^{te}_4)\) had to be less than the threshold for imbibition for a block the gas cluster \((P^{tt}_1)\). Fragmentation occurred when the mobilized block was located within a gas cluster as seen in Figure 5.1(c). In this case the gas from block 2 moved to block 4 (via block 3), fragmenting the original cluster into two gas clusters.

It is useful to characterize the potential for cluster mobilization in a given sand using a critical cluster length. Critical cluster lengths \((h_{crit})\) can be estimated using the capillary pressures at the bottom \((P^{bottom}_c)\) and top \((P^{top}_c)\) of the gas cluster as well as the hydrostatic pressure drop across the height of the cluster, as given by Mumford et al. (2009b) and Glass et al. (2000).

\[
h_{crit} = \frac{P^{top}_c - P^{bottom}_c}{\Delta \rho g}
\]
Values of $h_{crit}$ can be calculated by taking $P_{c}^{top}$ to be the capillary pressure at a gas saturation of 0.3 (using Eq. 5.11) and $P_{c}^{bottom}$ to be half of $P_{c}^{top}$ (Mumford et al., 2009b; Glass et al., 2000). The Bond number ($Bo$) which relates buoyancy forces to capillary forces can also be used as an indication of discrete gas movement (Brooks et al., 1999; Selker et al., 2007; Mumford et al., 2009b).

$$Bo = \frac{\Delta \rho gr^2}{\sigma}$$  \hspace{1cm} (5.15)

where $\Delta \rho$ is the difference in density between the wetting and non-wetting fluids (water and air, respectively), $r$ is the characteristic pore radius, and $\sigma$ is the interfacial tension. Typically, large Bond numbers and short cluster lengths correspond to high permeability soils where gas clusters tend to mobilize easier and faster (Mumford et al., 2009b).

When a bubble mobilized, the pressure in the invading block ($P_4$ from Figure 5.1(b)) was adjusted for the temperature based on conservation of mass between the invading block and the block from which the bubble is leaving ($P_1$), using the Ideal Gas Law:

$$P_4 = \frac{P_1 S_{g1} T_4}{T_1 S_{gcr}}$$  \hspace{1cm} (5.16)

Similarly, each time a gas cluster expanded or mobilized, the pressure within a gas cluster was modified. Since the temperature in a gas cluster was different at each block, the average temperature within a cluster was used and the pressure was adjusted in order to have the same average gas mass and pressure in each cluster block.

At the end of the gas movement module, if a bubble expanded or moved, new aqueous concentrations were calculated keeping the aqueous mass constant.

After the gas movement step, the water and gas concentrations and saturations for each grid block were calculated using the total mass ($M$) from the gas movement module and the equilibrium equation (5.10). If the equilibrium calculations resulted in gas saturations of zero (due to spatial change in temperature) in nodes where bubble mobilization or expansion occurred, the bubble would collapse. Bubble collapse would result in the mass in the gas phase being transferred to the aqueous phase:

$$C_w = \frac{M}{\phi}$$  \hspace{1cm} (5.17)
Figure 5.1: Gas clusters before and after (a) expansion (b) mobilization and (c) fragmentation (hatched squares represent gas occupied grid blocks while white squares are fully water saturated blocks); adapted from Wagner et al. (1997)
After each time step an energy and mass balance was performed on the system.

### 5.3 Simulation Description

To examine the effect of heat on bubble formation and resulting mass distribution, several soil and temperature scenarios were simulated using the ETM-MIP model. The simulation consisted of a 34 cm by 34 cm cell that represented a vertical cross section of the subsurface. Six electrodes were used in the simulation of ERH, using one phase heating. A Darcy velocity of $5 \times 10^{-6} \, m/s$ was specified at the left boundary. Three soils with different permeabilities and displacement pressures were examined and the corresponding parameters are listed in Table 5.1. Table 5.1 also lists the calculated critical cluster lengths and Bond numbers based on Eqs. (5.14) and (5.15) respectively.

At the beginning of the simulations, the subsurface was fully water saturated and no dissolved gases were present in the subsurface. A uniform subsurface temperature of $20^\circ C$ was assumed. The heat and mass transport boundary conditions were zero flux (Type II) for the top and bottom of the system, while a known water flow at $20^\circ C$ was specified on the left side boundary. In addition, the water pressure at the top of the domain was set to atmospheric pressure. All voltage boundary conditions were zero flux, assuming no current flow outside the boundaries of the simulated area. The linear equations for the discretized current, groundwater flow, heat, and mass transport were evaluated using the backslash ($\backslash$) operation in MATLAB which uses appropriate algorithms depending on the structure of the matrix. The ETM model is fully described in Chapter 2.

The organic compound chosen for this study was 1,1,1 TCA, a common groundwater contaminant with a relatively low boiling point and a solubility of $1,330 \, mg/L$ (at $20^\circ C$) (Lide, 2006; Pankow & Johnson, 1996). Table 5.2 lists the properties of the compound as well as the initial conditions of the simulated scenarios. An initial aqueous mass distribution of $1200 \, mg/L$ 1,1,1 TCA was specified in the center of the simulation area, presented on Figure 5.2. Each case was simulated at three target temperatures. To control the subsurface temperature, the power was turned off when the maximum temperature anywhere in the domain reached $70^\circ C$, $80^\circ C$, or $90^\circ C$ and then turned on once the maximum temperature dropped below the target level.

The reference permeabilities ($k_{rref}$), displacement pressures ($P_{dref}$), pore size distribution index ($\lambda$), and residual water saturations ($S_{wr}$) were obtained from Kueper (1989) and were used to develop a variable pore radius matrix based on the Young-Laplace rela-
Table 5.1: Simulation Scenarios

<table>
<thead>
<tr>
<th>Ottawa sand fraction (units)</th>
<th>Reference permeability $(cm^2)$</th>
<th>Mean pore radius (mm)</th>
<th>$P_{dref}$ $(cm)$</th>
<th>$\lambda$ (-)</th>
<th>$S_{wr}$ (-)</th>
<th>Bond number</th>
<th>$h_{crit}$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#25</td>
<td>$2 \times 10^{-6}$</td>
<td>0.257</td>
<td>4.43</td>
<td>3.51</td>
<td>0.069</td>
<td>$8.7 \times 10^{-3}$</td>
<td>2.5</td>
</tr>
<tr>
<td>#50</td>
<td>$5.3 \times 10^{-7}$</td>
<td>0.077</td>
<td>13.5</td>
<td>2.49</td>
<td>0.098</td>
<td>$7.8 \times 10^{-4}$</td>
<td>7.9</td>
</tr>
<tr>
<td>#70</td>
<td>$8.2 \times 10^{-8}$</td>
<td>0.034</td>
<td>33.1</td>
<td>3.30</td>
<td>0.189</td>
<td>$1.5 \times 10^{-4}$</td>
<td>19</td>
</tr>
</tbody>
</table>

Source: Kueper (1989)

To calculate the locally variable displacement pressures ($P_d$) in macroscopically homogeneous soils, the Young-Laplace equation and the variable pore radius matrix were used. Permeability distributions ($k$) were obtained using the Leverett relationship (Eq. 5.18), using the reference displacement pressures and permeabilities, where the porosity and surface tension were kept constant (Leverett, 1941; Kueper & Frind, 1988; Kueper & McWhorter, 1992).

$$k = \left( \frac{P_{dref}}{P_d} \right)^2 k_{ref}$$

(5.18)

Figure 5.2: Initial aqueous concentration (mg/L) in a vertical slice of the subsurface; red circles represent electrodes

The rise in subsurface temperature increased the velocity (due to a decrease in water viscosity) and produced buoyant groundwater flow in the heated zone (due to change in water density). The degree of buoyant flow depended on soil permeability, subsurface temperature, and groundwater velocity. If buoyant flow existed, the resulting temperature and contaminant distributions differed from a case where no convective flow was
CHAPTER 5. DISCRETE GAS BUBBLE FORMATION

Table 5.2: System Initial Conditions and Properties of 1,1,1 TCA

| $L_z, L_y$ | Simulation depth and width (mm) | 340, 340 |
| $dx, dy$ | Grid discretization (mm) | 4, 4 |
| $dt$ | Time step (s) | 10 |
| $n$ | Soil porosity (−) | 0.35 |
| $K_H$ | Soil Thermal Conductivity (W/mK)$^a$ | 2 |
| $T$ | Initial Temperature (°C) | 20 |
| $q$ | Darcy Velocity (m/s) | $5 \times 10^{-6}$ |
| $P_w$ | Water Vapour Pressure (Pa)$^b$ | $2.3 \times 10^3$ |
| $\sigma$ | Water Interfacial Tension (N/m) | 0.072 |
| $S$ | 1,1,1- TCA Solubility (mg/L)$^b$ | 1330 |
| $Bp$ | 1,1,1- TCA Boiling Point (°C)$^c$ | 74 |
| $H$ | Henry’s Coefficient (Pa.m$^3$/mol)$^b$ | $1.3 \times 10^3$ |
| $C_0$ | Initial Concentration (mg/L) | 1200 |
| $S_{gcr}$ | Critical Gas Saturation (−)$^d$ | 0.3 |


present (Chapter 3). When describing the simulations, the term “buoyant flow” referred to temperature induced convective groundwater flow, rather than gas buoyancy, unless otherwise specified.

5.4 Simulation Results

Thirty minutes of heating was simulated for all three scenarios, and temperatures, gas saturations and aqueous concentrations were recorded throughout the simulations. For ease of reporting the results, the “heated zone” was taken to represent the hatched area in Figure 5.3(a), in between the six electrodes. Although this zone corresponds to the highest temperature distribution, heating is not limited to this area.

At the beginning of the simulations, the dissolved mass was transported accordingly to the advection-dispersion equation. Once the subsurface temperature increased to a level where the total gas pressure was greater than the confining pressure, gas bubbles started forming. When the gas saturation reached $S_{gcr}$, the gas movement module was called and the contaminant mass was also transported by gas movement. The following section describes the results for the three soils for a single realization of the pore space.
5.4.1 Case 1 - Simulation of #25 Ottawa Sand

The temperature distribution for #25 Ottawa sand is presented in Figure 5.3. Bubble formation started when temperatures reached 65°C, in the area with the highest concentration and temperature and lowest confining pressure. Since incoming groundwater flow was simulated from the left side and temperature induced buoyant (convective) flow caused upward groundwater movement, this location was near the upper right electrode. To check the temperature at which bubble formation was first observed, the sum of the water vapour pressure and gas pressure was calculated at different temperatures. The gas pressure was based on Henry’s law (Gossett, 1987) using a concentration of 1200 mg/L 1,1,1 TCA. The calculated temperature at which this combined pressure was equal to atmospheric (upper boundary water pressure) was also 65°C.

Discrete bubble formation was followed by expansion and mobilization of the gas clusters within the heated section once gas saturation reached $S_{gcr}$. The effect of temperature on gas bubble formation and movement in #25 Ottawa sand is presented in Figure 5.4(a). Mass transfer of 1,1,1 TCA from the aqueous to the gas phase within the heated zone was observed at all temperatures, however gas phase mobilization only occurred at operating temperatures of 80°C and 90°C. High temperatures resulted in higher gas pressures leading to greater bubble expansion. In addition, higher temperatures resulted in increased groundwater velocities through the heated zone leading to faster advective mass transport. Rapid advective mass transport to the edge of the heating zone, along with the increased pressures, produced cluster expansion which led to mobilization of gas bubbles. As the cluster extended upward, the hydrostatic pressure decreased with elevation, promoting further mobilization.
CHAPTER 5. DISCRETE GAS BUBBLE FORMATION

Gas saturations with time in #25 Ottawa sand at 90°C are presented in Figure 5.5 where bubble activity was dominated by mobilization events. Although expansion also took place, mobilization occurred frequently, moving the contaminated mass upward. Once the bubbles reached cooler zones, they collapsed and mass was transferred from the gas phase to the aqueous phase. In addition, the progression of bubble movement followed the same pathways, corresponding to lowest entry pressures (i.e. largest pore radius) as shown in Figure 5.5, particularly Figures 5.5(c), 5.5(d), 5.5(f), and 5.5(g). This resulted in an accumulation of aqueous mass in areas of frequent gas mobilization and cooling-induced collapse, as seen in the resulting aqueous concentrations and enlarged the contaminated area (Figure 5.6(a), 90°C). The extent of contamination may possibly be greater than shown in this study since the extent of bubble mobilization was limited to the size of the modelled domain.

The aqueous concentration distributions modelled with just ETM, with no discrete bubble formation and movement, is presented in Figure 5.7(a). For higher temperature scenarios the ETM-MIP model predicted aqueous concentrations above the heated zone which was not captured by the advective (ETM) model. For lower temperatures, lower concentrations within the heated zone were predicted by the ETM-MIP model due to transfer of mass from the aqueous phase to the gas phase. These results demonstrate that although the presence of a discrete gas phase can result in rapid mass transport out of the heated zone, it does not significantly expand the area of impacted groundwater unless mobilization occurs.

The general upward movement of the aqueous mass observed in the high permeability soils at all temperatures was due to buoyant (convective) flow which developed as the subsurface was heated (Chapter 3). However, the presence of aqueous mass at the top of the modelled area in the 90°C scenario is also due to bubble mobilization. The distinction between mass movement due to temperature induced buoyant flow as opposed to gas mobilization is best observed by comparing the concentrations in Figures 5.6 (gas phase modelled with buoyant flow) and 5.7 (no gas phase modelled with buoyant flow occurring).

5.4.2 Case 2 - Simulation of #50 Ottawa Sand

Gas saturations and aqueous concentration after 30 minutes of heating #50 Ottawa sand are presented in Figures 5.4(b) and 5.6(b), respectively. Bubble mobilization in #50 Ottawa sand occurred less frequently than in the more permeable soil (#25 Ottawa
Figure 5.4: Gas saturations for different sands at 70°C, 80°C and 90°C, after approximately 9 min of heating
Figure 5.5: Gas saturation in #25 Ottawa sand at different times during heating. Maximum subsurface temperatures are indicated in brackets.
sand) and the extent of bubble movement was limited. The same trend was observed in experiments conducted by Mumford et al. (2009b).

Since #50 Ottawa sand had longer critical cluster lengths than #25 Ottawa sand, more bubble growth (expansion) needed to occur before bubble mobilization could take place. At 90°C, increased cluster gas pressure led to increased gas expansion, resulting in bubble mobilization. However, bubble mobilization occurred less often than in the more permeable soil allowing for more time for advective mass movement out of the heated area.

The 90°C scenario resulted in high aqueous concentrations at the top of the contaminated zone (Figure 5.6(b)) and similarly to #25 Ottawa sand, the concentration profiles with and without gas inclusion differed extensively, especially at 90°C (Figure 5.7(b)).

### 5.4.3 Case 3 - Simulation of #75 Ottawa Sand

Gas saturation (Figure 5.4(c)) and aqueous concentration profiles (Figure 5.6(c)) for #75 Ottawa sand, were similar to those of #50 Ottawa sand, especially at lower temperatures. At higher temperatures, rapid aqueous mass transport out of the heated zone occurred in #75 Ottawa sand through gas expansion where the gas bubbles either collapsed or got trapped by higher entry pressures. Since #75 Ottawa sand has very high critical cluster lengths, bubble activity was almost exclusively limited to bubble expansion (very little bubble mobilization occurred). This transfer of aqueous mass to the gas phase was especially pronounced at 90°C, where the heated zone was mostly gas filled (Figure 5.4(c), 90°C), resulting in low aqueous concentrations (Figure 5.6(c)). Using a conventional transport model, the aqueous concentration in #75 Ottawa sand would be overestimated in the central portion of the heated zone and underestimated at the edge, when heated to 90°C (Figure 5.7(c)).

Regardless of temperature or soil type, mobilization only occurred for a short period of time when the combination of subsurface temperature and sufficient mass was present in the heated zone. At the beginning of the simulation, temperatures were too low to induce bubble growth, whereas at the end of the simulation, significant amount of mass had moved out of the heated zone by both gas movement and aqueous advection. The effect of this can also be seen in the concentration distributions after 30 minutes of heating (Figure 5.6). Since bubble movement and collapse occurred for a short period of time and in the early part of the simulation (Figure 5.5), significant amount of spread
Figure 5.6: Concentration contours for different sands at 70°C, 80°C and 90°C, after 30 minutes of heating (last contour represents the maximum contaminant level (MCL) for 1,1,1 TCA (0.2 mg/L))
Conc Contours (mg/L) at time 1800 seconds, temp= 90°C, hd= 13.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 80°C, hd= 13.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 80°C, hd= 33.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 70°C, hd= 13.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 90°C, hd= 33.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 80°C, hd= 4.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 90°C, hd= 4.00 cm, no gas
Conc Contours (mg/L) at time 1800 seconds, temp= 70°C, hd= 4.00 cm, no gas

Figure 5.7: Concentration contours for different sands at 70°C, 80°C and 90°C, after 30 minutes of heating, gas phase not modelled (last contour represents MCL for 1,1,1 TCA (0.2 mg/L))
of the aqueous concentration was observed. Aqueous concentrations examined right after bubble mobilization resulted in much more discrete aqueous mass distribution, the location of the mass coinciding with the location of bubble movement and collapse.

5.5 Discussion

5.5.1 Entry Pressure

Longer cluster lengths occur in soils with higher entry pressures (Mumford et al., 2009b). In addition, since entry pressures are inversely related to the pore radius (Young-Laplace), less permeable soils have higher entry pressures and therefore longer cluster lengths. These values ($P_e$, $k$ and $h_{crit}$) are listed in Table 5.1 for the three modelled soils.

Expansion of gas bubbles to adjacent blocks is a function of the overall gas pressure within a cluster. Once the cluster pressure overcomes the entry pressure of an adjacent block, it expands into that grid block. The simulations showed that in less permeable soils, bubble expansion was the dominant gas movement mechanism due to longer cluster lengths required for mobilization. The discontinuous bubble growth and expansion acted as rapid mass transport pathway out of the heated zone where the bubbles became trapped or collapsed transferring the mass from the gas phase to the aqueous phase. This mass built up on the edge of the heated zone eventually led to mobilization events but the frequency of the events depended on the soil critical cluster lengths. Heating of the higher permeability soil (#25 Ottawa sand) resulted in more frequent bubble mobilization and higher bubble elevations than in less permeable soils. Figure 5.8 presents the maximum bubble elevation of different sands at different temperatures. The difference in bubble elevation was especially evident between the coarse #25 Ottawa sand and the other soils. The variation in bubble elevation was due to the time between mobilization events, which was longer for less permeable soils since longer critical cluster lengths were required for mobilization. This led to more time for advective transport of mass out of the heated zone, leaving less mass for mobilization and therefore limiting larger-scale vertical mobilization.

The effect of subsurface temperature on maximum bubble elevation is also shown on Figure 5.8. Bubble elevation was more impacted by the subsurface temperature in #25 Ottawa sand than in finer soils. In addition, since bubbles mobilized all the way to the top of the modelled domain (in #25 Ottawa sand heated to 90°C), bubble elevation may have been higher if a larger domain was used. Maximum bubble elevation for #50 and
#75 Ottawa sands did not significantly vary until the temperature reached 90°C, showing that significant gas mobilization did not occur in finer soils at lower target temperatures.

Lateral and downward movement of the bubbles was observed in lower permeable soils and not in #25 Ottawa sand, especially at high temperatures. In the more permeable soil, gas buoyancy was a larger contributing factor to bubble movement (i.e. larger Bond numbers) and therefore all bubbles moved upwards towards decreasing water pressure. In less permeable soils surface tension forces dominated and bubble expansion and mobilization was governed by the local entry pressures.

The presence of other dissolved gases in the groundwater, non-zero upgradient concentrations, as well as, kinetic mass transfer limitations would all slow the collapse of the gas bubbles. Therefore these modelled scenarios may be nonconservative in terms of how much gas mobilization may actually occur.

### 5.5.2 Groundwater Velocity

To limit the amount of cooling from incoming water, groundwater control is often implemented during the application of thermal remediation technologies (U.S. Army Corps of Engineers, 2009). This can be done through sheet pile or in situ barrier walls or dewatering wells. To examine the effect of low groundwater flow on discontinuous gas formation
and movement, a groundwater velocity of $5 \times 10^{-8} \, \text{m/s}$ was used and the simulations were repeated.

The effect of groundwater velocity on the aqueous concentrations after 30 minutes of heating to different temperatures is presented in Figure 5.9. Lowered groundwater velocity limited cooling from incoming water and resulted in circular buoyant flow through the heated region. This led to more uniform subsurface temperatures and aqueous concentration profiles (Figure 5.9) compared with higher groundwater velocities (Figure 5.6).

Maximum bubble elevation for different velocities in the three soils is presented in Figure 5.8. For the 80°C scenario, bubble elevations were higher at lower groundwater velocities. For finer soils this is due to less mass transfer from the gas to aqueous phase at the edge of the heated zone which allowed continued bubble growth to reach critical cluster lengths. For coarser soils, lower dissolution rates allowed for mobilized or trapped bubbles to remain in the soil longer, providing a pipeline route for larger-scale vertical mobilization through repeated coalescence events. However, at an operating temperatures of 90°C, bubbles reached higher elevations with higher groundwater velocities for #25 and #50 Ottawa sands. This difference may be due to the more circular, convective groundwater movement that results with lower groundwater velocities (Chapter 3), transporting the mass on top of the heated zone to the sides of the heated area, thereby reducing the amount of mass available for mobilization. Alternatively, since this simulation represents a single realization of a random pore field and the bubble elevations for the two velocities are similar, the difference could be a manifestation of the variability of entry pressures.

### 5.5.3 Solubility Limit and Mass Removal

The movement of discrete bubbles resulted in high aqueous concentrations outside the heated zone, in areas of repeated coalescence events. This was especially noticeable in low permeability soils with low groundwater velocities where dissolution rates were lower as shown in Figures 5.9(b) and 5.9(c) (90°C). High concentrations were also observed at the bottom of the heated zone in #75 Ottawa sand (Figure 5.9(c), 90°C) due to gas bubble expansion and collapse within the heated zone. These high concentrations were above the solubility limit of 1,1,1 TCA (1330 mg/L) signifying the possible formation of NAPL, which was not modelled using a conventional transport model (not shown). Additionally, the solubility of 1,1,1 TCA decreases with temperature (Pankow & Cherry, 1996) which
Figure 5.9: Concentration contours for the different sands at 70°C, 80°C and 90°C, after 30 minutes of heating, low groundwater velocity (last contour represents MCL for 1,1,1 TCA (0.2 mg/L)). Possible NAPL formation is seen in the 90°C scenario in (b) and (c), where the concentrations are above 1330 mg/L.
could result in significant NAPL formation at higher operating temperatures.

To examine the efficiency of mass removal out of the heated zone through bubble mobilization and the transfer of aqueous mass to the gas phase, the mass outside of the original contaminated area (defined in Figure 5.2 or by the heated zone shown in Figure 5.3(a)), was calculated with time for all three soils at different temperatures and velocity scenarios.

Figures 5.10(a) and 5.10(c) show the mass outside the heated zone when no gas phase is modelled with high and low groundwater velocities, respectively. The highest removal rate occurred in the most permeable soil at the highest temperature, since advection is the dominant mass transfer mechanism and velocities within the heated zone are highest in #25 Ottawa sand at the highest temperature.

The transport of mass out of the source zone when discontinuous gas phase is modelled is presented in Figures 5.10(b) and 5.10(d), with high and low groundwater velocities, respectively. Mobilization of bubbles is represented by the rapid increases in mass removed which only occurred in the higher temperature scenarios. Bubble mobilization stops around 12 minutes, due to the amount of mass that is removed by advection and bubble mobilization, leaving insufficient concentration in the source zone for bubble mobilization.

Figure 5.10 highlights similar trends that the concentration plots revealed (Figures 5.6 and 5.7), regarding the prediction of concentration using an advective model only. Figures 5.10(b) and 5.10(d) demonstrate how quickly mass moves out of the source zone if discontinuous bubble movement is included. This is especially significant for #50 Ottawa sand at 90°C, where the total mass removed at 12 minutes with gas phase modelled is almost equivalent to the mass removed at 30 minutes, with no gas phase modelled. In addition, at low groundwater velocities, the total mass removed at the end of heating is almost double the amount if no bubbles are modelled. This shows that discrete bubble expansion and mobilization may be an important mass transport mechanisms for less permeable soils. The mass removed would be greatly underestimated using an advective model alone.

Figure 5.10 also shows that bubble expansion and mobilization are prevalent at the beginning of the simulation, when enough mass is present in the source zone and has not yet been removed by advection or gas movement. If NAPL was present in the subsurface, it would act as a continuous source of mass and therefore lead to a much longer period of gas generation and movement.
Figure 5.10: Mass outside the source zone ($M_0$ = initial mass = 0.0218 mol)

(a) High groundwater velocity, no gas phase modelled

(b) High groundwater velocity

(c) Low groundwater velocity, no gas phase modelled

(d) Low groundwater velocity

#25 sand, T=90°C
#25 sand, T=80°C
#25 sand, T=70°C
#50 sand, T=90°C
#50 sand, T=80°C
#50 sand, T=70°C
#75 sand, T=90°C
#75 sand, T=80°C
#75 sand, T=70°C
5.6 Conclusions/Implications

This study examined how site conditions and subsurface temperatures resulting from ERH operation affect the formation, expansion and mobilization of discrete gas clusters. Three soil scenarios with different entry pressures were examined at three operating temperatures and two groundwater velocities. Expansion of gas bubbles was observed in the heated zones for all three of the soil types simulated. However, gas mobilization only occurred at higher temperatures. Soils with lower entry pressures experienced more frequent mobilization events leading to a greater impacted area. Gas expansion and mobilization in high entry pressure soils led to a significant amount of mass removal out of the heated zone, especially at low velocities, showing that the formation of a discrete gas phase in low permeability soils could be an important mass transport mechanism during thermal remediation.

This study outlines some important considerations when using ERH at contaminated sites. ERH is typically operated at water boiling temperatures in order to produce a continuous gas phase which can be extracted and treated. However, during pre-heating operations or at the edge of the heating zone, lower temperature may result in discrete gas formation. Current conceptual (and computer) models do not include the formation of discrete gas bubbles. This research showed that aqueous concentrations could be significantly impacted if formation of a discrete gas phase was considered. This is especially true for low entry pressure soils where gas mobilization could result in the contamination of unsuspected areas. In addition, even with an aqueous phase source below the solubility limit, concentrations over the solubility are possible due to repeated expansion and mobilization events, especially in high pressure entry soils at low groundwater velocities.

Lastly, the formation and mobilization of discrete gas bubbles is dependent on subsurface temperature as well as contaminant concentrations. In this study, a finite mass of 1,1,1 TCA was assumed and with only aqueous phase contamination, it was found that gas mobilization was limited to a time when temperature and aqueous concentrations were high. However, if NAPL phase was present, the duration and extent of bubble growth and mobilization would be much greater. It is possible that bubble growth and mobilization would occur even at lower temperatures ($70^\circ$C), leading to widespread contamination. This scenario should be studied further to understand the potential risks, and possibly remedial benefits, of heating NAPL sources to below water boiling temperatures.
Chapter 6

Conclusions and Recommendations

Any knowledge that doesn’t lead to new questions quickly dies out:
it fails to maintain the temperature required for sustaining life.

Wisława Szymborska, 1923 -

6.1 Overall Conclusions

This thesis examined the effect of sub-boiling subsurface temperatures on mass and energy distributions using a newly developed 2D electro-thermal model capable of simulating a contaminant site heated with ERH. The topics investigated include: the onset and effect of temperature induced buoyant flow, soil heterogeneity, and discrete bubble formation. Based on the results from this research, the following overall conclusions were made:

1. Temperature induced buoyant flow impacts groundwater flow and mass transport. This effect was observed in 2D experiments and simulated with an electro-thermal model (Chapter 2).

2. Modelling of low temperature remediation activities requires the inclusion of temperature dependent properties such as water density and viscosity (Chapter 2).

3. The strength of buoyant flow in porous media depends on the subsurface temperature as well as groundwater velocities. The onset of buoyant flow is a function of Rayleigh and thermal Peclet numbers. This relationship, referred to as the buoyancy number, can be simplified in terms of temperature, hydraulic gradient and thermal expansion coefficient (Chapter 3).
4. Buoyancy ratios greater than unity result in buoyant flow. For a contaminated site heated for 200 days to 80°C, buoyant flow significantly impacts contaminant transport when the buoyancy ratio is above one and Rayleigh number is over 60 (Chapter 3).

5. Modelling results show a dependence of energy distribution on the soil electrical conductivity (EC). Higher EC values result in stronger buoyant flow and faster heating rates. The effect of EC is independent of the level of soil heterogeneity examined (Chapter 4).

6. Groundwater flux significantly effects mass and energy distributions. Lower flux values result in stronger buoyant flow leading to greater upward movement of solute and energy plumes. In addition, buoyant flow can dominate over flow through higher permeability zones and override heterogeneity effects. The effect of applied groundwater flux on heat and mass distribution is dependent on the level of heterogeneity, within the range that was examined (Chapter 4).

7. Simulations using the electro-thermal model combined with the macroscopic invasion percolation (MIP) model, show discrete gas bubble formation in soils with different entry pressures at different subsurface temperatures (Chapter 5).

8. Gas movement mechanisms differ depending on the soil entry pressures. In less permeable soils (high entry pressures), such as silty sands, gas expansion dominates due to the longer cluster lengths required for mobilization. For these types of soils, the growth and expansion of discrete bubbles provides a rapid mass transport pathway out of the heated zone. Once bubbles reach colder zones, they collapse and transfer the mass from the gas phase to the aqueous phase. Downward expansion of bubbles can occur in low permeability soils due to low Bond numbers (Chapter 5).

9. In more permeable soils, such as clean sands, discrete gas mobilization is extensive, especially at higher temperatures (Chapter 5).

10. The elevation of bubble mobilization depends on the time between mobilization events, which is a function of critical cluster lengths. Therefore, higher bubble elevations and more frequent mobilization events occur in more permeable soils (Chapter 5).
11. Simulations with initial aqueous phase contamination show that concentrations over the solubility limit of the contaminant are possible due to repeated expansion, mobilization and condensation events. This is especially true for low permeability soil at low groundwater velocities (Chapter 5).

12. Sub-boiling temperatures, either during ERH heat-up and cool-down phases or from operating ERH at low temperatures, can result in discrete bubble growth and mobilization (Chapter 5).

6.2 Contributions

This work resulted in several original contributions:

1. The 2D ETM model is the first fully combined electro-thermal model with temperature dependent properties. It is capable of simulating power and temperature distributions resulting from ERH operations, as well as, temperature induced buoyant flow and mass transport (Chapter 2).

2. The buoyancy number, which indicates the onset of buoyant flow, was derived in terms of temperature, hydraulic gradient and thermal expansion coefficient. This simplification makes the buoyancy number more applicable to subsurface thermal activities. It can be used to check if buoyant flow is occurring at a given site, or alternatively if designing low temperature ERH, the buoyancy number can determine the operating temperature resulting in buoyant flow (Chapter 3).

3. This is the first study to examine the effect of temperature induced buoyant flow on mass transport. The criteria developed to determine if there is significant impact on mass distribution is the first relationship established between site conditions, operating temperatures and mass transport (Chapter 3).

4. The effect of heterogeneity with changing electrical conductivity values has not been studied before. These results quantify the effects of EC and indicate shorter heating times with higher electrical conductivity values. The independence of EC on heterogeneity has not been demonstrated before (Chapter 4).

5. This is the first modelling study showing buoyant flow overriding flow through higher permeability zones (Chapter 4).
6. The discrete bubble formation and mobilization simulations provide useful information about the type of soil that would result in significant bubbling as a result of thermal remediation. This research provides the first evidence of discrete bubble formation during thermal subsurface remediation (Chapter 5).

7. The simulations using the ETM-MIP model show that concentrations over the solubility limit of the contaminant could develop during heating of a site initially contaminated with an aqueous phase (below solubility limit). In addition, the simulations demonstrate that bubble expansion and movement can serve as an important mass transport mechanism for low permeability soils. These results provide insight into the effects of a discontinuous gas phase during thermal remediation (Chapter 5).

6.3 Future Work

Based on the results from this research, several recommendations for future work are outlined:

1. Extend the electro-thermal model to three dimensions and incorporate a total variation diminishing (TVD) scheme to simulate sharp concentration fronts. This would allow for a more accurate representation of mass transport during buoyant flow.

2. Incorporate the electro-thermal model with a multiphase simulator, such as COMP-SIM (Sleep & Sykes, 1993a), to simulate thermal remediation of NAPL contaminated sites.

3. The criteria established in Chapter 3 for buoyant flow impacting mass transport is specific to the time simulated (200 days) and subsurface temperature (80°C). A more general criteria should be established by repeating the simulations at different temperatures and times.

4. Conduct experiments to observe the onset of buoyant flow with time, under different temperatures and hydraulic gradients. This would validate the buoyancy criteria established in Chapter 3.

5. Simulate heterogeneity scenarios using a bigger domain and run simulations for a longer time period.

7. Incorporate a relationship between porosity and soil permeability to generate a variable EC distribution. Examine the effect of variable EC on energy and mass transport.

8. Simulate the heating of a NAPL contaminated sites with the combined ETM-MIP model and examine the extent of bubble formation and mobilization.

9. Use the ETM-MIP model to simulate the heating of sites contaminated with more than one compound and with dissolved gases in the subsurface.
Bibliography


Appendix A

ERH Background Theory

A.1 ERH Process and Governing Equations

Typically, ERH is performed using 3 phase or 6 phase heating where a series of electrodes are placed in the soil in a hexagonal or triangular pattern and connected to an AC voltage source (Figure A.1). The current generated is conducted through the soil and since the soil acts as resistance to the current, energy is dissipated and transformed into heat (U.S. EPA, 1997; Vermeulen & McGee, 2000). The increase in temperature increases the vapour pressures, solubility, volatility, and diffusion of DNAPLs, while lowering viscosity, and sorption coefficients (Looney & Falta, 2000; Boulding & Ginn, 2004). Table A.1 summarizes these effects. Moreover, temperature change can have an effect on heat transfer properties such as electrical and thermal conductivities.

The governing equations of voltage and current distribution through soil can be described using Maxwell and Ohm equations.

\[ \nabla \cdot \vec{J} = -\frac{\partial \rho_v}{\partial t} \quad (A.1) \]

\[ \nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t} \quad (A.2) \]

\[ \nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} = \vec{J} + \epsilon \frac{\partial \vec{E}}{\partial t} \quad (A.3) \]

where \( \vec{J} \) is the current density (A/m\(^2\)), \( \rho_v \) is electric charge density (C/m\(^3\)), \( \vec{E} \) is the electric field strength (V/m), \( \vec{B} \) is the magnetic flux density, \( \vec{H} \) is the magnetic field strength (A/m), and \( \vec{D} \) is electric flux density (C/m\(^2\)). \( \frac{\partial \vec{D}}{\partial t} \) is referred to as the displacement current density and can be rewritten as \( \epsilon \frac{\partial \vec{E}}{\partial t} \), where \( \epsilon \) is the electric permittivity.
Figure A.1: Typical Three Electrode ERH Layout

Table A.1: Temperature Dependent Properties

<table>
<thead>
<tr>
<th>Fate and Transport Property</th>
<th>Effect as Temperature Increases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid Density</td>
<td>Decreases moderately (less than 100 percent)</td>
</tr>
<tr>
<td>Vapour Pressure</td>
<td>Increases significantly (10 to 20 fold)</td>
</tr>
<tr>
<td>Liquid viscosity</td>
<td>Decreases significantly until boiling point and drops markedly upon conversion from liquid to vapour</td>
</tr>
<tr>
<td>Vapour viscosity</td>
<td>Increases slightly as vapour temperature increases</td>
</tr>
<tr>
<td>Diffusivity</td>
<td>Increases</td>
</tr>
<tr>
<td>Solubility</td>
<td>Increases as temperature increases</td>
</tr>
<tr>
<td>Henrys constant</td>
<td>Increases (more likely to volatilize from water)</td>
</tr>
<tr>
<td>Partition coefficient</td>
<td>Decreases (less likely to partition to organic matter in soil)</td>
</tr>
<tr>
<td>Biological degradation</td>
<td>Increases (may decrease at very high temperatures)</td>
</tr>
<tr>
<td>Abiotic degradation</td>
<td>Increases</td>
</tr>
</tbody>
</table>

Source: U.S. EPA (2004); Davis (1997)
Table A.2: Governing Equation in the Electrical Model

<table>
<thead>
<tr>
<th>All Frequencies</th>
<th>Low Frequencies</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$</td>
<td>$\nabla \times \vec{E} = 0$</td>
</tr>
<tr>
<td>$\nabla \times \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t}$</td>
<td>$\nabla \times \vec{H} = \vec{J}$</td>
</tr>
<tr>
<td>$\nabla \cdot \vec{J} = -\frac{\partial \rho}{\partial t}$</td>
<td>$\nabla \cdot \vec{J} = \nabla \cdot (\sigma \nabla V) = -\frac{\partial \rho}{\partial t} = 0$</td>
</tr>
<tr>
<td>$\vec{J} = \sigma \vec{E}$</td>
<td>$U = \sigma</td>
</tr>
</tbody>
</table>

These equations can be applied to calculate the electrical field of any material at any frequency. However since ERH is usually performed at low frequencies (50-60 Hz), the above formulas can be simplified by removing several terms with negligible contributions. Table A.2 summarizes low frequency formulas arising from such simplifications. A more detailed explanation follows.

At high frequencies the magnetic fields induce additional electric fields and hence additional currents, as seen by Equation A.3. However, as the frequency approaches zero, the currents which flow between the electrodes approach those that would flow in static fields (Hiebert et al., 1986). In other words, the time-variant portion of the magnetic field is neglected and Equation A.3 is replaced by

$$\nabla \times \vec{E} = 0 \quad (A.4)$$

Assuming the displacement currents ($\frac{\partial \vec{D}}{\partial t}$) are insignificant compared to the conduction currents ($\sigma \vec{E}$) at low frequencies (Vermeulen et al., 1979), Equation A.3 becomes:

$$\nabla \times \vec{H} = \vec{J} \quad (A.5)$$

This simplification can be used, as long as the largest system dimension is much less than any electromagnetic wavelength measured within the system (Hiebert et al., 1986; Hiebert, 1987).

In order to model the energy within the soil during the ERH process, Ohms Law is used to relate electrical conductivity ($\sigma$), electrical potential ($V$), and current density ($J$).

$$\vec{J} = \sigma \vec{E} \quad (A.6)$$
Since the curl of the electric field is zero (Eq. A.4), this implies that the electric field can be expressed in terms of a gradient of a function $V$ \[^1\] and Equation A.6 becomes:

$$\vec{J} = -\sigma \nabla V$$  \hfill (A.7)

Combining Equations A.1 and A.7 yields

$$\frac{\partial \rho}{\partial t} = \nabla \cdot (\sigma \nabla V)$$  \hfill (A.8)

Since there is no accumulation of charge in the soil, Equation A.8 will equal zero everywhere except for the electrode locations. For the case where the electrical conductivity does not change (initial conditions), Equation A.8 becomes the Laplace equation:

$$\nabla^2 V = 0$$  \hfill (A.9)

However in most cases $\sigma$ is a function of temperature as well as the amount of water present in the soil (or type of soil). Therefore $\sigma$ varies spatially and cannot be moved outside the divergence operator in Equation A.8. The resulting equation is used to calculated the voltage distribution everywhere except for the electrode locations:

$$\nabla \cdot (\sigma \nabla V) = 0$$  \hfill (A.10)

$$\frac{\partial}{\partial x} \left( \sigma_x \frac{\partial V}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_y \frac{\partial V}{\partial y} \right) + \frac{\partial}{\partial z} \left( \sigma_z \frac{\partial V}{\partial z} \right) = 0$$  \hfill (A.11)

The voltage at the electrodes is a function of time since an alternating voltage source is usually used in ERH. It can be described using the following equation:

$$V = V_o \cos(\omega t + \phi)$$  \hfill (A.12)

where $V_o$ is the peak voltage (V), $\omega$ is the angular velocity (rad/s) which describes how rapidly the curve oscillates, and $\phi$ is called the phase angle (rad). The resulting phase-shifted voltage distribution for three electrodes is shown in Figure A.2. The figure also shows the time dependence of the voltage which must be accounted for when modelling

---

\[^1\]If $\text{curl}(E) = 0$, then $E$ is conservative and a function $f$ exists such that $\nabla f = E$ (Hiebert, 1987).
ERH Section A.2 describes the three methods of modelling this dependence.

Once the voltage distribution is obtained, the electrical field (E) is calculated by taking the gradient of the potential.

\[ E = -\nabla V \]  \hspace{1cm} (A.13)

Finally, the power dissipation (U) in the subsurface can be calculated from the following relationship and used in the heat equation.

\[ U = \sigma |E^2| \]  \hspace{1cm} (A.14)

### A.2 Power Calculations

In order to accurately predict the temperature change in the subsurface, the power generated by the electrodes needs to be properly modelled. To do this, the time dependence of AC voltage must be taken into account. Three methods of modelling this dependence are described in this section. Method 1 involves using the general equation which describes the potential (Eq. A.12), Method 2 uses complex numbers to describe the resulting potential, and Method 3 incorporates root mean square (RMS) values of the voltage. The following description of the methods assumes that the soil electrical conductivity is constant.

The power dissipation can be modelled using just the real portion of the potential and
time-stepping through one power cycle in order to obtain an average power dissipation value (Method 1). However, this can be quite time consuming. Consequently, several authors have modelled the potential and power distribution throughout the soil using different methods. Buettner & Daily (1995) used an analytical method where the current was broken up into real and imaginary values, while Carrigan & Nitao (2000) approached the problem by separating the time dependent portion of the potential from the rest of the solution. This is similar to representing the potential in real and imaginary numbers and averaging the time dependent portion (Method 2). Lastly, Hiebert et al. (1986) and McGee & Vermeulen (2007) separate the voltage distribution into real and imaginary roots with Hiebert et al. (1986) using RMS values for all the voltages (Method 3).

The different methods were analyzed for accurateness, computational time and ease of use. It was found that all methods resulted in the same potential and power distribution but Methods 2 and 3 are much easier to implement and are faster to run than Method 1. ETM used Method 3 to calculated the system power.

A.2.1 Method 1: Time Stepping

The time stepping method prescribes a phase shifted voltage at each electrode. For example, for three electrodes, the electrode boundary conditions would be:

\[
\begin{align*}
V_1 &= V_o^1 \cos(\omega t + \phi_1) \\
V_2 &= V_o^2 \cos(\omega t + \phi_2) \\
V_3 &= V_o^3 \cos(\omega t + \phi_3)
\end{align*}
\]  

(A.15)

where \(V_o^e\) is the voltage amplitude of electrode \(e\) (where \(e = 1, 2\) or \(3\) in this case). The phase shift for three electrodes is 120°, resulting in three \(\phi\) values of 0, 120 and 240, respectively.

The resulting voltage at any point would be:

\[
V_{tot}(x, y, z, t) = V_o^1(x, y, z) \cos(\omega t + \phi_1) + V_o^2(x, y, z) \cos(\omega t + \phi_2) + V_o^3(x, y, z) \cos(\omega t + \phi_3)
\]  

(A.16)

Since this voltage is time dependent, the time stepping method divides one period \((T)\) of the alternating voltage into a number of time steps and calculates the voltage
and subsequently the electric field and power at different times during one period of the alternating voltage. Since the period of a wave is the reciprocal of the frequency and the frequency of alternating current used in North America is 60 Hz, then the voltages and power terms are averaged over a period of $1/60 \text{s}$ at each node of the finite difference grid.

Therefore, the average power of the system is calculated as follows:

$$U_{ave} = \frac{1}{T} \int_0^T U(t) dt = \frac{\sigma}{T} \int_0^T (\nabla V(x,y,z,t))^2 dt$$  \hspace{1cm} (A.17)

As the system is discretized using finite difference technique, the above integral is approximated as:

$$U_{ave} = \frac{\sigma}{n} \sum_{0}^{n} (\nabla V(x,y,z,t))^2$$  \hspace{1cm} (A.18)

where n is the number of time steps per period.

### A.2.2 Method 2: Complex Numbers

Another technique that simplifies the average power calculation relies on the complex number notation. The electrode voltages are transformed using trigonometric identities to obtain the following boundary conditions:

$$V_1 = V_o^1 (\cos(\omega t) \cos(\phi_1) - \sin(\omega t) \sin(\phi_1))$$

$$V_2 = V_o^2 (\cos(\omega t) \cos(\phi_2) - \sin(\omega t) \sin(\phi_2))$$

$$V_3 = V_o^3 (\cos(\omega t) \cos(\phi_3) - \sin(\omega t) \sin(\phi_3))$$  \hspace{1cm} (A.19)

The resulting voltage at any point would then be:

$$V_{tot}(x,y,z,t) = (V_o^1(x,y,z) \cos \phi_1 + V_o^2(x,y,z) \cos \phi_2 + V_o^3(x,y,z) \cos \phi_3 \cos(\omega t)) \cos(\omega t)$$

$$- (V_o^1(x,y,z) \sin \phi_1 + V_o^2(x,y,z) \sin \phi_2 + V_o^3(x,y,z) \sin \phi_3) \sin(\omega t)$$  \hspace{1cm} (A.20)
The equation can be simplified using:

\[
\begin{align*}
\mathbf{V}_1(x, y, z) &= \left( V_1^1(x, y, z) \cos \phi_1 + V_1^2(x, y, z) \cos \phi_2 + V_1^3(x, y, z) \cos \phi_3 \right) \\
\mathbf{V}_2(x, y, z) &= \left( V_2^1(x, y, z) \sin \phi_1 + V_2^2(x, y, z) \sin \phi_2 + V_2^3(x, y, z) \sin \phi_3 \right)
\end{align*}
\]  

(A.21)

And even further simplified using complex notation.

\[
V_{tot}(x, y, z, t) = \mathbf{V}_1 \cos \omega t + \mathbf{V}_2 \sin \omega t = \mathbf{V}_1 - j \mathbf{V}_2
\]  

(A.22)

where \( \mathbf{V}_1 \) and \( \mathbf{V}_2 \) are the real and imaginary roots of the voltage, respectively. This notation can also simplify the power calculation. Instead of time stepping through a period, the average power can be calculated as follows:

\[
U_{ave} = \frac{1}{T} \int U(t) dt = \frac{\sigma}{T} \int \left( \mathbf{V}_1(x, y, z) \cos \omega t - \mathbf{V}_2(x, y, z) \sin \omega t \right)^2 dt
\]

\[
= \frac{\sigma}{T} \int \left( \mathbf{V}_1^1(x, y, z) \cos \phi_1 + \mathbf{V}_1^2(x, y, z) \cos \phi_2 + \mathbf{V}_1^3(x, y, z) \cos \phi_3 \right) \left( \mathbf{V}_1^1(x, y, z) \cos \phi_1 + \mathbf{V}_1^2(x, y, z) \cos \phi_2 + \mathbf{V}_1^3(x, y, z) \cos \phi_3 \right) dt
\]

\[+ \mathbf{V}_2(x, y, z)^2 \int_0^T (\sin^2 \omega t) dt
\]

\[= \frac{\sigma}{T} \left( \frac{T}{2} \mathbf{V}_1^1(x, y, z)^2 - 0 + \frac{T}{2} \mathbf{V}_2(x, y, z)^2 \right)
\]

\[= \frac{\sigma}{2} \left( \mathbf{V}_1^1(x, y, z)^2 + \mathbf{V}_2(x, y, z)^2 \right)
\]  

(A.23)

As this method does not need to discretize time to calculate average power, it results in significant computational savings. In addition, the real (\( \mathbf{V}_1 \)) and imaginary (\( \mathbf{V}_2 \)) voltage conditions can be calculated separately and added together at the end, providing an opportunity to exploit concurrency.

**A.2.3 Method 3: RMS Values**

This last method is similar to the previous technique except that instead of amplitude voltages, RMS values are calculated. By taking the RMS of the voltage distribution, an average voltage is assumed and therefore it replaces the averaging method of Method 2.
with a RMS value. The relationship between RMS value and the amplitude voltage is:

\[ V_{rms} = \frac{V_o}{\sqrt{2}} \]  \hspace{1cm} (A.24)

Therefore the electrode boundary conditions would be:

\[ V_1 = V_{rms}^1 \cos \phi_1 + V_{rms}^1 \sin \phi_1 \]
\[ V_2 = V_{rms}^2 \cos \phi_2 + V_{rms}^2 \sin \phi_2 \]
\[ V_3 = V_{rms}^3 \cos \phi_3 + V_{rms}^3 \sin \phi_3 \]  \hspace{1cm} (A.25)

Similarly to the second method, these boundary conditions can be broken up to real and imaginary roots and evaluated separately however, the voltages that are obtained are RMS values. Therefore, average power can be calculated through the original equation

\[ U = \sigma |E^2| = \sigma (\nabla V_{rms(real)}^2 + \nabla V_{rms(imaginary)}^2) \]  \hspace{1cm} (A.26)

Note that the factor of \( \frac{1}{2} \) does not appear in this equation since the averaging over one period is done using RMS values of the potential rather its complex representation.
Appendix B

Model Validation

This appendix details the tests conducted to validate the electrical and thermal modules of the electro-thermal model (ETM). To test the voltage and power calculated by ETM, a one dimensional (1D) example was used and an analytical solution derived. To test the thermal module, the Ogata Banks equation was employed.

B.1 One Dimensional Voltage and Power Measurements

The results of the ETM was compared to a one dimensional example solved analytically. The example was similar to one used by Hiebert (1987) and consisted of two electrodes 15 m apart, with three different electrical conductivity zones as seen on Figure B.1. A voltage of 50 V at a phase of 45° was applied to Electrode 1 while a 50 V at a phase of 225° was applied to Electrode 2.

The analytical solution was found by approximating the problem with a circuit (Figure B.2) and calculating the voltage drop according to Ohms Law, where the resistance is inversely related to the conductivity of the material:

\[ V = IR \quad \text{where} \quad R = \frac{L}{\sigma A} \quad (B.1) \]

where \( V \) is the voltage (V), \( I \) is the current (A), \( R \) is the resistance (ohm), \( L \) is the length (m), \( \sigma \) is the conductivity (S/m) and \( A \) is the cross sectional area (m²). The total current through the system was calculated using Ohms Law, where \( R_{tot} \) is the total
resistance of the system.

\[ I_{tot} = \frac{\Delta V}{R_{tot}} = \frac{50 - (-50)}{3.05} = 32.8 \text{A} \]  

Figures B.3 and B.4 show the potential and power distribution, respectively for the analytical and modelled solutions.

### B.2 One Dimensional Heat Measurements

In order to verify the heating portion of the electro-thermal model, a solution to a one dimensional example was obtained using the Ogata-Banks equation, modified for heat, and compared to the results using the electro-thermal model.

The Ogata-Banks solution is based on the one dimensional advection dispersion equation as given below:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} \]  

where \( D \) is the dispersion coefficient \((m^2/s)\), \( C \) is the concentration \((kg/m^3)\), \( \bar{v} \) is the seepage velocity \((m/s)\) \((v = q/n)\) and \( x \) is the distance from the source of contamination \((m)\).
Figure B.3: Comparison of Simulated and Analytical Voltage Distribution for 1D Voltage Example

Figure B.4: Comparison of Simulated and Analytical Power Distribution for 1D Voltage Example
APPENDIX B. MODEL VALIDATION

The Ogata-Banks equation (Ogata, 1970) is an analytical solution to the 1D advection-dispersion equation and is given as follows:

$$C(x, t) = \frac{1}{2} C_0 \left[ \text{erfc} \left( \frac{x - vt}{2\sqrt{Dt}} \right) + \exp \left( \frac{vx}{D} \right) \text{erfc} \left( \frac{x + vt}{2\sqrt{Dt}} \right) \right]$$  \hspace{1cm} (B.4)

and where the solution to Equation B.4 is subject to these boundary conditions:

$$C(x, 0) = 0 \quad x > 0$$  \hspace{1cm} (B.5)
$$C(0, t) = C_0 \quad t \geq 0$$  \hspace{1cm} (B.6)
$$C(\infty, t) = 0 \quad t \geq 0$$  \hspace{1cm} (B.7)

The one dimensional heat equation is given as:

$$(\rho c)_{\text{comb}} \frac{\partial T}{\partial t} = K_H \frac{\partial^2 T}{\partial x^2} - \rho_w c_p q \frac{\partial T}{\partial x}$$  \hspace{1cm} (B.8)

where $K_H$ is the heat conduction coefficient ($W/mK$), $T$ is the temperature ($^\circ C$), $c_p$ is the water heat capacity ($J/kg^\circ C$), $\rho_w$ is the density of water ($kg/m^3$), and $(\rho c)_{\text{comb}}$ is the combined heat capacity and density of soil and water ($J/^\circ C m^3$).

Since the 1D advection dispersion equation (B.3) and the heat equation (B.8) are both second order partial differential equations, the Ogata Banks solution can be used to estimate the temperature distribution a distance of $x$ away from the heat source in a 1D system as follows:

$$T(x, t) = \frac{1}{2} T_0 \left[ \text{erfc} \left( \frac{x - Aqt}{2\sqrt{Bt}} \right) + \exp \left( \frac{Aqx}{Bt} \right) \text{erfc} \left( \frac{x + Aqt}{2\sqrt{Bt}} \right) \right]$$  \hspace{1cm} (B.9)

where

$$A = \frac{c_p \rho_w}{(\rho c)_{\text{comb}}} \quad B = \frac{K_H}{(\rho c)_{\text{comb}}}$$

Using the electro-thermal model (with the electrodes turned off) a pulse of warm water ($20^\circ C$) was simulated as it entered into a layer of soil of initial temperature of $0^\circ C$. The inlet velocity of the water was taken to be $3 \times 10^{-5} \text{ m/s}$ and the thermal conductivity was assumed to be $2 \text{ W/mK}$. The electro-thermal model results were compared to the Ogata Banks solution at different times. As shown in Figure B.5 there is good correspondence
Figure B.5: Comparison of a Plug Heat Example using the Electro-Thermal Model and the Ogata Banks Solution

Error between the results can be reduced by decreasing the grid discretization. Figure B.5 shows results for a grid discretization (in both x and y) of 0.5 cm.
Appendix C

Model Flowcharts

This appendix presents a schematic of the different modules of the electro-thermal model (ETM) (Figure C.1, the ETM flowchart (Figure C.2), flowchart of the combined ETM and macroscopic invasion percolation (MIP) models (Figure C.3), and MIP model flowchart (Figure C.4).
Chapter 2 – Model Development

Electro-Thermal Model

Thermal Module

- Calculates EC
- Calculates voltage
- Calculates power
- Calculates temperatures
- Calculates water density and viscosity
- Calculates velocities
- Iterates velocity and temperature
- Calculates dispersion coefficient
- Calculates mass

Mass Transport Module

Electrical Module

- Calculates EC
- Calculates voltage
- Calculates power

Figure C.1: ETM Modules
Calculate voltage ($V_t$) and power ($U_t$) using $\sigma_0$.

Calculate $T_i$ using $q_0$.

Is $|T_{i+1} - T_i| \leq$ convergence criteria?

Calculate $\sigma_{i+1}$ then $V_{t+1}$ and $U_{t+1}$.

Does $T =$ exit criteria?

Calculate $q_i$ using $T_i$.

Calculate $T_{i+1}$ using $q_i$.

Set initial $T_0$, $q_0$, and $\sigma_0$ values.

Calculate voltage ($V_t$) and power ($U_t$) using $\sigma_0$.

$T_1 = T_0$.

$N = \#$ of iterations.

$t = \#$ of time steps.

Figure C.2: Electro-thermal model flowchart
APPENDIX C. MODEL FLOWCHARTS

Calculate voltage and power using \( T \) and \( \sigma \)

Iterate \( T_i \) and \( q \)

Calculate \( P_w, H_{\text{coef}} \), and \( P_{v_{\text{water}}} \)

as functions of \( T \)

Calculate \( S_g \) and \( P_g^{\text{tot}} \) using equilibrium equations, using \( C \)

obtained from transport step

Calculate new concentrations

with transport equations

Calculate \( S_g \) and \( P_g^{\text{tot}} \) using equilibrium equations, using \( C \)

obtained from transport step

Is \( P_g^{\text{tot}} > P_w \)

YES

Link to MIP model **

NO

Continue to time-step in the electro-thermal model using the new

concentrations and \( S_g \) values as \( t-1 \)

Is \( S_g > S_{\text{crit}} \)

NO

Redistribute \( S_g \) with equilibrium

calculations, using concentrations

from MIP module

YES

Set initial \( T_0, q_0, \) and \( \sigma_0 \) values

Figure C.3: Combined electro-thermal model and the macroscopic invasion percolation model flowchart (** see Figure C.4)
Calculate Pe, Pt and assign Pg(1) as the contaminant gas partial pressure and Pg(2) as the water vapour

Is sum(G) >0 (do clusters exist?)

Separate clusters

For each cluster calculate the cluster perimeter and entry and terminal thresholds

Calculate the average gas mass in each cluster and assign an average pressure in each cluster node (modified for temp)

Are any saturations in the cluster > Sg_{crit}

** Bring in P_{g1}^\text{tot}, P_g, S_g, Hcoef, P_o from ETM model (equilibrium equations)

Assign G = 1 for all nodes where S_g>S_g_{crit}

Scale pressures and S_g; Calculate new aqueous conc, if bubbles have formed or moved; Go out of MIP program

Reassemble gas clusters

• Include E node as part of cluster
• Take E node off D list
• Remove T node of G list
• Add T pressure to E pressure
• Adjust Pressure in E for temp
• Sg of T node = 0
• Sg of E node = S_g_{crit}

• Include E node as cluster
• Take E node off D list
• Sg of E node = S_g_{crit}

Is Pt_{avg} > I_{min}

Mobilization

Expansion

E = node being invaded by gas
T = node being drained of gas
G = connected gas cluster group
D = disconnected gas group

Pt_{avg} = total average pressure
I_{min} = minimum entry pressure
RI = terminal pressure

Figure C.4: Macroscopic invasion percolation model flowchart (** see Figure C.3)