LABORATORY STUDY EVALUATING ELECTRICAL
RESISTANCE HEATING OF POOLED TRICHLOROETHYLENE

by

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A thesis submitted to the Department of Civil Engineering
In conformity with the requirements for
the degree of Master of Science (Engineering)

Queen’s University
Kingston, Ontario, Canada
(March, 2009)

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Abstract

A laboratory scale study was conducted to evaluate the thermal remediation of trichloroethylene (TCE) in a saturated groundwater system using electrical resistance heating (ERH). Two experiments were conducted using a two-dimensional polycarbonate test cell, the first consisting of a single pool of TCE perched above a capillary barrier, the second consisting of two pools of TCE each perched on separate capillary barriers. Temperature data was collected during the heating process from an array of 32 thermocouples located throughout the test cell. Visualization of the vaporization of liquid phase TCE, as well as the upward migration of the produced vapour was recorded using a digital camera. Chemical testing was performed 48 hours after experiment termination to measure post heating soil concentrations. A co-boiling plateau in temperature was found to be a clear and evident earmark of an ongoing phase change in the pooled TCE. Temperature was found to increase more rapidly in the second experiment that included a fully spanning barrier. As temperatures increased above the co-boiling plateau, vapour rise originating from the source zone was observed, and was found to create a high saturation gas zone beneath the upper capillary barrier when no clear pathway was available for it to escape upwards. When the source zones had reached the target temperature of 100°C and the ERH process stopped, this high saturation gas zone condensed, leading to elevated TCE concentrations below as well as within the capillary barrier itself. The water table within the experimental cell was also noted to drop measurably when the gas zone collapsed. Post-testing chemical analysis showed reductions in TCE concentrations of over 99.04% compared to the source zone, although due to condensation of entrapped gas and convective mixing, there was a net redistribution of TCE within the experimental domain, especially within confined areas below the capillary barriers.
A secondary set of experiments were conducted using a homogenous silica sand pack with no chemical contaminants to determine the effect, if any, of the wave shape of electrical input on the ERH process. It was found that in early time heating, square wave inputs consistently produced a more localized heating pattern when compared to the standard sine wave electrical input. This effect equalized between the two experiments as the ERH process went on, perhaps due to the increased dominance of conduction and convection as the mode of heat transfer in the test cell at higher temperatures. It is believed that the localization of heating in square wave experiments is due to a consistent power supply due to the lack of a sinusoidal ramping in power delivery.
Acknowledgements

This research project was supported by Queen’s University through student scholarships to the author and by the Natural Sciences and Engineering Research Council of Canada through a Discovery Grant to Dr. B. Kueper.

I would like to express my gratitude and appreciation of my supervisor, Dr. Bernard H. Kueper, who allowed me the opportunity to work on this project, which has challenged and extended my skills, knowledge and experience. Your knowledge, guidance, advice and motivation has helped me complete this phase of my ongoing education and would not have been possible without your guiding hand. Technical support graciously provided by Stan Prunster, Neil Porter, Paul Thrasher, Jamie Escobar, Dave Tryon and Bill Boulton cannot go without a great deal of thanks. Dr. Allison Rutter at Queen’s Analytical Services Unit and machine work performed by Andy Bryson of the Mechanical Engineering department was invaluable to the completion of this project. Additionally, the support of Fiona Froats, Maxine Wilson, Cathy Wagar, Dian King and Rosalia Escobar is greatly appreciated.

A great deal of thanks must also be extended to members of the groundwater research group who served as good friends, colleagues and office mates. Among them, Mike West, Luis Bayona, Ashley Wemp, Scott Hansen, John Kosustanich, Sasha Richards, Grace Yungwirth, Titia Praamsma, Steph Grell, Daniel Baston, Brenda Cooke, Erin Clyde, David Rodriguez and Shawn Trimper, who were always willing to extend their hand in assistance, encouragement and friendship.
Lastly, I must express my profound gratitude to my parents and brother whose love, support, encouragement and tolerance of having a stress-ball for a son/sibling has exceeded what anyone could have expected. Thank you for sitting through so many dry technical explanations and always giving me the strength to continue onwards and upwards. Finally, special thanks to Michelle, whose support and reassurance has helped me incredibly.
Foreword

This thesis has been written in a manuscript format. Chapter 1 is intended as a general introduction to the subject matter, Chapter 2 presents a review of relevant literature and Chapter 3 is a complete independent manuscript to be submitted for publication. Chapter 4 is a technical note regarding an investigation conducted into the influence of wave shape on the ERH process. Eric John Martin is the lead author of the manuscript and technical note. Appendix A contains complete graphical data collected from temperature sensors during the experimental process covered in the main manuscript. Appendix B consists of analysis reports from Queen’s University Analytical Services Unit (ASU), and Appendix C includes sample calculations of threshold soil concentrations for free-phase existence of TCE.
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<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Thermal Diffusivity</td>
<td>(m$^2$/s)</td>
</tr>
<tr>
<td>$\alpha_{lf}$</td>
<td>Liquid Fraction</td>
<td>(--)</td>
</tr>
<tr>
<td>$\frac{\partial T}{\partial z}$</td>
<td>Thermal Gradient</td>
<td>($^\circ$ C/cm)</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Porosity</td>
<td>(--)</td>
</tr>
<tr>
<td>$\phi_a$</td>
<td>Air Filled Porosity</td>
<td>(--)</td>
</tr>
<tr>
<td>$\phi_w$</td>
<td>Water Filled Porosity</td>
<td>(--)</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>Surface Tension</td>
<td>(mN/m)</td>
</tr>
<tr>
<td>$\mu_1, \mu_2, \mu_\infty$</td>
<td>Fluid Velocity</td>
<td>(m/s, cm/s)</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
<td>(g/cm$^3$)</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Bubble Density</td>
<td>(g/cm$^3$)</td>
</tr>
<tr>
<td>$\rho_{bulk}$</td>
<td>Dry Bulk Density</td>
<td></td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>Liquid Density</td>
<td>(g/cm$^3$)</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Solid Density</td>
<td>(g/cm$^3$)</td>
</tr>
<tr>
<td>$\rho_{resis}$</td>
<td>Electrical Resistivity</td>
<td>($\Omega \cdot $m)</td>
</tr>
<tr>
<td>$\rho_{resis\ r}$</td>
<td>Rock Electrical Resistivity</td>
<td>($\Omega \cdot $m)</td>
</tr>
<tr>
<td>$\rho_{resis\ w}$</td>
<td>Water Electrical Resistivity</td>
<td>($\Omega \cdot $m)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
<td>(--)</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Mole Fraction</td>
<td>(--)</td>
</tr>
<tr>
<td>$A$</td>
<td>Area</td>
<td>(cm$^2$)</td>
</tr>
<tr>
<td>$a, m$</td>
<td>Empirical Parameters <em>(Balberg, 1985)</em></td>
<td>(--)</td>
</tr>
<tr>
<td>$A_a, B_a, C_a$</td>
<td>Antoine Constants</td>
<td>(--)</td>
</tr>
<tr>
<td>AWG</td>
<td>American Wire Gauge</td>
<td>(--)</td>
</tr>
<tr>
<td>$C_a$</td>
<td>Capillary Number</td>
<td>(--)</td>
</tr>
<tr>
<td>$C_T$</td>
<td>Total Soil Chemical Concentration</td>
<td>(mg/kg)</td>
</tr>
<tr>
<td>$C_w$</td>
<td>Chemical Concentration in Pore Water</td>
<td>(mg/l)</td>
</tr>
<tr>
<td>$c_i, d_i$</td>
<td>Empirical Parameters <em>(Liao et al, 2003)</em></td>
<td>(--)</td>
</tr>
</tbody>
</table>
c_l  Liquid Specific Heat Capacity at Constant Pressure  (J/kg•K)
c_p  Specific Heat Capacity at Constant Pressure  (J/kg•K)
c_pl  Specific Heat Capacity of Liquid at Constant Pressure  (J/kg•K)
c_ps  Specific Heat Capacity of Solid at Constant Pressure  (J/kg•K)
c_s  Solid Specific Heat Capacity at Constant Pressure  (J/kg•K)
CEC  Cation Exchange Capacity  (meq/g)
d  Mean Pore Diameter  (mm)
Eo  Eötvös Number  (--)  
F  Frequency  (Hz)
F_{oc}  Fraction Organic Carbon  (--)  
F_v  Vertical Buoyancy force  (N)
g  Gravitational Acceleration  (m/s^2)
H_e  Henry’s Constant  (--)  
\bar{h}  Convective Heat Transfer Coefficient  (W/m^2•K)
h_{fs}  Latent Heat  (J/kg)
I  Current  (A)
I_{peak}  Peak Current  (A)
I_{rms}  Root Mean Square Current  (A)
K_d  Distribution Coefficient  (ml/g)
K_{oc}  Organic Carbon Partitioning Coefficient  (ml/g)
k  Thermal Conductivity  (W/m•K)
k_e  Effective Thermal Conductivity  (W/m•K)
k_f  Thermal Conductivity of Fluid  (W/m•K)
k_s  Thermal Conductivity of Solid  (W/m•K)
L  Length  (m)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>Moles</td>
<td>(--)</td>
</tr>
<tr>
<td>$P$</td>
<td>Power</td>
<td>(W)</td>
</tr>
<tr>
<td>$P_i$</td>
<td>Pressure</td>
<td>(Pa)</td>
</tr>
<tr>
<td>$q$</td>
<td>Heat Flux</td>
<td>(W/m²)</td>
</tr>
<tr>
<td>$Q_c$</td>
<td>Charge</td>
<td>(C)</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
<td>(Ω)</td>
</tr>
<tr>
<td>$R_{uni}$</td>
<td>Universal Gas Constant</td>
<td>(= 8.2057 x 10⁻⁵ atm•m³/mol•K)</td>
</tr>
<tr>
<td>$T_1$, $T_2$, $T_n$ etc.</td>
<td>Temperature</td>
<td>(° C, K)</td>
</tr>
<tr>
<td>$\nabla T$</td>
<td>Heat flux tensor</td>
<td></td>
</tr>
<tr>
<td>$u_i$</td>
<td>Fluid Velocity</td>
<td>(cm/s)</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
<td>(V)</td>
</tr>
<tr>
<td>$V_b$</td>
<td>Buoyancy Velocity</td>
<td>(cm/s)</td>
</tr>
<tr>
<td>$V_{bulk}$</td>
<td>Bulk Volume</td>
<td>(cm³)</td>
</tr>
<tr>
<td>$V_{peak}$</td>
<td>Peak Voltage</td>
<td>(V)</td>
</tr>
<tr>
<td>$V_{ps}$</td>
<td>Volume of Pore Space</td>
<td>(cm³)</td>
</tr>
<tr>
<td>$V_{rms}$</td>
<td>Root Mean Square Voltage</td>
<td>(V)</td>
</tr>
<tr>
<td>$V_s$</td>
<td>Volume of Solids</td>
<td>(cm³)</td>
</tr>
<tr>
<td>$VA$</td>
<td>Volt-Amp</td>
<td>(V•A)</td>
</tr>
<tr>
<td>$v_b$</td>
<td>Velocity due to Buoyancy</td>
<td>(cm/s)</td>
</tr>
<tr>
<td>$z_i$</td>
<td>Point in Linear Space</td>
<td>(m, cm)</td>
</tr>
<tr>
<td>$\Delta z$</td>
<td>Spatial Distance</td>
<td>(m, cm)</td>
</tr>
</tbody>
</table>
Abbreviations

AC Alternating Current
BTEX Benzene, Toluene, Ethylbenzene and Xylene
DC Direct Current
DNAPL Dense Non-Aqueous Phase Liquid
ERH Electrical Resistance Heating
LNAPL Light Non-Aqueous Phase Liquid
PCB Polychlorinated Biphenyl
PCU Power Control Unit
ppb Parts Per Billion
ppm Parts Per Million
PCE Perchloroethylene / Tetrachloroethylene
PCU Power Control Unit
REV Representative Elementary Volume
SEE Steam Enhanced Extraction
SPH Six Phase Heating
SVE Soil Vapor Extraction
TCE Trichloroethylene
TCH Thermal Conductive Heating
TPH Three Phase Heating
USEPA United States Environmental Protection Agency
VDMME Virginia Department of Mines Minerals and Energy
VOC Volatile Organic Compound
Chapter 1

Introduction

1.1 Research Objectives

The primary objective of this study was to perform laboratory experiments to evaluate the use of electrical resistance heating (ERH) for the remediation of pooled trichloroethylene (TCE) in a fully saturated subsurface environment with partially and fully confining capillary barriers in the absence of vapour extraction systems. Treatment was evaluated by using visual observation, temperature data and post-treatment chemical analysis. Clean silica sand was packed under water into a polycarbonate (Makrolon™) cell, arranged in a layered fashion producing a high permeability environment with two low permeability lenses. The silica sand was then impacted with TCE, with pools perched upon both of these lenses. To date, the published literature does not include the results of ERH experiments using pooled DNAPL in the presence of a capillary barrier.

1.2 Chlorinated Solvents and DNAPL

Chlorinated organic solvents have become recognized as a major problem facing groundwater quality in the industrialized world over the last several decades. Substances such as TCE and tetrachloroethylene (PCE) pose serious risks to both human and environmental health. Years of use have resulted in numerous cases of site contamination of the subsurface as these and similar
substances have infiltrated groundwater. Such chemicals are produced in great volumes for industrial and manufacturing purposes on the order of millions of litres a year (Pankow and Cherry, 1996). Most of these solvents have infiltrated groundwater systems by improper disposal in years past, leakage from piping, storage tanks or evaporation ponds and accidental releases occurring during transportation (Longino and Kueper, 1995).

The health hazards linked to chlorinated solvents are varied and numerous including both suspected and confirmed carcinogenic and mutagenic effects, central nervous system damage, and in some cases liver and kidney damage (USEPA, 2006). When a chlorinated solvent is denser than water in liquid form, it is referred to as a dense non-aqueous phase liquid (DNAPL). DNAPLs exhibit limited solubility in water although as much as 1100 mg/L of TCE can exist dissolved in water at 25°C, which is enough to pose health concerns to living organisms. As a result, groundwater contaminated with DNAPL can contain both free-phase liquid as well as DNAPL dissolved in the water itself. Since DNAPLs exhibit a higher weight per volume than water, they can penetrate deeply into saturated porous media, often pooling on and traveling through bedrock via fractures. Both vertical and horizontal travel is observed in a DNAPL release, resulting in these pools as well as disconnected ganglia and blobs in areas where DNAPL has traveled, known as residual. Pools are formed when the capillary pressure of the DNAPL is not great enough to overcome the entry pressure of a capillary barrier that it has encountered. Assuming more DNAPL continues to infiltrate the area downwards, the height of this pool will continue to grow until the entry pressure is exceeded, at which point it will continue downward penetration into the barrier. If the width of the pool reaches the edge of the layer, it can also spill over, and travel downwards around the capillary barrier (Kueper et al., 1989).
The water-solvent interface of both pooled and residual DNAPL is the site of dissolution of the solvent into the groundwater flowing around them, creating what is known as a solvent plume, which is carried away from the source zone. Eventually, these source zones are completely depleted by this dissolution, but it is a very lengthy process, which can be measured on the order of decades to hundreds of years (Kueper et al. 2003). Because residual has much more surface area than pooled solvent, the dissolution of a pool would take longer to reach full depletion than residual. Even though the DNAPL may not be in a separate organic liquid phase, water contaminated with the substance will continue to be carried down gradient. It should also be noted that the low solubility of TCE is still much higher than the concentrations that are generally accepted as dangerous to human health. As such, the remediation of DNAPL impacted areas is a high priority in many developed countries.

1.3 Thermal Remediation

Remediation of DNAPL impacted areas has become a high priority in many developed countries, spurring a great deal of research in the field directed at improvements in efficiency and cost-effectiveness of remediation technologies. Recently, a class of thermally-based methods including steam-flushing, conductive heating, radio-wave heating, and electrical resistance heating (ERH) have received a great deal of attention due to unique properties of the techniques. Thermal technologies are effective in overcoming mass transfer limitations prevalent in older, more traditional methods such as pump-and-treat, and soil-vapour extraction (SVE). The introduction of thermal energy to the subsurface can alter both the physical and chemical
properties of compounds that increase the potential of mobility. Vaporization, steam distillation, boiling, and in some cases degradation occurs at elevated temperatures along with other favourable effects, such as decreased viscosity, density and adsorption (Davis, 1997).

Thermal remediation techniques applied in-situ utilize thermal energy in the subsurface as a means to mobilize and remove contaminants. Such technologies have become very popular in recent years because of several unique properties specific to thermal remediation that decrease the effect of rate-limiting properties that commonly come into play in conventional in-situ remediation techniques. Thermal technologies, and ERH in particular are not negatively influenced by low permeability soils to the extent that a method such as the popular ‘pump and treat’ method is. Some of the mechanisms that contribute to enhanced remediation in thermal treatments include evaporation, vaporization or full-out boiling. In addition to this a decrease in adsorption and viscosity, an increase in Henry’s constant and solubility aid remedial activities. In addition, the ability of contaminants to migrate through the soil is increased by volatilization of liquids into the gas phase allowing greater mass transfer.

A small collection of popular methods for the application of thermal remediation are currently practiced, including electrical resistance heating (ERH), steam enhanced extraction (SEE) and thermal conductive heating (TCH). TCH relies on heating elements placed in the subsurface which conduct heat throughout the affected area. SEE uses wells to inject pressurized steam transferring thermal energy. ERH uses electrodes to pass a current through the pore water and generate heat by way of Ohmic heating.
Most of these technologies were originally developed to enhance the efficiency of oil recovery in the petroleum industry, and after demonstration projects, adapted for environmental uses once their benefits were realized (USEPA 2004). ERH has been applied to compounds belonging to the DNAPL family such as PCE, TCE and poly-chlorinated biphenyls (PCBs). Light non-aqueous phase liquids (LNAPLs) have also been treated using thermal remediation methods.
1.4 Literature Cited


Chapter 2

Literature Review

2.1 Fundamentals

2.1.1 Internal Energy

Joule discovered that as water is stirred, the mechanical energy used to agitate the water could be extracted later as thermal energy (Cardwell, 1991). This means that the energy is stored in the fluid as internal energy. In the case of monatomic molecules, this is kinetic energy, mainly internal and rotational motion. In larger molecules, bond vibrations and rotations are also a means of storing internal energy. In addition to increases in internal energy produced by the application of work to a fluid, the direct transfer of heat to that fluid object will raise the overall level of internal energy (Smith and Van Ness, 1987). Included in the definition of internal energy is potential energy, which is caused by interaction between the charged portions of molecules as well as chemical bonds holding these particles together. Internal energy is differentiated from overall energy because it does not include the macroscopic conditions of the object, such as position or movement.

2.1.2 Temperature

Temperature is a measurement of thermal energy and provides a numerical value that can be assigned to quantify the amount of thermal energy contained within a system. Temperature is typically expressed in units of degrees Celsius, degrees Fahrenheit, or Kelvin. Temperature
measurements are somewhat unique in that they do not directly measure the total amount of thermal energy in an object, but rather they only reflect changes in thermal energy. The most commonly known example of this is the mercury/glass thermometer, which consists of a liquid metal housed in a narrow glass tube. The amount of thermal expansion that mercury undergoes throughout changes in temperature is used with a glass channel of a size calibrated so that one reference temperature, being the freezing point of water is 0°C.

2.1.3 Heat Transfer and Thermal Equations

Since heat transfer is in essence a transfer of kinetic energy between particles, it cannot be instantaneously conveyed from one part of an object to another. Rather, it diffuses over time throughout objects, and to the surrounding environment. This can be done through direct contact of solid objects; conduction, or through contact with a moving fluid; convection. Heat may also be transferred through radiation, which can be observed at any temperature.

Heat is actually a form of motion, although not on the macroscopic scale. It is a result of kinetic energy due to the motion of molecules and within those molecules, through vibrational and rotational motions. This kinetic energy, due to its nature cannot be contained within an object, but is in a constant state of transfer, dispersing itself throughout the object from areas of high energy to low energy, and also to the surroundings. The rate of this transfer of energy is proportional to the magnitude of the difference in temperature that exists, as can be seen in the basic definition of a temperature gradient (Beardsmore and Cull 2001):
\[
\frac{\partial T}{\partial z} = \frac{(T_2 - T_1)}{(z_2 - z_1)}
\]  \hfill (2-1)

where \( T_1 \) and \( T_2 \) are temperatures at two points in space, \( z_1 \) and \( z_2 \) are locations of the respective points, and \( \frac{\partial T}{\partial z} \) is the gradient driving heat transfer between those points. Naturally, if the temperature throughout an object, or between an object and its surroundings is uniform, there will be no heat transfer as there will be no gradient to facilitate the transfer of thermal energy.

### 2.2 Conduction

Conductive heat transfer occurs when static particles are in direct physical contact with one another. When thermal energy is higher in one part of this system, heat will be transferred from high energy areas to low energy portions due to a thermal gradient (Smith and Van Ness, 1987). The basis of this gradient effect is related to the kinetic thermal energy of particles at different temperatures. Molecules with a high degree of thermal energy move more quickly than those with lower energies. Because of this, kinetic energy is transferred from hotter to cooler molecules. The diffusion of this energy will eventually result in a thermal equilibrium, with every molecule affecting surrounding molecules equally. This is particularly the case in static fluid systems. Solids behave similarly, but because of the non-fluid nature of solids, this diffusion effect is attributed to kinetic waves in the lattice caused by the same types of vibrational motion observed in fluids. Also, because of the greater spacing between molecules in a fluid, conductive heat transfer is less efficient than in a solid lattice structure (Incropera and DeWitt, 1990).
Fourier’s law expresses the rate of heat transfer by conduction. The equation is not based on first principles, but rather is phenomelogical, being based on observed phenomena. Heat flux \( q \) is defined as the rate of heat transfer per unit area (Incropera and DeWitt, 1990), and is defined in Cartesian coordinates as:

\[
q = -k \nabla T
\]  

(2-2)

As heat flux is a directed occurrence, it is naturally a vector quantity with both a magnitude and direction. The three dimensional operator, \( \nabla \) is therefore required. Heat is conducted perpendicular to lines of equal temperature, or isotherms, in an isotropic system (Incropera and DeWitt, 1990).

### 2.2.1 Specific Heat Capacity

Specific heat capacity \( (c_p) \), also sometimes known simply as specific heat, is defined as the amount of thermal energy required to raise the temperature of a unit mass of a material by a unit measure of temperature at a constant pressure. For example, the specific heat of a substance could be measured in J/gK, or the number of joules of thermal energy required to raise the temperature of one gram of the material one Kelvin.

### 2.2.2 Thermal Diffusivity

The thermal diffusivity of a material \( (\alpha) \) is defined as the ratio of thermal conductivity to volumetric heat capacity. High thermal diffusivity materials heat and cool very quickly, and therefore take less time to reach thermal equilibrium with their surroundings. The opposite would
be true of a thermal diffusivity that is lower. Thermal diffusivity can be expressed as (Incropera and DeWitt, 1990):

\[ \alpha = \frac{k}{\rho c_p} \]  

(2-3)

where \( k \) is thermal conductivity, \( \rho \) is density and \( c_p \) is specific heat capacity. Since thermal diffusivity is essentially a function of specific heat capacity and thermal conductivity, it can be determined when these two values and the density of the material are known variables. Thermal diffusivity is a useful value in predicting a material’s response to increases and decreases in the ambient temperature, as is observed in thermal remediation properties.

2.3 Convection

Convection is a form of heat transfer that involves the movement of fluid with a surface. Illustrations of this process are commonly found, such as water in the radiator of an automobile. When heat is transferred by the bulk motion of fluid, it is termed advection.

Boundary layers play a key role in the transfer of heat by convection. The velocity of a fluid passing over a solid surface is not constant with respect to height above the plate. Due to viscous action, there is a velocity profile that appears in the fluid, as illustrated in Figure 2-1. The velocity of the fluid that is in contact with the surface is zero, and increases as the distance between the fluid and the surface is increased to a finite value (\( u_\infty \)). Since the fluid at zero height has zero velocity, transfer of heat is achieved through conduction only. As discussed earlier, the
driver of thermal energy transfer is the heat gradient between two points in space. Since energy is conducting through the static boundary layer, the flow rate of the fluid above the boundary layer becomes very important in determining the net flux of thermal energy exchanged.

Figure 2-1 - Heat transfer through fluid flow over a flat plate (Reproduced from Holman, 1997)

Aside from conduction through the boundary layer, heat transfer is also achieved in the bulk fluid passing around the solid object by convective mixing, the advective portion of heat transfer involved in the convection process, illustrated in Figure 2-2.

Figure 2-2 - Convection regime between a flowing fluid and a solid body (Reproduced from Lienhard, 1981)
Heat is then transferred in the bulk fluid purely by hotter fluids coming in contact with cooler regions (Lienhard, 1981). When this mixing is caused by temperature differences causing a density change in the hotter fluid, the process is called natural or free convection. When there is an external force applied to the fluid to induce mixing, it is known as forced convection.

The rate of heat transfer between such a solid and a fluid moving around it can be described by Newton’s Law of cooling (Lienhard, 1981):

\[ q = \bar{h}(T_w - T_\infty) \]  

(2-4)

where \( T_w \) is the wall temperature of the solid object, \( q \) is the amount of thermal energy transferred and \( T_\infty \) is the temperature of the bulk fluid, and \( \bar{h} \) is the heat transfer coefficient, which is a term that is dependent on the physical characteristics of the fluid, the geometry of the solid itself, and the flow regime of the fluid across the solid surface. It should be noted that this term is generally averaged over a representative area of the solid surface.

### 2.3.1 Phase Change

When a fluid experiences a change of state, not only does sensible heat come into play, but so does the latent heat, that is the heat required to convert a fluid from one phase into another, such as the act of boiling, in which there is a conversion of liquid phase into vapour phase or in condensation, from vapour to liquid. The latent heat can be defined as the amount of thermal energy that must be transferred before such a change occurs. It is generally denoted as \( h_{fg} \). Since this energy precedes a change of phase, either boiling or condensation, the overall temperature of
the fluid will remain constant until the phase change occurs. Both the processes of boiling and condensation typically involve the movement of a fluid on a solid-liquid interface, and is therefore classified as forms of convection.

2.4 Electrical Power and Ohmic Heating

2.4.1 Electricity and Electric Power

Electricity is a term used to describe charge, and in particular the movement of charge. When charge is not moving, a more appropriate term is static electricity. Charge is a fundamental property of matter, and as a form of energy, is conserved; it cannot be created or destroyed. Charges can exist in two polarities: positive and negative. Like charges repel, while opposite charges attract, which is the phenomenon that holds atoms together. Positively charged protons retain negatively charged electrons in orbit around the central nucleus. Charge is expressed in units of the Coloumb (C) and is generally designated by the symbol $q_c$. Electrical current is the movement of charge, and a current is simply a measure of quantity of charge moving per unit time. The measure of current is the Ampere ($A$), which is one C per second. To put this in perspective, the charge of a single electron is $-1.602 \times 10^{-19}$ C.

The potential energy of voltage is depleted when it is passed through a load. A load is something that causes resistance in the electrical pathway. A conceptual analogy following the lines of the fluid comparison would be a continuous loop of hose, or a circuit, as pictured below in Figure 2-3.
The analogy runs along the same lines of logic as an electrical circuit where the pump and turbine are replaced with a battery and light bulb respectively. Electrical energy is converted to light and heat energy, leaving a potential drop across the bulb. Therefore the voltage before the bulb will be higher than after. This phenomenon is known as resistance, and will be discussed below.
2.4.2 Alternating and Direct Current

Current is utilized in everyday electric and electronic applications in two basic forms: alternating (AC) and direct (DC) currents pictured in Figure 2-4. The difference between the two lies in the direction of the current. A direct current travels only in one direction through the circuitry at a value specified by the battery used. Alternating current, however, reverses its direction of movement. Most often, this reversal follows a sinusoidal pattern. The number of times the direction of the current changes is known as frequency, denoted by \( f \) and measured in hertz (Hz).

In North America, standard delivery frequency is 60Hz.

![Sine Wave](image1.png)  
![Direct Current (DC)](image2.png)  
![Square Wave](image3.png)

**Figure 2-4 - An alternating sine current, direct current (DC) and alternating square current**
(Modified from Rizzoni, 2004)

Voltage and current magnitude can be expressed with DC current easily as a simple numerical value, considering that the magnitude of the voltage or current is static with respect to time. AC currents and voltages are generally expressed as a root mean square (RMS) value since the values are in a constant state of transition. These values can be obtained from peak values by the following expressions:
RMS is also known as the quadratic mean, and is particularly useful in describing the average voltage, current or power of any alternating waveform which dips into the negative.

2.4.3 Resistance and Conductance

Electrical resistance and its reciprocal, electrical conductance are the basic concepts that govern the travel of electricity through a conducting medium. Resistance is a ratio of the degree to which a material opposes an electrical current, whereas conductance is a measurement of the ease with which electricity can travel through the material. The units used in resistance and conductivity are ohms (Ω) and Siemens (S) respectively. Resistance can be expressed as:

\[ R = \frac{L \rho_{resis}}{A} \]  \hspace{1cm} (2-7)

Where \( L \) is the length, \( A \) is the cross sectional area and \( \rho \) is the specific electrical resistance of the material. Also known as resistivity, specific electrical resistance is the value that denotes how strongly a material opposes the flow of an electrical current.

Materials that conduct electricity well do so because of the number of valence electrons in their outer shells. The best conductors, or worst resistors, only have one valence electron which is
easily detached and allowed to flow through the material, transporting charge as a result. Materials that exhibit this quality include silver, copper and gold. Factors such as impurities reduce the number of atoms with only one valence electron, and hence, reduce the conductivity of the material.

Conduction can also occur in ionic liquids, such as water that contains ionic material, typically salt or minerals, as it is almost always found in everyday life (as opposed to distilled, de-ionized laboratory grade water). In this case, charge is not carried by individual electrons, but rather entire ionic species, and as such the conductivity is highly sensitive to the concentrations of ions present. Distilled water is a near insulator, while biological fluids and tap water conduct quite well, allowing electrical charges to be transferred through the nervous system.

Non-conductors or insulators have their valence electrons very firmly bound to their respective atoms, disallowing any detachment and net flow of charge throughout the medium. This type of material, such as rubber, will not conduct electricity until the intensity of the applied electric energy overcomes the dielectric strength of the material, forcing valence electrons to become disrupted and freed from their host atoms. Examples of conductors, insulators and semi-conductors can be found in Table 2-1.

Resistance in metals can be attributed partially to impurities that exist in the material. Additionally, resistance is highly temperature dependent. The reason for this is tied to kinetic motion of the atoms that make up the material. At higher temperatures, the motion of atoms is greater than at low temperatures, which can disrupt the flow of electrons, a phenomenon known
as electron-scatter. The longer the electrical path that must be traveled, the more temperature affects the efficient flow of charge, creating a greater resistive effect. Conversely, at low temperatures, lessened atomic motion contributes far less to electron scatter, allowing charge to flow in an undisrupted manner. At temperatures approaching absolute zero, good conductors such as gold become nearly perfect conductors, showing no measurable signs of electrical resistance.

With ionic liquids, lowering temperatures actually hinders ionic transport due to constricted motion, and eventually leads to a phase transition resulting in a solid form. The most profound factors affecting conductivity in liquids are the aforementioned ionic content, as well as the addition of non-conducting media, such as water existing in the pore space of soil, which has an impact much like impurities in a metal.

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity (20°C) (Ω•m)</th>
<th>General Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>1.72x10^{-7}</td>
<td>Conductor</td>
</tr>
<tr>
<td>Carbon</td>
<td>3.45x10^{-5}</td>
<td>Semiconductor</td>
</tr>
<tr>
<td>Glass</td>
<td>1.0x10^{12}</td>
<td>Insulator</td>
</tr>
</tbody>
</table>

The base equations that express the relationships held between Resistance in a medium with voltage current and electrical power are rearrangements of Ohm’s law with additions of Joule’s laws, and are as follows:
Where $R$ is resistance, $V$ is voltage in volts ($V$), $I$ is current in Amperes ($A$) and $P$ is power in watts ($W$). Since potential, or voltage is reduced when a current is passed through a resistor, it can be seen from the equation above that the total electrical power must be reduced, as power is merely the product of voltage and current. This fact is exploited often in everyday life to produce mechanical motion, light, sound, or, as it pertains to this particular study, heat energy. The power that is lost during transmission of moving charge through a resistive element is converted to thermal power, the same basis that electric heating elements and range-tops rely on. It can also be seen from the above equations that if the current entering a resistor is held constant, the greater the resistance applied, the more power is produced. A very impure element, such as an electric stove will produce a great amount of heat when current is applied, whereas a good conductor such as copper wiring in one’s home, which is carrying the same current and voltage as the stove, will remain relatively cool, producing very little waste heat. This is a phenomenon known as Ohmic heating, joule heating, or electrical resistance heating (ERH). The theory behind ERH has been extensively studied, and is very well understood. Recently, novel approaches have been examined using Ohmic heating for the thermal remediation of the subsurface.
2.4.4 Ohmic Heating

Ohmic heating is the application of current to a resistive material to produce thermal energy. Excited particles increase their vibrational movements, causing friction and an increase in temperature. The name ‘Ohmic heating’ is derived from the relation of heat generation to Ohm’s law, the original form of which was published in 1827 (Irwin and Kerns, 1995).

\[ V = IR \quad (2-12) \]

The power produced by resistance is converted into thermal energy, creating an increase in temperature described by the expression (Cardwell, 1991):

\[ P = RI^2 \quad (2-13) \]

A third common name for the process is resistive heating. As charged particles are accelerated by an electric field their velocity increases, and so does the number of collisions between particles. With each collision, an amount of this energy is lost, and dissipated as heat. This is the principle on which electrical heating systems are based on. It is also the basis of power losses in transformers and electronic equipment, which is a negative effect of Ohmic heating.
2.5 Thermal Properties of Porous Media

Heat transfer to this point has been discussed in terms of solids and fluids. The process is actually much different in non-homogenous porous media, as particulate transfers heat much differently than the fluid that exists in the pore space. Geological materials, for example, are composed of either a matrix in the case of rock, or tightly packed particles as is the case with soils. A fluid, generally water, air, or a mixture of the two exists in the space of the stationary solids (Ho, 2004).

The same is true of electrical properties in a porous medium, where the fluid will conduct electricity differently than the solid phase. It should also be noted that since both thermal and electrical conductivities vary with temperature, the difference in properties of each will also change in relation to each other as the ambient temperature is varied.

2.5.1 Porosity

Porosity (\(\phi\)) is the ratio of void space, which is the volume of the media which is not solid (\(V_{ps}\)) to the volume that the bulk of the media exists in (\(V_{bulk}\)). Although literature exists that quantifies the porosity of different types of soils and rocks, they can only be regarded as guidelines. Actual porosities are very site-specific, depending on the type of media and the conditions under which it exists. As such, actual porosities must be measured to obtain an accurate assessment. The actual porosity of a soil greatly impacts the heat transfer properties of that soil, since it will determine the balance of solid matrix and fluid filled pore space, both having unique heat transfer
properties. In addition, high porosity materials will be more efficient at transferring heat through convection and advection, since the additional fluid allows greater movement and transfer.

2.5.2 Heat Transfer Mechanisms in Porous Media

Heat transfer in a porous medium is based on the thermodynamic properties of the constituents that comprise the medium itself. When such a medium has a moving fluid passing through it, which is generally the case in groundwater investigations, heat may be transferred by conduction and convection.

The ways in which conduction and convection contribute to the overall movement of thermal energy in a porous medium (Bear, 1972) can be summarized as transfer through the solid phase by conduction, through the liquid phase by conduction, through the fluid phase by convection, through the liquid phase by dispersion and transfer from the solid to the fluid phase by convection.

The term dispersion is the same that is used in the study of mass transfer. In this case, heat would be transferred by the hydrodynamic mixing of fluid, which can be observed on the pore scale (Nield, 2006). Tortuosity in the flow path of the fluid can cause this mixing action, as well as when all pores are not accessible to the fluid once it enters a flow path, causing the fluid to turn around at these dead ends.
2.5.3 Thermal Conduction in Porous Media

Heat transfer by conduction in porous media is influenced by both the solid matrix of the specific medium as well as the fluid that fills the pore space. The arrangement of solid particles as well as the thermal properties of the solids and those of the fluid combine to determine the efficiency with which the medium can transfer heat by conduction. Typical values of thermal conductivity in various types of soil can be found in Table 2-2.

Table 2-2 - Typical $k$ values for various common soil types (VDMME, 2006)

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>$k$ ($\frac{W}{m \cdot K}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry sand</td>
<td>0.7615233</td>
</tr>
<tr>
<td>Saturated sand</td>
<td>2.492258</td>
</tr>
<tr>
<td>Dry clay</td>
<td>1.10767</td>
</tr>
<tr>
<td>Saturated clay</td>
<td>1.661505</td>
</tr>
<tr>
<td>Loam</td>
<td>0.8999821</td>
</tr>
</tbody>
</table>

As with mass transfer, heat transfer is most easily described by using a macroscopic approach using a representative elementary volume (REV), which is basically a control volume used to represent an average collection of pore-scale processes (Benard et al, 2005). Also, as with most heat transfer analyses, local thermal equilibrium must be assumed, meaning that at very small scales, it can be said that fluid and solid temperatures are equal. When this assumption is made, and averaged over the representative elementary volume conduction can be described by (Hsu, 1999):

$$\varnothing \rho_f c_{pf} + (1 - \varnothing)\rho_s c_{ps} = \nabla \cdot (k_e \nabla T) \tag{2-14}$$
where $\rho_f$ and $\rho_s$ are the fluid and solid densities, respectively, and $C_{pf}$ and $C_{ps}$ are the specific heat capacities of the fluids and solids, respectively. The effective thermal conductivity $k_e$, is defined as the heat transfer potential of a stagnant, non-flowing solid matrix with pore space occupied by a fluid (Kaviani, 1991). There are various definitions of the effective conductivity dependant on the specific geometry of the solid/fluid regime, whether it be in series, parallel, or a combination of these two, as represented by a geometric mean model of the two presented by Woodside and Messmer (1961a):

$$k_e = k_f^\varnothing k_s^{1-\varnothing}$$

(2-15)

Where $k_f$ and $k_s$ are the conductivity of the fluid and solid respectively, and $\varnothing$ is the porosity of the medium.

### 2.5.4 Thermal Convection in Porous Media

A porous medium consists of a solid skeleton of particles with space allowing the presence and possibly the flow of a fluid, either water or gas between these particles. This flow can either be applied by a gradient due to a mechanical implement, or by natural convective flow due to density differences in the fluid. As with investigations into the conductive behavior of porous media, an REV approach is generally taken, resulting in an averaged flow throughout a specified area to compensate for velocity differences on the pore-scale.

The migration of hotter liquids upwards, while the cooler, more dense liquids travel downwards results in a net rotational motion, as shown in Figure 2-5 and Figure 2-6.
Understanding of the convective patterns involved in thermal systems is particularly useful in the harnessing of geothermal resources. Much research has been conducted to better understand these patterns, which have been shown to be nearly symmetrical when a heat source is centrally located in a generally homogenous medium.

Figure 2-5 - Convective mixing due to conductive heat transfer (Reproduced from Freeze and Cherry, 1979)

Figure 2-6 - Convective mixing and isotherms due to a heated object in a porous matrix (Reproduced from Freeze and Cherry, 1979)
2.5.5 Boiling in Porous Media

When the application of thermal energy to a porous medium is great enough to cause boiling of the liquid present in the pore space, three distinct regions can be readily identified. It is most convenient to represent these regions by means of a one-dimensional conceptual model. Closest to the heat source is where the majority of the vapourization will occur, resulting in a vapour region. As temperature decreases with increasing distance from the heat source, a region exists that contains both vapour and liquid; a two-phase zone. Even further from the heat source the temperature will decrease further, resulting in a one-phase liquid zone. Because of the close spacing of solids in the vapour zone and limited ability for vapour to transfer heat convectively compared to liquid, heat transfer in the vapour zone is dominated by conduction. Rising concentrations of liquid in the two-phase and liquid zones lead to an increasing role of convection in the transfer of thermal energy. In the case of ERH, often the saturated region is heated, leading to a higher concentration of bubbles in the zone being directly heated, with fewer bubbles below, leading to the one phase liquid zone. Above the treatment zone, the temperature decreases into a single phase vapour zone. Naturally, liquid saturation is highest bordering the cool single-phase liquid zone, and lowest at the hotter vapour zone.

2.5.6 Buoyancy and Bubble Rise in Porous Media

Bubbles produced from the process of boiling in porous media have a lower density than the liquid surrounding them, so buoyancy draws the vaporized liquid upwards. The upward force acting on the bubble is simply proportional to the difference in density between the gas and the liquid which surrounds it (McGee, 2004):
\[ F_v \propto (\rho_b - \rho_l) \]  

(2-16)

where \( \rho_b \) is the density of the bubble created by boiling, and \( \rho_l \) is the density of the surrounding fluid. Naturally, factors that actually determine the upward velocity of a bubble include the density of the liquid, tortuosity and permeability of the solid matrix. Since the upward movement of a bubble rising in fluid is constrained by the difference in density, the bubble will always reach a terminal velocity. This velocity is greatly reduced by the presence of a solid matrix (McGee and Huang, 2004):

\[ v_b = \frac{\gamma}{d} C_a \]  

(2-17)

where \( \gamma \) is the surface tension between the two fluids, \( d \) is the mean pore diameter and \( C_a \) is the capillary number defined as:

\[ C_a = c_1 Eo^{d_1} + c_2 Eo^{d_2} \]  

(2-18)

in this expression \( c_1 \) and \( d_i \) are parameters fit using numerical results, such as those found in Liao (2003). For a square, \( c_1 = 6.7 \times 10^{-5}, c_2 = 2.3 \times 10^{-5}, d_1 = 1.03, d_2 = 2.61 \). \( Eo \) is the Eötvös number, a dimensionless value used to characterize the shape of bubbles rising in a fluid, defined as:

\[ Eo = \frac{\Delta \rho g l^2}{\gamma} \]  

(2-19)
where $\Delta \rho$ is the difference in density between the bubble and the fluid, $g$ is acceleration due to gravity, and $L$ is the characteristic length. Combined, these can be used to roughly approximate the upward velocity of a bubble rising in saturated porous media (McGee and Huang, 2004)

$$V_v = \tau \phi (1 - \alpha_{lf}) v_b = \tau \frac{\phi (1 - \alpha_{lf})}{d} (c_1 E_0 d_1 + c_1 E_0 d_2)$$ (2-20)

where $V_v$ is the vertical flow velocity of the bubble, $\tau$ is the tortuosity of the porous medium, $\phi$ is porosity, and $\alpha_{lf}$ is the liquid volume fraction present.

This relationship is particularly helpful in the design of vapour extraction systems often used in ERH and Thermal Conductive Heating (TCH). This is because it is extremely important to provide a great enough negative pressure at these extraction points to capture rising bubbles before they reach cooler areas close to the ground surface, which may lead to condensation and ultimately, the inability to capture vaporized solvents.

### 2.6 Electrical Properties of Porous Media

The most basic relationship concerning electrical measurements of porous media is Archie’s Law, developed in 1942. Empirically determined, the simple relationship draws the connection between the electrical resistivity of rock and the water content of the pore space:

$$\rho_{\text{resist}} = a \rho_{\text{resist, w}} \phi^{-m}$$ (2-21)
Where $\rho_{resi}r$ is the electrical resistivity of the solid bulk rock, $\rho_{resi}w$ is the resistivity of the liquid water in the pore space, $\varnothing$ is the porosity of the rock, and the parameters, $a$ (0.62-3.5) and $m$ (1.37-1.95) are parameters determined through laboratory analysis (Balberg, 1985). The expression used for rock has also been successfully applied to saturated soils (Jinguuji et al, 2007). Archie’s law shows that the bulk conductivity of a porous material is a function of the porosity and the connectivity of this pore space, implying that electrical charge travels only through the electrolytic fluid existing between the soil grains, assuming that there is a continuous path available to close the electrical circuit between two electrodes.

Archie’s law is limited in the respect that it only concerns itself with ‘clean soils’, meaning that the matrices are poor conductors, such as silica sand. Otherwise, in a case such as cation-rich clays, for example, minerals contained in the lattice of the matrix formation would contribute to ion exchange, thereby affecting the overall electrical conductivity of the soil (Bussian, 1983). A number of modified models have since been developed to address this limitation.

One of the first attempts to develop a model of this type was conducted by Waxman and Smits (1968), which similarly to Archie’s law, was based on empirical data. The model however included contributions to bulk conductivity from both the pore water volume as well as the cation exchange capacity (CEC) of the clay minerals present in the porous medium (Wildenschild et al, 2000). CEC is a measure of the number of cations that a soil particle is able to hold, or the total negative charge of a particle and is a function of clay content as well as organic matter present. Further expansion on this model was developed by Johnson and Sen (1988) followed by Samstag
and Morgan (1991), Revil et al (1998) and Mojid and Cho (2008). These later expressions included descriptions of the vadose zone, parameters such as ionic content of the pore water, the electrical double layer and more advanced concepts which will not be discussed here. Some examples of typical resistivity values of common soils and rock types can be found in Table 2-3:

Table 2-3 - Typical electrical resistivities of soils and rocks (FLHP, 2008)

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Resistivity (Ω•m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay</td>
<td>1-20</td>
</tr>
<tr>
<td>Sand, wet to moist</td>
<td>2-200</td>
</tr>
<tr>
<td>Shale</td>
<td>1-500</td>
</tr>
<tr>
<td>Porous Limestone</td>
<td>100-1,000</td>
</tr>
<tr>
<td>Dense Limestone</td>
<td>1,000-1,000,000</td>
</tr>
<tr>
<td>Metamorphic Rocks</td>
<td>50-1,000,000</td>
</tr>
<tr>
<td>Igneous Rocks</td>
<td>100-1,000,000</td>
</tr>
</tbody>
</table>

2.7 Mechanisms of Contaminant Removal

2.7.1 Boiling and Co-Boiling

Vaporization and boiling are two major influences on the aggressive remediation enhancement seen in thermal remediation method. There are two types of vaporization, evaporation, which is the change of a liquid to a gas below the boiling point of that particular liquid, and boiling, which occurs at the boiling point. Raoult’s law can be used to determine the total pressure of the substance ($P_t$), which is a summation of the vapour pressures of each of the components ($P_n$).
When the substance is an ideal, multi-component mixture, these pressures are known as partial pressures (Smith and Van Ness, 1987).

\[ P_t = x_1 P_1 + x_2 P_2 + x_3 P_3 \ldots + x_n P_n \]  

(2-22)

where \( P_n \) is the vapour pressure of the pure substance at a given temperature, and \( x_n \) is the mole fraction of the substance present in the mixture. Clearly, a substance that exists in a higher quantity in the mixture will contribute more greatly to the total pressure than one that is only present in trace amounts (Smith and Van Ness, 1987).

The vapour pressure of a pure substance can be determined using the Antoine equation (Zumdahl, 1998):

\[ \ln P = A_a - \left( \frac{B_a}{T + C_a} \right) \]  

(2-23)

Where \( A, B \) and \( C \) are constants empirically determined for each substance, and can be found in references such as Coulson’s and Richardson’s Chemical Engineering (2005). The values for TCE and PCE are listed below in Table 2-4:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Antoine Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>TCE</td>
</tr>
<tr>
<td>( A_a )</td>
<td>14.1469</td>
</tr>
<tr>
<td>( B_a )</td>
<td>3259.27</td>
</tr>
<tr>
<td>( C_a )</td>
<td>-52.15</td>
</tr>
</tbody>
</table>

The total vapour pressure of a substance is useful in describing the tendency of a liquid to change into the gas phase, as it is the pressure exerted by a vapour in equilibrium with its liquid phases.
Higher vapour pressures are indicative of a substance very prone to vaporization. The boiling point of a liquid is defined as the temperature at which the vapour pressure is equal to the ambient pressure. Vapour pressures are highly sensitive to changes in temperature, and increase as this temperature is raised. As the boiling point of an ideal binary solution is dependent on the molar composition of the liquid, the temperature of boiling will always be between the temperatures that either pure component boils.

Although this is true for solutions, immiscible mixtures behave differently as they are 2-phase liquid-liquid binary systems. Considering Raoult’s law, a 2-phase liquid-liquid system is comprised of two substances that do not mix, forcing the mole fraction to reduce to 1. This changes Raoult’s law to the simplified (Smith and Van Ness, 1987):

\[ P_t = P_1 + P_2 \]  

(2-24)

As the mole fraction is no longer a factor in determining the total pressure of the liquid, the boiling temperature of an immiscible system is actually lower than either pure substance, as each partial pressure contributes a greater amount to the total pressure. This theory applies to chlorinated solvents, which are immiscible in water, and presents an added benefit to thermal remediation techniques as the boiling temperature will be significantly reduced (USEPA 2004). A plot of the vapour pressure of TCE and TCE in the presence of water can be found in Figure 2-7.
This phenomenon is particularly useful when contaminants have extremely high boiling points, such as PCBs, used as an insulator in high temperature electrical transformers. A common term for this process is steam distillation, or co-distillation, and has been used in many areas, such as the extraction of oils from plant matter, as in the fragrance industry.

The mole fraction of the resulting vapour mixture obtained from the steam distillation process can be determined very simply by employing the ideal gas law:

\[ PV = nRT \]  \hspace{1cm} (2-25)

where \( P \) is pressure, in this case the vapour pressure at the point of boiling, \( V \) is volume, \( n \) is moles, \( R \) is the universal gas constant and \( T \) is temperature. Since there is a net transfer of all the liquid to the vapour phase, it is clear that the gas comprised of two components will occupy
one finite volume. The composition of the vapour can be expressed as a mole fraction of vapour phase water and vapour phase TCE:

\[ P_{\text{water}} V_{\text{water}} = n_{\text{water}} R T_{\text{water}} \]  \hspace{1cm} (2-26)

combined with:

\[ P_{\text{organic}} V_{\text{organic}} = n_{\text{organic}} R T_{\text{organic}} \]  \hspace{1cm} (2-27)

forming the ratio:

\[ \frac{P_{\text{water}} V_{\text{water}}}{P_{\text{organic}} V_{\text{organic}}} = \frac{n_{\text{water}} R T_{\text{water}}}{n_{\text{organic}} R T_{\text{organic}}} \]  \hspace{1cm} (2-28)

Because the vapour occupies one volume, the V terms can cancel out, and since the temperature in that volume does not vary, so will T. R being a universal value also reduces to unity, leaving a final expression:

\[ \frac{P_{\text{water}}}{P_{\text{organic}}} = \frac{n_{\text{water}}}{n_{\text{organic}}} \]  \hspace{1cm} (2-29)

By this expression we can see that the proportion of each component present in the vapour phase on a molar basis is proportional to the vapour pressure at the distillation temperature.
2.7.2 Increase in Porosity

The boiling of water in the subsurface also has the effect of increasing pore volume in the medium. Especially affected are low permeability soils, such as clays and silts which normally act as a barrier to mass transfer. Due to the relatively sudden expansion of fluids which are vaporized during the boiling process, the build-up of pressure forces the creation of pore space. This phenomenon is illustrated in Figure 2-8.

![Figure 2-8 - Increased porosity due to subsurface boiling (Reproduced from McGee, 2004)](image)

The creation of large pores interconnected with striated micro-fractures results in a medium with a much greater porosity than before it was thermally altered (McGee, 2004).
2.7.3 Viscosity, Adsorption and Solubility

Thermal remedies produce several other mechanisms by which contaminants may be efficiently removed from a treatment area. Some of the more notable effects of elevated temperatures include a decrease in viscosity of DNAPL, decreased sorption and increased solubility into the aqueous phase.

Viscosity is reduced as temperature is increased. Organic solvents, such as TCE have been shown to have a viscosity drop of approximately 1% for every degree °C that temperature is increased. When extraction wells are being used for mass removal of contaminant, as is common in thermal remediation, the lowered viscosity of solvents is a benefit, as it facilitates the migration of source zones to these extraction points.

Adsorption is also decreased as temperatures are elevated, as it is a function of organic carbon fraction, surface area available, and the partitioning of contaminant between the liquid and vapour phases. It has been found that Henry’s constant increases dramatically with temperature (Heron et al, 1998a), skewing the partitioning towards the vapour phase fluids, decreasing the overall adsorption in the porous medium. This decrease also contributes to a greater ease of contaminant mobilization, making collection at extraction wells more efficient than at lower temperatures.

Solubility has been studied in the case of TCE as a function of temperature (Knauss et al, 2000). It was found that between the temperatures of 20.85 °C and 116.85°C, the solubility in water increased from 0.010763 mol/L to 0.037889 mol/L. The practical advantage of this is that water
removed from the treatment area contains a greater concentration of TCE when remediation is conducted in higher temperature ranges, facilitating the ease of mass removal.

2.7.4 Thermal Conductive Heating

Thermal conductive heating (TCH) is a method of contaminant removal that utilizes the implantation of heating elements to raise the temperature of soils impacted with hydrocarbon contaminants. Heat is carried through both conductive and to some extent, convective transfer. TCH is generally applied in conjunction with a vacuum extraction system to remove volatilized components faster and more efficiently than through upward movement due to buoyancy alone.

Wells are drilled in the area to be treated in a hexagonal arrangement surrounding the area of interest. Each well contains an electrical heating element, and a seventh well containing both a heating element and the extraction system lies in the centre of the hexagon. Conduction, being the most prominent form of heat transfer in this method raises the temperature of the subsurface. This leads to the upward mobilization and possibly destruction of contaminants if the heat flux is great enough. Steam distillation, accelerated oxidation and thermolysis are all triggered in conjunction to achieve mass removal. TCH methods can achieve temperatures that typically range from 100°C up to 500°C, dependant on the compounds present at the site and the specific goals of treatment. This magnitude of heat flux is generally made by considering the most efficient heat at which the compounds may be mobilized and/or destroyed. Lighter, more volatile compounds such as TCE, PCE and BTEX boil at low temperatures, and require smaller fluxes of heat. Heavier, less volatile compounds, such as
PCBs, however, may require a greater input of energy to achieve similar effects (Stegemeier and Vinegar, 2001).

One limitation to TCH is that while heat is generated in-situ, it is only done so at the elements in the wells. As such, a sufficient gradient must be established between these wells and cooler regions to induce heat transfer. The time to produce such a gradient leads to a less efficient heating method than electrical resistance heating (ERH). With electrical resistance heating, the thermal energy is created by resistance between electrodes, meaning that heat is actually generated in the resistive areas between electrodes, which in practice, is the area containing contaminant.

2.7.5 Steam Enhanced Extraction

Steam enhanced extraction (SEE), uses the introduction of high-temperature water vapour injected into the subsurface in order to promote heat flux into an area to be treated. Unlike TCH, destruction of compounds is not generally observed, so all treatment of hazardous materials must be performed ex-situ after the extraction process. As with TCH and ERH, wells are drilled into a site in a similar hexagonal pattern, or a ring fashion utilizing another number of wells. A central well for extraction is also required.

The outer wells are all outfitted with steam injection pipes which force the water vapour into the subsurface, where the thermal energy of the steam is transferred to the porous media. As the liquid zone comes into contact with the compounds of concern, the temperature is still low, and
the main effect is the flushing of contaminant from pores by means of simple displacement. As the cool water is replaced with the two-phase liquid/vapour zone, temperatures increase, causing a lowering of viscosity and increase in solubility, making mobilization of the compounds towards the extraction point easier. Finally, when the single-phase steam zone reaches the compounds, temperatures are sufficiently high to induce vaporization and steam distillation, causing vapour phase contaminant to be drawn towards the negative pressure of the extraction well.

The main drawback to the SEE approach is the high sensitivity of the method to the permeability of the subsurface. As low permeability features within a generally high permeability site present a significant barrier to mass transfer, injection of steam into such areas is greatly hindered. This can result in uneven heating or a complete inability to heat sites. Hydraulic conductivity varies much more than thermal conductivity in soils, limiting the effectiveness of SEE alone. There have been several cases however, of SEE being combined with ERH or TCH in order to boost efficiency of each in such situations, adding conductive elements to the mass-transfer based SEE. ERH has particularly been investigated as the higher resistance and thus, higher rate of ohmic heating in low permeability soils is a highly synergistic pairing to SEE considering the latter’s limitations in such areas (Heron, 1998b).

2.7.6 Electrical Resistance Heating

Electrical resistance heating is a thermal technology that relies on the application of an alternating electrical current into the subsurface in order to generate heat. ERH was originally developed by the United Stated Department of Energy as a dewatering technique to be used in the petroleum
industry (Beyke and Flemming, 2005). The inherent electrical resistivity of the soil matrix results in electrical energy being converted to thermal energy. As dictated by Ohm’s law, the targeted area is heated by this energy conversion from the electrical to thermal form. Because moisture is the primary conductive vehicle for the transfer of electrical charge, ERH may be implemented in both the saturated and vadose zone. ERH also does not suffer from the mass transfer limitations of other thermal technologies such as SEE since heat is generated in-situ rather than relying on the mechanical transport of hot fluids to carry thermal energy to affected areas. Additionally, low permeability areas are preferentially heated in practice, as they often are composed of clay or high-clay-content soils, which are efficient electrical conductors due to ion exchange.

In practice, it is usually applied in both three and six-phase varieties. The overlapping of these electrical phases in these cases increases the total power delivery of the system and the choice between six phase heating (SPH) and three phase heating (TPH) is dependent on the size and shape of the area to be treated. Current is drawn from local transmission lines that are connected directly to a power control unit (PCU), which is housed in a trailer on site. The role of the PCU is to regulate the amount of power that is delivered to the subsurface. The amperage and by extension, power delivered to the site will be dictated by water saturation, electrode spacing and electrical properties of the subsurface.

SPH is set up with a hexagonal array of electrodes with one neutral ground in the centre of the ring as shown in Figure 2-9 (Cacciatore and Clark, 2004). Electrical phases are periodically alternated between these electrodes to provide a more even heating distribution avoiding ‘hot spots’ within the treatment area. When this is done, the heating pattern of SPH is very even,
although due to electrical resistance inherent in the soil, the maximum size of the hexagonal array is somewhat limited.

TPH is an alternative to SPH that is more appropriate for large treatment areas. TPH electrodes are set in triangular arrays, but may also be placed adjacent to each other, allowing very large and irregularly shaped treatment areas.

![Figure 2-9 - Schematic of a typical SPH equipment setup (Reproduced from USEPA, 1999)](image)

As with SPH, vapour extraction wells are placed in the centre of each array to vent off volatilized solvents, and may also be used in conjunction with other technologies such as air-sparging (USEPA, 2003) steam enhanced extraction (SEE) (Hudson et al., 2002) and bio-technologies. Contaminants that are extracted are routed to a containment apparatus and are subsequently treated.
2.7.7 Laboratory Studies and Computer Modeling

Bench scale laboratory studies have been conducted investigating the efficacy of ERH in remedial operations, although there have been few published works on this topic. These investigations generally involve a column apparatus, rectangular soil cell, or predictive mathematical models. Although there have been some published accounts of such trials, there is little research conducted on the bench scale investigating electrical resistance heating in relation to groundwater remediation, especially those concentrating on pooled DNAPL.

Heron et al. (1998b) conducted studies on a bench scale using ERH in combination with steam enhanced extraction (SEE) to remove dissolved phase (1120 mg/L) TCE from water in silty soil. The experiment was conducted in a two dimensional column in which an electrical current was applied. The cell was filled with a low permeability soil, which contained a water table, segmenting the domain into a saturated and vadose zone. During testing, ERH raised the temperature to 85°C, then with higher amperage, elevated even higher to 100 °C. During this time, steam was also injected into the experimental domain. Mass removal from the source zone was reported to be 99.8%.

A study was also performed at Umeå University investigating ERH and vacuum extraction in conjunction on ground water contaminated with dissolved phase PCE rather than a single, coherent pool. (Näslund, 2003) Using a cylindrical column, with a homogenous soil packing regime, contaminated groundwater was thermally treated showing concentration reductions of 98%, and no formation of degradation products.
Hendricks et al (2006) and Carrigan and Nitao (2000) have both proposed mathematical models to describe mass transfer processes applicable to the simulation of ERH implementation combined with vapour extraction. The models presented a set of governing equations for a multiphase, multi-component system under the influence of an applied heat flux, making them appropriate for a number of thermal remedies including ERH and possibly TCH.

### 2.7.8 Pilot Scale Studies

A number of pilot scale studies have been conducted using ERH technology, primarily in the U.S. Due to the small size of pilot scale studies, six phase heating (SPH) is generally preferred as it provides a high degree of uniformity in heating patterns, and due to symmetry, works most efficiently in small areas.

Notable examples of pilot scale trials of ERH that have been conducted include a six month project in Alameda Point, California (Cacciatore and Clark, 2004) from June 2002 to January 2003. Six phase heating was the chosen technology because of the small scale of the project, and resulted in a reduction of chlorinated volatile organic compounds (CVOCs). They were reduced from an initial level of 35,000 ppb to 700 ppb, accounting in a total of 81 lbs (36.7 kg) of solvent being collected and condensed. SPH was also used at a superfund site in Massachusetts in 2002-2003 which was contaminated with VOCs, BTEX, aromatic compounds and styrenes. Heating took place over a three-month period, and produced shallow water VOC concentrations (up to 24 ft below ground surface (bgs) or 7.3 m bgs) to drop by more than 99% and deeper water concentrations to be reduced by 84% (Scaramuzzo, 2004).
2.7.9 Full-Scale Studies

Full scale implementation of ERH has been conducted at many sites, and has increased since
ERH became a commercially available remediation technique in 1997. ERH has been applied to
remediate both LNAPL and DNAPL varieties of chlorinated solvents in such industrial sites as
adhesive film plants (Pope, 2002) and uranium enrichment facilities, (Smart, 2004), and have
been proven effective in various permeability soils (Francis and Wolf, 2004).

The non-invasive nature of ERH technology has presented many benefits, including remediation
activities conducted underneath existing structures as documented by McGee et al., (2003), who
conducted a form of ERH underneath an occupied apartment building. Fain et al., (2002)
conducted similar trials in an industrial manufacturing environment.

Other types of sites that have been treated using ERH include a waste pit in the Lowry Landfill
Superfund site in Denver Colorado. Approximately 12,000 gallons (54.6 m³) of LNAPL and
17,000 kg of VOCs were extracted during the course of the trial, demonstrating the effectiveness
of ERH where buried debris and drums are present (Palehn et al., 2004). ERH has also been
combined with successful results with SEE (Heron et. al., 2004) and soil vapour extraction (SVE)
(Hudson et al., 2002).
2.8 Literature Cited


http://www.epa.gov/tio/download/remed/epa542r04010.pdf


http://www.epa.gov/safewater/dwh/t-voc/trichlor.html


http://www.geo4va.vt.edu/A1/A1.htm


Chapter 3

Laboratory Study Evaluating Electrical Resistance Heating of Pooled Trichloroethylene

Abstract

A laboratory scale study was conducted to simulate the thermal remediation of pooled trichloroethylene (TCE) perched on a capillary barrier in a saturated groundwater environment using electrical resistance heating (ERH). Two scenarios were examined in a 2-dimensional polycarbonate test cell, the first consisting of a single pool of TCE underneath a partial capillary barrier, and the second with two pools of TCE, each perched on a capillary barrier positioned one above the other, both of which spanned the entire width of the cell. The soil was heated using ERH until the source zones had reached a target temperature of 100°C. Data was collected to examine processes occurring during the heating process including temperature readings from an array of 32 thermocouples. The vaporization and disappearance of liquid phase TCE in the source zones, as well as the upward migration of the vapour produced was recorded using a digital camera. Chemical samples were collected 48 hours after experiment termination and subsequently analyzed to evaluate efficacy of treatment in each case. A co-boiling plateau in temperature was found to be a clear and evident sign of an ongoing phase change in the pooled TCE. Temperature was found to increase more rapidly in the fully spanning barrier experiments as a result of heat retention due to its insulating properties. As temperatures increased above the co-boiling plateau, vapour rise continued to be observed visually, and was found to create a zone of gas saturation beneath the capillary barrier when no clear pathway was available for it to escape upwards. When the source zones had reached the specified target temperature and the
ERH process stopped, this gas zone condensed, leading to elevated TCE concentrations below as well as within the capillary barrier itself. The water table within the experimental cell was also noted to drop measurably at the time of gas condensation. Post-experimental chemical analysis showed reductions in TCE concentrations of over 99.04% compared to the source zone, although due to condensation of entrapped vapour and convective mixing, there was a net redistribution of TCE within the experimental domain especially within confined areas below the capillary barriers.
3.1 Introduction

Contamination of groundwater by dense, non-aqueous phase liquids (DNAPLs) has become a major problem worldwide, impacting water quality and subsequently, human health. Remediation of DNAPL impacted areas has become a high priority, spurring a great deal of research in the field directed at improvements of remediation technologies. Recently, a class of thermally-based methods including steam-flushing, thermal conductive heating (TCH) and electrical resistance heating (ERH) have received a great deal of attention due to unique properties of the techniques. Thermal technologies can be effective in overcoming mass transfer limitations prevalent in more traditional methods such as pump-and-treat, and soil-vapour extraction (SVE) (USEPA, 2003; USEPA, 2004; Heron, 1998b; Näslund, 2003; Hendricks, 2006).

Bench scale laboratory studies have been conducted investigating the efficacy of ERH in remedial operations, although there have been few published works on this topic. None of these deal with pooled DNAPL, nor do they investigate DNAPL entrapped beneath capillary barriers under conditions of ineffective or non-existent vapour extraction.

Heron et al (1998b) conducted studies on a bench scale using ERH in combination with steam enhanced extraction (SEE) to remove trichloroethylene (TCE) from a solution of water (1120 mg/L) in medium of silty soil. The experiment was conducted in a two dimensional column across which an electrical current was applied.

The cell was filled with a low permeability soil, which contained a water table, segmenting the domain into a saturated and vadose zone. During the experiment, ERH raised the temperature to
85°C, then with a higher applied amperage, to 100 °C. During this time, steam was also injected into the experimental domain. Mass removal from the source zone was reported to be 99.8%.

A study was also performed at Umeå University investigating the use of ERH coupled with vacuum extraction on ground water contaminated with dissolved phase tetrachloroethylene (PCE) (Näslund, 2003). Using a cylindrical column, with a homogenous soil packing regime, contaminated groundwater was thermally treated showing concentration reductions of 98%, and with no observed formation of degradation products.

Hendricks et al (2006) and Carrigan and Nitao (2000) have both proposed mathematical models to describe mass transfer processes applicable to the simulation of ERH implementation combined with vapour extraction. The models presented a set of governing equations for a multiphase, multi-component system under the influence of an applied heat flux, making them appropriate for a number of thermal remedies including ERH.

The objective of this study is to observe, through visualization and temperature monitoring, the ERH process on pooled DNAPL which to this point has not been documented. Interactions with partially and fully confining low permeability capillary barriers will be included to determine their impact on the heating and upward migration of vapour during the ERH process.

3.2 Materials

The ERH experiments were conducted in a 76.2 cm wide, 16.51 cm thick, 40.64 cm high test cell constructed from 1.27 cm thick Makrolon brand polycarbonate plastic sheeting. The internal
The dimensions of the box were 73.66 cm x 13.97 cm x 38.1 cm, and all seams were joined with a high temperature epoxy (CLR 1390 resin with CLH 6120 hardener, Crosslink Technology Inc.). The inside surfaces of the cell were laminated with optically clear 10 mil Teflon film (Fluorogrip-F HD-FEP Teflon, Integument Technologies Inc.) and backed with an acrylic adhesive. Seams in the lamination were sealed using a viton rubber caulking compound (SC-200 Fluorogrip Elastomer Caulk, Integument Technologies Inc.). A sheet of glass was placed against the inside viewing face of the cell to ensure that the DNAPL would be non-wetting with respect to water.

![Figure 3-1 - Design view of test cell showing basic dimensions and key features](image)

The rear face of the cell was held in place by 1.91 cm long 8-32 thread size screws holding down a 0.794 mm viton rubber o-ring stock held in a square groove providing a gas-tight seal. The edges of the soil cell were further reinforced by an aluminum frame constructed of 2.54 cm square structural aluminum tubing with 3.18 mm wall thickness held tight by a series of clamps.
The rear face of the experimental cell was equipped with 32 thermocouple ports sealed with viton rubber o-rings. The thermocouples were arranged in a rectangular grid with 4 thermocouples in the vertical direction and 8 in the horizontal. The tips of the thermocouples extended into the centre of the test cell. The spacing between thermocouples, both vertically and horizontally, was 7.62 cm as shown in Figure 3-3. The thermocouples used were ungrounded T-type, stainless steel probe design (Omega Engineering Inc.). Each thermocouple measured 10.16 cm in length, and 0.3175 cm in diameter. Temperature data was collected from the array of thermocouples by a Keithley 2700 digital multimeter, equipped with a Keithley 7708 40-channel multiplexer with internal cold-junction circuit.
Figure 3-3 – Dimensions and thermocouple locations (red circle) in test cell in single pool (top) and double pool (bottom) experiments. The grid spacing is 5 cm square

Electrical current was delivered to the sand pack using two electrodes. The electrodes were constructed of stainless steel plates 30.48 cm tall, 10.16 cm wide and 0.3175 cm thick, and were connected by a bolt-attached crimp connector to 14 AWG temperature-rated cabling. The spacing between electrodes was maintained at a distance of 35 cm, and the electrodes spanned both the upper and lower boundaries in the single and double pool experiments.
The test cell was also equipped with a water delivery system that could replenish moisture lost from the cell during the experiment due to vaporization and collection. This system consisted of a pair of perforated Teflon wells placed vertically in the sand pack on the outside of each electrode. The wells extended to the same depth as the electrodes themselves, and ran to sealed ports that protruded through the top of the pressure cell alongside ports for cabling and vapour out lines. The wells were plugged with gas tight viton rubber stoppers. When additional water was required to be added, these stoppers were opened, the water was introduced to the cell, and the stoppers were immediately resealed. Water that was introduced during experiments was pre-heated to the average temperature of the cell so as not to introduce any thermal gradients or major cooling effects within the experimental domain.

Well graded sand was purchased then #16 and #50 mesh sands were extracted using mechanical sifting to ensure a narrow grain distribution and uniformity in each size. The #16 and #50 sands had permeability values of $5.04 \times 10^{-6}$ cm$^2$ and $5.26 \times 10^{-7}$ cm$^2$, respectively (Kueper et al., 1989). The porosities of the sands were also measured at $\phi=0.45$ and $\phi=0.41$ respectively, using a water-displacement method. Forensic grade TCE was used (Fischer Scientific Inc.), pigmented with a hydrophobic dye (Oil Red O, Sigma Aldrich Inc.) at a concentration of approximately 144 mg/L to increase ease of visualization.

A collection system which had its own designated port in the top of the test cell was constructed to vent vaporized TCE and water. The port and exit line were constructed of Teflon (PTFE), and the port was sealed using viton caulking to ensure a gas tight seal. The Teflon tubing leading away from the port was insulated using neoprene foam wrapped tightly around the tube
preventing any condensation before the vapour reached a glass collection vessel, which was placed in an ice bath to ensure it remained in liquid form and that a minimum of volatiles were lost. The collection vessel also featured a gas line leading to a fume hood as a safety precaution to handle any possibility of re-vaporization of TCE as well as to allow equalization to avoid a pressure build-up that would prevent filling of the vessel.

The rear of the test cell was designed with an overflow port, intended to act as a runoff channel to carry away liquid in the cell that reached a height of less than 2.5 cm from the top of the cell. During heating, liquid expansion forced the water level to rise, which was carried out through this system and into a glass collection vessel which had the same design as the one used in the condensation system. The source of AC power used was a Hewlett-Packard Agilent 6811B programmable AC power supply. The unit is capable of a 375 volt-amp (VA) output, with a maximum of 300Vrms.

3.3 Methodology

3.3.1 Experimental Setup

In both experiments, the main body of the packing comprised the #16 mesh sand, with horizontal barriers made from the lower permeability #50 mesh sand. Both schemes were constructed using a wet packing technique where sand was added to the test cell partially filled with water to prevent the entrapment of air bubbles in the pore space. Water and sand were added to the cell in an alternating fashion so that the water level never fell below the top of the sand pack.
The first experiment included a base layer of the low permeability sand, which was used as a capillary barrier to support a pool of TCE, which was added halfway through the packing process, pictured in Figure 3-4. The base layer was formed in a bowl shape. The 5 cm deep bowl spanned approximately 30 cm in the centre of the cell.

Figure 3-4 - Schematic representation of soil packing regime for single pool experiment (top) and double pool experiment (bottom). Each grid square is 5 cm tall and 5 cm wide.
Approximately 16 cm above the bottom of the bowl (where the bottom of the DNAPL pool was situated) and centered above it was a barrier of the low permeability silica measuring 5 cm in height and 25 cm in width. The remainder of the cell was packed using the high permeability sand.

The second experiment was created in a similar method, using a packing method with a layer of water. It consisted of a bowl similar to the first experiment (A depth of 5 cm and a span of approximately 30 cm horizontally). Another barrier composed of low permeability sand was constructed 10 cm above the bottom point of the lower bowl. The upper barrier spanned the entire width of the cell, and had the same dimensions as the base layer with a 5 cm deep, 30 cm wide bowl shape intended to support the second DNAPL pool.

In both experiments the addition of DNAPL was completed before the upper barrier was placed, avoiding any possible disruption of the fine grained sand. The TCE was added using a 50 ml glass pipette held vertically into the sand pack by hand. The DNAPL was allowed to drain under gravity out of the pipette and subsequently spread laterally above the capillary barrier. The volumes of the pools used in both experiments are summarized in Table 3-1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Number of Pools</th>
<th>Lower Pool Volume (ml)</th>
<th>Upper Pool Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Barrier</td>
<td>1</td>
<td>298</td>
<td>--</td>
</tr>
<tr>
<td>Double Barrier</td>
<td>2</td>
<td>293</td>
<td>296</td>
</tr>
</tbody>
</table>
Given the soil properties and cross-sectional area of the cell, a pool height was calculated using a goal seek function in Microsoft EXCEL with values found in Table 3-2 and the relation (Longino and Kueper, 1995):

\[
V_{NW} = A \phi \left( L_2 - S_r L_2 - \frac{(1 - S_r) (P_d^A)}{(-\lambda + 1) (\Delta \rho g)} \times \left\{ (P_D + \Delta \rho L_2)^{-\lambda+1} - P_d^{-\lambda+1} \right\} \right)
\] (3-1)

where \( V_{NW} \) is volume of non-wetting fluid, \( A \) is the plan view area of the pool, \( \phi \) is the porosity of the sand, \( L_2 \) is the height of the pool and \( S_r \) is the residual wetting phase saturation, \( \lambda \) is the pore size distribution index, \( P_d \) is the displacement pressure, \( g \) is the acceleration due to gravity and \( \Delta \rho \) is the difference in density between the wetting and non-wetting fluids. Equation 3-1 assumes that the entire pool is under drainage conditions, consistent with the experiment conditions.

<table>
<thead>
<tr>
<th>Sand</th>
<th>( P_d ) (cm water)</th>
<th>( \lambda )</th>
<th>( S_r )</th>
<th>Permeability (cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>#16 Silica</td>
<td>3.77</td>
<td>3.86</td>
<td>0.078</td>
<td>5.04 x 10(^{-6})</td>
</tr>
<tr>
<td>#50 Silica</td>
<td>13.5</td>
<td>2.49</td>
<td>0.098</td>
<td>5.26 x 10(^{-7})</td>
</tr>
</tbody>
</table>

Using the modified Raoult’s law for immiscible liquids, the vapour pressure of TCE and water can be determined from (Smith and Van Ness, 1987):
\[ P^* = P_1^{sat} + P_2^{sat} \]  

where \( P^* \) is the total vapour pressure of the immiscible liquid system, \( P_1^{sat} \) is the vapour pressure of the first immiscible liquid, water in this case, and \( P_2^{sat} \) the vapour pressure of the second, pure TCE, at a defined temperature.

Substituting atmospheric pressure (101.325 KPa) for \( P^* \) and Antoine’s law used to calculate \( P_1^{sat} \) and \( P_2^{sat} \) (Felder and Rousseau, 2000), the following expression can be derived:

\[
101.325 = \exp\left( A_{water} - \frac{B_{water}}{T + C_{water}} \right) + \exp\left( A_{TCE} - \frac{B_{TCE}}{T + C_{TCE}} \right)
\]  

(3-3)

<table>
<thead>
<tr>
<th>Substance</th>
<th>( A_s )</th>
<th>( B_s )</th>
<th>( C_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>16.5362</td>
<td>3985.44</td>
<td>-38.9974</td>
</tr>
<tr>
<td>TCE</td>
<td>14.1654</td>
<td>3028.13</td>
<td>-43.15</td>
</tr>
</tbody>
</table>

Table 3-3 - Antoine constants for water and trichloroethylene (Sinnott, 2005)

where \( T \) is temperature. By solving for \( T \) using the Antoine constants in Table 3-3, the co-boiling temperature of separate phase TCE in water can be estimated as 73.36°C. When TCE is dissolved in the water at 1100 mg/L the boiling temperature is slightly lower than that of pure water, 99.8°C.
3.3.2 Sample Locations and Methods

Both the single and double pool experiments were sampled and analyzed to determine the TCE soil concentration after treatment. A total of 19 samples were taken in the single barrier case and 20 in the double barrier case, with sample areas concentrating on areas above the pools, the low permeability layers, as well as the capillary barriers upon which the TCE pools were placed (Figure 3-5). The samples were taken following removal of the top of the cell.

![Figure 3-5 - Schematic representation of soil sampling locations for single pool experiment (left) and double pool experiment (right)](image)

Post treatment samples were collected using a 5 g Terra core disposable plastic sampler (En Novative Technologies, Inc.). The samples were collected horizontally relative to the orientation of the performed experiments and immediately placed into a 20 ml glass vial sealed with a Teflon lid. The samples were analyzed for TCE concentration using purge-and-trap gas chromatography.
by the Queen’s University Analytical Services Unit (ASU). In addition to the samples taken from
the test cell, one blank sample of uncontaminated silica was submitted as a baseline for
comparison. Original laboratory analysis result reports are provided in appendix B.

The heating process was conducted at a set voltage of 300 \( V_{\text{rms}} \) (\( \pm 0.3V \)) to prevent any possible
safety hazards associated with a set current. Increases in resistivity with a set current can lead to
over-powering and eventual overheating (Heron et al, 1998b). Photographs of the viewing pane
were taken every 30 minutes, and temperature readings were logged every 60 seconds.

3.4 Results

3.4.1 Temperature and Visual Observations – Single Pool Experiment

Temperature readings for all thermocouples rose rapidly in the first 24 hours of heating. A
representative sample of temperature readings is pictured in Figure 3-6. The thermocouples
whose temperature readings are presented in this figure form a vertical line, centred above the
DNAPL pool. These TC readings show the general trend representative of thermocouples
between the ERH electrodes, and demonstrate a greater rate of heating in the upper areas of the
cell, and lower rates near the bottom. The faster heating regions also demonstrated a reduction in
heating rate earlier in time than the lower, as can be seen when the plots of thermocouple 5 (TC5)
and TC13 are compared to TC21 and TC29. Temperature readings for individual thermocouples
can be found in Appendix A.
A reduction in the rate of temperature increase was observed first in TC5 and TC6, the thermocouples on the uppermost row, followed shortly thereafter by thermocouples on the left and right. TC5 and TC6 also reported the highest absolute temperatures. Thermocouples in the lower rows exhibited similar curves that showed reductions in the rate of heating later than those above them, the last being TC32 at the bottom right of the array, which began to slow at approximately 30.6 hours.

Figure 3-6 - Temperature versus time at selected thermocouples in single pool experiment. See Figure 3-3 for thermocouple positions
No obvious evidence of a co-boiling plateau was observed from any thermocouples implanted in the pool itself, although anomalous readings were recorded in TC30, situated in the centre of the source zone. At 30.2 hours, a downward trend was observed in the temperature readings distinct from the smooth transition of slopes recorded by adjacent thermocouples. This anomalous slope spanned from 30.2 hours to approximately 40 hours, ranging from 73.1°C to 74.3°C. The reading of TC29, situated on the left hand side of the source zone showed no abrupt change of slope during this period, but did show a slowing of temperature rise until 40 hours. It resumed a slope typical of surrounding thermocouples at a temperature of 75.3°C.

This anomaly does coincide with visual observations of source zone depletion, which was captured photographically. Photographs taken every 30 minutes between 32.5 hours and 35 hours shown in Figure 3-7 chart the visual disappearance of the TCE pool.

During the heating process temperature readings climbed in a smooth curve at each thermocouple location. Two major drops were observed, most prominently in the top row of thermocouples at 154.0 hours and 276.0 hours, which coincided with the addition of water to the cell. Water was added when the water table had dropped by 2.5 cm. 3L of tap water, heated to 83°C and 95°C respectively to match the average temperature of water contained in the soil cell was added. The momentary drop observed in the temperature readings was due to a shut off of electrical power (less than 5 minutes in each case) required to add this water safely. As temperatures reached the boiling point of water, readings reached and maintained a plateau until the ERH process was terminated.
After 24 hours of heating, evidence of gas accumulation underneath the capillary barrier was observed. The gas bubbles were very faint, and transitory in nature. By 96 hours of heating, greater amounts of vapour were clearly visible by eye under and around the barrier, appearing to
bypass it predominantly on the left hand side, dispersing as it travelled upwards as seen in Figure 3-8.

![Figure 3-8 - Enhanced image of vapour bypass in single pool experiment](image)

By 120 hours of heating, no continuous streams of vapour were visible, although gas appeared to be evenly dispersed throughout the #16 mesh silica.

### 3.4.2 Temperature and Visual Observations – Double Pool Experiment

The temperature readings for thermocouples rose rapidly throughout 7.5 hours of heating. A representative sampling of thermocouples is pictured in Figure 3-9. These thermocouples were aligned vertically at the centre of the DNAPL pools, and represent the general behaviour of thermocouples between the ERH electrodes. Full thermocouple readings can be found in Appendix A. TC12 and TC28 demonstrate plateaus at the co-boiling point of a TCE-water system. As with the single pool experiment, thermocouples in the upper regions of the cell showed a greater rate of heating than those in lower areas. A marked reduction in slope occurred at the 7.5 hour point, beginning with TC4 and TC5, positioned in the centre of the electrode array.
on the top row of thermocouples. This preceded the visual evidence of pool depletion. This event was followed by the other thermocouples in this row, with the centre thermocouples rate of heating slowing first, and the outside slowing last. This trend was observed with every row of thermocouples, with the rate of heating and absolute temperatures being higher in the centre of the electrode span, and cooler moving outwards from the centre-line.

![Graph](image)

**Figure 3-9 - Representative temperature readings from double pool experiment. See Figure 3-3 for thermocouple locations**

Thermocouples placed directly in the upper pool demonstrated a reduction in slope that was more extreme and more prolonged than thermocouples outside of the source zone. Both TC11 and TC12, on the left hand side of the top source zone showed a zero slope at a temperature of 73.9°C from time 6.3 hours to 8.6 hours. This preceded visual source zone of reduction, and ended while visual observations showed obvious signs of source zone decay on the left side. The
thermocouples in the right hand side of the source zone, TC 13 and TC14, reached a similar plateau temperature of 74.0°C beginning at time 7.7 hours. TC13 resumed a greater rate of heating at 9.1 hours and TC14 at 9.3 hours as pictured in Figure 3-10. This was consistent with visual observations showing the source zone remaining last at its rightmost point, shown in Figure 3-11.

After the co-boiling plateaus, the thermocouples showed slopes similar to those in their own row, a trend that was largely followed throughout the remainder of the ERH process. The four thermocouples placed in the lower pool exhibited a boiling plateau somewhat later than those placed in the upper pool. The leftmost thermocouple (TC27) reached a slope of 0 at approximately 14.2 hours, and maintained a plateau of approximately 74.2°C until 29.25 hours. To the right of that thermocouple, TC28 began a plateau of 74.2°C at 14.9 hours which ended at 30.1 hours. TC29 and TC30 displayed plateaus similar to each other ranging between 74.8°C and 75.1°C. They both began at 9.4 hours, with TC29 demonstrating increased temperature rise at 22.2 hours, and TC30 at 22.5 hours. In the case of the lower source zone, the visual observation of TCE vaporization showed no sign of TCE even while co-boiling plateaus persisted. In addition, co-boiling plateaus on the right hand side of the pool were the first to end, even though visual observations suggested that TCE was vaporized from the left first, moving towards the right hand side, suggesting that TCE that was not visible in the viewing pane was still in liquid form within close proximity to the thermocouples.

A possible co-boiling plateau was also observed on TC18 and TC23, which sit below the capillary barrier and to the and right of centre, on the outside of the thermocouple array. Between
the times of 13.35 hours and 29.1 hours, TC18 remained between 74.1°C and 74.3°C, with markedly greater slopes in the temperature readings both before and after this time range. TC23, situated on the right side of the cell, showed a possible plateau between 15.5 hours and 29.4 hours, in which time it slowly ramped from 74.2°C to 76.0°C.

Figure 3-10 - Close-up of boiling plateaus from single pool experiment (top) and double pool experiment (bottom)
There were no visually observed events that coincide with this timeframe other than the slow appearance of entrapped gas below the capillary barrier, which was barely discernable by eye and too subtle to be captured by camera.

At 48 hours, it was obvious by visual observation that entrapped gas was present in the test cell. It could be observed moving upwards in the areas above and below the capillary barrier, but too faint and transitory in nature to be recorded on camera. The gas appeared as slightly lighter patches pressed against the viewing pane that slowly formed over the course of several hours, and subsequently faded. A very prominent zone of high gas saturation had established itself immediately below the capillary barrier after 120 hours of ERH treatment. It was much lighter in colour than the smaller gas pockets observed earlier, and was easily photographed. This high saturation gas zone remained static until the ERH process was terminated.

After the co-boiling plateau phase, temperature readings climbed in a stepwise fashion, somewhat consistent with Heron et al. (1998b). Two major drops were observed, most prominently in the top row of thermocouples at 47.3 hours and 118.0 hours, which coincided with the addition of water to the cell. Water was added when the water table had dropped by 2.5 cm. 3L of tap water, heated to 83°C and 93°C to match the average temperature of water contained in the soil cell was added. The momentary drop observed in the temperature readings was due to a shut off of electrical power (less than 5 minutes in each case) required to add this water safely. As temperatures reached the boiling point of water, readings reached and maintained a plateau until the ERH process was ceased.
Figure 3-11 - Front view of pool vaporization in double pool experiment
When the lower source zone had reached 100°C, a vapour layer was still present below the capillary barrier. It measured approximately 5 cm in height and remained static and fairly uniform in height, spanning the entire width of the test cell.

After ERH treatment was discontinued, the high saturation gas layer rapidly shrank from the top down, suggesting condensation of the vapour present and liquid phase penetrating from the capillary barrier.

Figure 3-12 - Enhanced images of collapse of unsaturated zone in double pool experiment
This interpretation is supported by the observation of an approximately 5 cm drop in water level within the cell. The collapse of this vapour phase was recorded photographically, and enhanced by using contrast adjustment in Figure 3-12.

Given the volume that the gas saturated zone occupied, approximately 5 cm tall, 73.66 cm wide and 13.79 cm deep and a porosity of 0.41 the volume of void space can be calculated to be approximately 2104 ml. The pressure the vapour is under can be approximated as atmospheric pressure plus 20 cm of hydraulic head due to water above the vapour phase. The total pressure would then be calculated 103.286 kPa. By treating the gas saturation as an ideal gas mixture, a molar volume of 30.31 L at this pressure and 373.15 K is calculated by the ideal gas law:

\[ V = \left( \frac{RT}{P} \right) \]  \hspace{1cm} (3-4)

where R is the universal gas constant, T is temperature in K and P is pressure in kPa. By this molar volume, the number of moles present in the vapour cloud can be calculated as 0.0702 mol.

Using the expression relating vapour pressure to mole fraction in the process of Coboiling:

\[ \frac{P_{TCE}}{P_{water}} = \frac{n_{TCE}}{n_{water}} \]  \hspace{1cm} (3-5)

the mole fraction of TCE in the gas mixture would be 0.65, and water would be 0.35. With TCE and water having molar weights of 131.4 g/mol and 18.02 g/mol respectively, the weights of each when condensed to standard temperature and pressure are 5.99 g of TCE and 0.44 g of water. This amount of TCE would be enough to produce concentrations in the soil below the barrier as
high as 115 mg/kg if it were evenly distributed throughout the volume of soil beneath the capillary barrier.

3.4.3 Chemical Analysis

In both cases, soil samples were collected and analyzed 48 hours after heating had been stopped. This allowed time for the cell to cool to temperatures that would allow handling. The results of chemical analysis performed by Queen’s University Analytical Services Unit (ASU) are represented both graphically and in tabular form in Figure 3-13 and Tables 3-4 and Table 3-5 respectively. For the single pool experiment, the total reduction of TCE in the soil cell was 99.98%, and 99.35% in the double pool experiment based on calculations averaging the soil analysis throughout the entire cell.

Figure 3-13 – Soil sample results (mg/kg) for single and double pool experiments
TCE concentrations calculated on a dry weight basis in ppm are shown in Table 3-4 and Table 3-5. In both the single and double barrier experiments, no concentrations exceeded the threshold concentration for free phase TCE in the silica, calculated to be 238 mg/kg. Full calculations can be found in Appendix C. The single barrier experiment showed a high degree of reduction in TCE concentration compared to the solubility of TCE with a maximum recorded concentration of 6.61 ppm, which was found below the original pool location. Areas between the capillary barriers ranged in concentration from 1.16 ppm centered immediately beneath the barrier to 0.435 ppm, which was centrally located between the source zone and the partial barrier. Lower concentrations were noted on the left side of this barrier where visualization of vapour bypass was more evident than on the right. Higher concentrations were also noted within the barrier itself, particularly towards the centre, immediately above the source zone. TCE was present in all samples collected, demonstrating transport either by vaporization and subsequent re-condensation or through convective mixing.
The double pool experiment tested higher for TCE concentration in the upper barrier, and the upper pool was more effectively remediated than the lower. The area above the upper barrier ranged in concentrations from 10.1 ppm to 34.8 ppm, while the region between the upper and lower barrier ranged from 97.0 ppm to 136.0 ppm. Higher concentrations were also found below the upper barrier than in the barrier interior itself, which coincides with the area immediately below the observed gas saturated zone recorded photographically.
Table 3-5 - Tabular chemical analysis results for post-experimental TCE concentrations in double pool experiment

<table>
<thead>
<tr>
<th>Sample #</th>
<th>TCE ppm</th>
<th>Moisture</th>
<th>Percentage Reduction Compared to Source Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank 1&amp;2</td>
<td>&lt;.05</td>
<td>&lt;.005</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.11</td>
<td>0.26</td>
<td>99.95%</td>
</tr>
<tr>
<td>2</td>
<td>10.1</td>
<td>0.29</td>
<td>99.91%</td>
</tr>
<tr>
<td>3</td>
<td>34.8</td>
<td>0.29</td>
<td>99.70%</td>
</tr>
<tr>
<td>4</td>
<td>43.7</td>
<td>0.31</td>
<td>99.62%</td>
</tr>
<tr>
<td>5</td>
<td>57.0</td>
<td>0.28</td>
<td>99.50%</td>
</tr>
<tr>
<td>6</td>
<td>57.2</td>
<td>0.31</td>
<td>99.50%</td>
</tr>
<tr>
<td>7</td>
<td>28.4</td>
<td>0.29</td>
<td>99.75%</td>
</tr>
<tr>
<td>8</td>
<td>35.5</td>
<td>0.3</td>
<td>99.69%</td>
</tr>
<tr>
<td>9</td>
<td>27.0</td>
<td>0.27</td>
<td>99.76%</td>
</tr>
<tr>
<td>10</td>
<td>90.9</td>
<td>0.28</td>
<td>99.20%</td>
</tr>
<tr>
<td>11</td>
<td>63.7</td>
<td>0.31</td>
<td>99.44%</td>
</tr>
<tr>
<td>12</td>
<td>96.7</td>
<td>0.31</td>
<td>99.15%</td>
</tr>
<tr>
<td>13</td>
<td>109</td>
<td>0.32</td>
<td>99.05%</td>
</tr>
<tr>
<td>14</td>
<td>126</td>
<td>0.33</td>
<td>99.90%</td>
</tr>
<tr>
<td>15</td>
<td>106</td>
<td>0.28</td>
<td>99.07%</td>
</tr>
<tr>
<td>16</td>
<td>136</td>
<td>0.32</td>
<td>99.81%</td>
</tr>
<tr>
<td>17</td>
<td>124</td>
<td>0.29</td>
<td>99.91%</td>
</tr>
<tr>
<td>18</td>
<td>97.0</td>
<td>0.32</td>
<td>99.15%</td>
</tr>
<tr>
<td>19</td>
<td>110</td>
<td>0.29</td>
<td>99.04%</td>
</tr>
<tr>
<td>20</td>
<td>126</td>
<td>0.29</td>
<td>99.90%</td>
</tr>
</tbody>
</table>

3.5 Conclusions

A set of two separate experiments were conducted demonstrating the visualization of the ERH process in the remediation of pooled trichloroethylene. It can be concluded that there were clear indications of pool vaporization in both cases as temperatures in the source zone approached 73.4°C. Co-boiling plateaus were evident in both TCE pools in the experiment with two full
capillary barriers, but less so in the single pool experiment. Co-boiling plateaus were not observed at any thermocouples located outside of the TCE pools. In both cases, temperature readings indicative of the co-boiling process coincided with visual observations of the phenomenon occurring. There were later indications of co-boiling at higher vertical layers in the cell and further out laterally, which may suggest upward and lateral movement of liquid phase TCE that continued to be converted into vapour phase.

It can also be concluded that the ERH treatment reduced TCE concentrations within the test cell, with all concentrations between 99.04% and 99.99% of the original source zone, which are similar to reductions found with dissolved DNAPL experiments run by Heron (1998b) and Näslund (2003), who also found reductions upwards of 98% under similar conditions. Visualization of vapour migration demonstrated the bypass and continued upward migration of vaporized TCE in the partial barrier scenario, which allowed vapour to escape upwards. Photographic evidence suggested a greater bypass on the left side of this partial barrier, and chemical results confirmed lower concentrations of TCE after treatment on the side where upward vapour migration was most evident. In both cases, higher concentrations of TCE were found beneath the barriers, demonstrating the restriction in upward movement of vapour-phase TCE under its own buoyancy force.

Importantly, there was visualization of the fully-spanning barrier experiment demonstrated a high degree of vapour restriction and accumulation underneath this capillary barrier with a subsequent condensation and collapse as heating was ceased. Chemical analysis confirmed high concentrations of TCE beneath this low permeability layer. Higher concentrations of TCE were
also found within the capillary barriers as they inhibit mass transfer, especially in the absence of an extraction system. Chemical results also show higher TCE concentrations throughout the cell, demonstrating dispersion of TCE either by convective mixing or re-condensation once heating had stopped.

The aspect of entrapped TCE vapour and the suggested convective mixing demonstrates some of the processes involved when vaporized NAPL is trapped underneath a barrier. Although re-condensation after incomplete solvent recovery has been a noted problem, the dissolution and effect of mass transfer in situations in which vapour and pooled NAPL coexist are only beginning to be investigated (Mumford et al, 2008).
3.6 Literature Cited


http://www.epa.gov/tio/download/remed/epa542r04010.pdf

Chapter 4

Technical Note: Wave Shape Analysis on the Delivery of Electrical Power to the Subsurface in Electrical Resistance Heating

Abstract

Electrical resistance heating (ERH) was performed in a test cell packed with uncontaminated, homogenous silica sand over a 24 hour period to test the effects of the frequency and wave shape of the electrical input on the heating process. Electrical power was supplied by a single-phase 375 volt-amp (VA) programmable power source to electrodes embedded in the sand to generate heat by Ohmic heating. Four frequencies were tested, 10 Hz, 60 Hz, 500 Hz and 1000 Hz using both sine and square wave shapes. Direct current (DC) was also tested. Temperature data was collected throughout the experiments by an array of 32 thermocouples and the data converted to two-dimensional spatial profiles of temperatures during the ERH process. Square wave heating consistently produced a narrow, localized pattern of heat distribution between the electrodes while sinusoidal heating patterns were broadly dispersed predominantly upward from the central area between the electrodes. The frequency at which electricity was provided had no clear effect on the time or pattern of heat distribution. The variations in spatial heating patterns between sine and square wave experiments were most pronounced during early time heating, and became more equalized during later stages as the heating process continued to progress.
4.1 Introduction

Electrical resistance heating (ERH) has become a popular thermal remediation technique to create elevated temperatures in the subsurface to aid in the recovery of dense, non-aqueous phase liquid (DNAPL). In ERH, an electrical current is supplied to electrodes installed in wells bored into the subsurface. The conduction of this electricity allows the electrical resistance of the soil to convert electrical energy to thermal energy as dictated by Ohm’s law (Rizzoni, 2004). The resultant increase in temperature affects the subsurface in several ways, facilitating vapourization, a decreased density and viscosity, decreased absorption and increased solubility which can be advantageous to the recovery of DNAPL (Davis, 1997).

The most common forms of ERH are six phase heating (SPH) and three phase heating (TPH) models, which use the overlap of voltage and current wave forms to maximize power delivery. This electrical energy is generally drawn from transmission lines and processed by a power control unit (PCU). The PCU regulates the voltage and current injected to each electrode, which is calculated based on the electrode spacing and electrical properties of the subsurface to optimize heating and meet project goals (Cacciatore and Clark, 2004). As such, the electrical signals, although modified in magnitude, remain at standard transmission form, sinusoids at 60 Hz.

There have been few laboratory investigations including the spatial heating patterns of ERH in soils, and none to the author’s knowledge focusing solely on this aspect of ERH. Heron et al (1998b) conducted 2-dimensional ERH experiments using porous media containing dissolved TCE, and produced spatial profiles of the resultant heating patterns using 60 Hz sine wave
electrical input. The experiment however, was focused on contaminant removal, and did not investigate heating patterns or effects of the electrical input signal.

There is no physical relationship between basic resistivity and frequency or wave shape in passive resistors, which are only factors in complex resistance, termed as impedance. It can also be safely assumed that soils show little reactive resistance at low frequencies (Rizzoni, 2004). Work in the field of arc welding however has shown that in many respects a square wave electrical input is preferable to a sinusoid input (Correy, 1962), due mainly to the rapid transition of the wave shape from the maximum value to the minimum, which provides a very steady delivery of power. Inherent sloping of power delivery found in a sine wave between maximum values allows for periods of lower power delivery, and lower quality welds. Similar work has been conducted in flash welding, finding that square wave inputs have the ability to produce more constant flashing than sine waves (Sato and Ishida, 2005). It has been found that when the root-mean-square power of a sine wave and that of a square wave are equal, the welds produced by the square wave exhibited greater strength due to this consistent delivery of power over a set period of time (Klingman, 1998). Combinations of square and sine wave forms have also been investigated because of their combination of power delivery and other qualities of importance in welding such as molten metal droplet detachment, which is heavily facilitated by a sine wave input (Zheng and Kovacevic, 2001). The objective of this work is to investigate the effects of this uniform power delivery described in such works in relation to the role of signal input in ERH.
4.2 Materials

The ERH experiments were conducted in a 76.20 cm wide, 16.51 cm thick, 40.64 cm high test cell constructed of 1.27 cm thick polycarbonate plastic sheeting (Makrolon, Bayer Inc., pictured in Figures 4-1 and 4-2). The internal dimensions of the box were 73.66 cm x 13.97 cm x 38.10 cm as illustrated in Figure 4-1, and all seams were joined with a high temperature epoxy (CLR 1390 resin with CLH 6120 hardener, Crosslink Technology Inc.). The inside surfaces of the cell were laminated with optically clear Teflon film (Fluorogrip-F HD-FEP Teflon, Integument Technologies Inc.) with a thickness of 0.254 mm, and backed with an acrylic adhesive. Seams in the lamination were sealed with a viton rubber caulking compound, (SC-200 Fluorogrip Elastomer Caulk, Integument Technologies Inc).

![Figure 4-1 - Design view of test cell showing basic dimensions and key features](image)

The rear face of the cell was held in place by 8-32 thread size screws, 1.91 cm in length holding down a 0.794 mm viton rubber o-ring stock held in a square groove providing a gas-tight seal,
The edges of the soil cell were further reinforced by an aluminum frame constructed of 2.54 cm square structural aluminum tubing with 3.18 mm wall thickness held tight by a series of clamps.

![Photograph of assembled test cell showing thermocouple placement, retaining plates, o-ring and viewing pane](image)

**Figure 4-2 - Photograph of assembled test cell showing thermocouple placement, retaining plates, o-ring and viewing pane**

The rear face of the experimental cell was equipped with 32 thermocouple ports sealed with viton rubber o-rings. The thermocouples were arranged in a rectangular grid with 4 thermocouples in the vertical direction and 8 in the horizontal. The spacing between thermocouples, both vertically and horizontally was 7.62 cm, as shown in *Figure 4-3*. The thermocouples used were ungrounded T-type, stainless steel probe design (Omega Engineering Inc.). Each Thermocouple measured 10.16 cm in length, and 0.3175 cm in diameter. Information was collected from the array of
thermocouples by a Keithley 2700 digital multimeter, equipped with Keithley 7708 40-channel multiplexer with internal cold-junction circuit.

Electrical current was delivered to the sand pack using two electrodes spaced 35 cm apart. The electrodes were constructed of stainless steel plates 30.48 cm tall, 10.16 cm wide and 0.3175 cm thick and were connected by a bolt-attached crimp connector to 14 AWG temperature-rated cabling. In all cases the root-mean-square voltage was maintained at 300 V (± 0.3V) to ensure equal power delivery between sine, square and DC signals supplied to the soil.

Figure 4-3 – Dimensions and thermocouple locations in test cell in the experiments. The grid spacing is 5 cm square. Thermocouples are marked as red circles and ascend from left to right by row

The soils used was industrial grade silica sand (Unimin Inc.), which has 75% retention on 20 mesh or coarser. The resistivity of the soil was measured as 300 Ω•m (± 5 Ω•m) by a voltage drop method.
A venting system was constructed to release volatilized water, which had its own designated port in the top right corner of the test cell leading to a fume hood to allow pressure equalization. The source of AC power used was a Hewlett-Packard Agilent 6811B programmable AC power supply. The unit is capable of a 375 volt-amp (VA) output, with a maximum of $300V_{\text{rms}}$.

4.3 Methodology

4.3.1 Experimental Setup

In all experiments, the main body of the packing comprised the industrial grade silica sand. A wet packing technique was used, where sand was added to the test cell partially filled with water to prevent the entrapment of air bubbles in the pore space. Water and sand were added to the cell in an alternating fashion so that the water level never fell below the top of the sand pack.

The heating regime consisted of delivering electrical energy to the soil in the test cell for a period of 24 hours. The frequency and wave shape of the electrical signal used to achieve ohmic heating are detailed in Table 4-1. Frequencies ranged from a direct current (DC) to 1000 Hz, and the two wave shapes investigated were sine and square.
Table 4-1 - Summary of frequencies and wave shapes tested

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Frequency (Hz)</th>
<th>Wave Shape</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>Sine</td>
<td>300</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>Sine</td>
<td>300</td>
</tr>
<tr>
<td>3</td>
<td>500</td>
<td>Sine</td>
<td>300</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>Sine</td>
<td>300</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>Square</td>
<td>300</td>
</tr>
<tr>
<td>6</td>
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<td>Square</td>
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</tr>
<tr>
<td>8</td>
<td>1000</td>
<td>Square</td>
<td>300</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>DC</td>
<td>300</td>
</tr>
</tbody>
</table>

After the heating process had reached 24 hours in duration, electrical power was shut off from the test cell and it was allowed to cool back to room temperature, which was held constant by an air conditioner/dehumidifier, which was controlled by a thermostat set to 24°C. The ambient temperature of the laboratory was confirmed by a mercury thermometer before the start of each experiment.

4.3.2 Temperature Measurements

The heating process was conducted at a set voltage of 300 V<sub>rms</sub> to prevent any possible safety hazards associated with a set current. Increases in resistivity with a set current may lead to over-powering and eventual overheating in the case of an accidental dry-out of the soil pack (Heron et al., 1998b). The test cell remained saturated with water throughout the experiments, allowing a constant 1.25 A of current delivery at all times, resulting in 375 W of power available for heating.
Photographs of the viewing pane were taken every 30 minutes, and temperature readings were logged every 60 seconds. The temperature data collected was logged directly to a PC in Microsoft EXCEL format. The data was subsequently processed in Tecplot 360 (Tecplot Inc.) software to produce 2-dimensional contour maps of the temperature readings at designated points in the heating process. These included the points in time when the highest thermocouple reading reached 40°C and 60°C and when the average reading of all thermocouples in the test cell was equal to 40°C and 60°C.

4.4 Results

Temperature readings at the point in time when the highest thermocouple reading in each experiment was equal to 40°C are pictured in Figure 4-4. At all frequencies except for 1000 Hz, the square wave experiments reached 40°C slightly sooner than sine wave experiments. Sine wave experiments took between 1.00 hours and 1.85 hours to reach 40°C, while square wave experiments ranged between 0.97 hours and 1.97 hours. The direct current experiment required 0.90 hours to reach 40°C at its hottest point. A discrepancy in the spatial heating pattern was observed as a trend between experiments using sine wave and square wave electrical signals. Although the highest temperature in the test cell at the time pictured is identical, and times of heating are similar, the experiments heated by square wave show a greater localization of heat distribution central to the cell as well as slightly higher average and low temperatures. Sine wave heating produced a more dispersed heating pattern, extending upwards towards the top of the test
cell, suggesting a greater degree of convective heat transfer. The high degree of localization of the peak temperatures at that point in time is also observed in the DC experiment.
Figure 4-4 – Temperature profiles in test cell when the highest thermocouple reading equals 40°C
When a similar comparison is made at the point in time when all experiments had an average thermocouple reading of 40°C, a similar trend is apparent as pictured in Figure 4-5. The square wave heating experiments produced a more localized high temperature zone than sine wave heating, which again, produced an upwardly extending heat distribution pattern, suggesting convective heat transfer. The maximum temperature in the timeframe was consistently higher in the sine wave heating experiments, while the lowest temperatures of the square wave heating experiments were higher than that produced in sine wave heating. The times required to achieve an average temperature of 40°C in the test cell, similar to the previous comparison were always lower in the square wave experiments, with the exception of heating at a frequency of 1000 Hz. In addition to this, the DC experiment achieved a 40°C average temperature sooner than square or sine wave experiments conducted at a set frequency and again produced a heating pattern localized to the centre of the test cell, showing little heat transfer in the vertical direction.
Figure 4-5 - Temperature profiles in test cell when the average thermocouple reading equals 40°C
Comparisons of temperature profiles made at later time showed a greater degree of uniformity in the heat distribution in the interior of the test cell. Graphs of thermocouple readings when the highest temperature in the cell was equal to 60°C are pictured in Figure 4-6. The times required for sine wave heating to achieve a high of 60°C ranged from 3.23 hours to 4.78 hours compared to square wave heating, which ranged from 2.45 hours to 6.28 hours. Again, square wave heating was slightly faster in achieving this benchmark than sine wave with the exception of heating conducted at 1000 Hz. The fastest time was DC heating, which required only 2.2 hours. At this time, the heating patterns of sine wave heating and square wave heating are much more similar, with no centralized localization of high temperature readings, suggesting the increased prevalence of convection as the dominant mode of heat transfer between hotter and cooler portions of the packed silica sand. The range between the highest and lowest temperatures in both sine and square wave, as well as the average temperatures, are very similar between the two wave forms. The lowest average temperature was observed in the DC heating experiment.

A comparison of temperature profiles when the average temperature in the test cell was equal to 60°C, seen in Figure 4-7, demonstrated a greater equalization between sine wave and square wave experiments. Times to achieve this temperature ranged between 5.23 hours and 7.57 hours in sine wave experiments and 4.75 hours to 11.5 hours in square wave heating. Sine wave heating was slightly faster at 500 Hz and 1000 Hz, while square wave was slightly faster at 10 Hz and 60 Hz. DC heating was again the fastest at 3.82 hours. Additional heating produced similar heating patterns, rising in magnitude of temperature values, but static in spatial distribution of heat.
Figure 4-6 - Temperature profiles in test cell when the highest thermocouple reading equals 60°C
Figure 4-7 - Temperature profiles in test cell when the average thermocouple reading equals 60°C
4.5 Conclusions

It can be concluded that differences in spatial heating patterns when ERH is applied to silica sand have been observed between sine wave and square wave electrical signal inputs, as well as when the signal is DC. It was found that sine wave inputs produce a wider area of overall heating while square wave and DC inputs produce a more localized heating pattern centralized in the path of electrical conduction between the electrodes. This effect is most notable at early times in heating, due to a lower overall temperature gradient within the porous medium, limiting conductive and convective heat transfer from the central area of applied current.

It is possible that the cause of the spatial difference in heating between a sine and square wave is due to the mode of energy delivery. The similarities between DC and square wave input heating is reasonable considering that a square wave is, in essence, a DC current alternated at a set frequency. While the total power delivered is equal in all cases the DC and square wave power delivery is constant. The ramping of voltage and current found in sinusoidal pattern cause periods of both high and low power delivery. The sine wave signal delivers a lower amount of power during its ramp to a peak value, and a much higher amount when it approaches that peak. This results in times of much higher conversion of electrical to thermal energy compared to square wave or DC. The high power delivery at the peak of the sine wave increases the overall temperature gradient between portions of the porous medium, facilitating heat transfer within the medium through conduction and convection, predominately in the upward direction. These momentary peaks in heat delivery cycling between 10 and 1000 times a second could provide a means for a broader distribution of thermal energy in the silica medium compared to a more tightly concentrated temperature profile observed in square wave and direct current heating.
It is unclear as to why the experiments at 1000 Hz square wave input were slower to reach the high and average 40°C benchmarks, and the 500 Hz and 1000 Hz square waves were slower at the 60°C benchmarks. This may be due to resonance of the electrical frequencies causing an improved heating at lower frequencies or simply outlying time values. This aspect of the work could be subjected to additional investigations to confirm the cause of this phenomenon, although it falls outside of the scope of this particular investigation.
4.6 Literature Cited


Chapter 5

Recommendations for Future Work

In future work, collection of more data may provide a better understanding of the internal workings of a subsurface system undergoing ERH treatment. Limitations of the current study include discreet point temperature measurements provided by thermocouples. Higher resolution temperature collection such as infra-red sensory equipment would eliminate the need of interpolation between points where temperature data was collected. A system to provide pressure measurements throughout the experimental domain would also allow for a more complete composite of factors that come into play as contaminants are vaporized. Finally, a grid of sampling ports with data collection at specific time intervals could allow for constant monitoring of contaminant presence throughout the experimental domain would provide researchers a means by which to track contaminant migration during ERH rather than a before/after approach.

Future work using waveform variations could further expand the frequency range studied and amplitude of electrical signal input to identify the influence waveform has on the ERH process. Higher amplitude experiments would be particularly valuable to accentuate the effect of each wave shape on spatial heating patterns before convective and conductive heat transfer becomes a major factor. Lastly, the use of other wave forms such as saw tooth, triangle, and white noise could provide insight on the effect differences in wave forms have on electrical resistance heating.
Appendix A

Temperature Readings – Single and Double Pool Experiments
Single Pool Experiment
Double Pool Experiment
Appendix B – Soil Sample Result Reports
**AMENDED REPORT**

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*TCE results of multiple analyses.

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Prepared by: [Signature]

Authorised: [Signature]

Paula Whitley, BSc
Laboratory Manager

**Queens University**

Preparing Leaders and Citizens for a Global Society

**Page 1 of 1**

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School of Environmental Studies
Biocenosis Complex
Queen's University, Kingston, Ontario, Canada K7L 3N6
Tel: 613-533-2643  Fax: 613-533-2997

---

Report of Analysis:

**ASU#**: 10915  
**Client**: Dr. Keeper  
**Dept. of Ch-8 Engineering**  
**Queen's University**

**Date Submitted**: 7-Jan-98  
**Date Tested**: 29-Jan-98  
**Date Reported**: 30-Jan-98  
**Matrix**: Soil

---

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#11  | 1560 | 28
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*Note: TET results of duplicate analyses.

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Prepared by: [Signature]  
Keepr-10915-TCE Report-2  
Page 1 of 1

Authorization: [Signature]  
P. Weithey, BSc  
Laboratory Manager
Report of Analysis

AST # 11100
Client: Dr. Kapoor
Dept. of Civil Engineering
Queen's University

Report ID: Kapoor-11100-TCE
Date Submitted: 1-Apr-08
Date Taught: 9-Apr-08
Date Reported: 14-Apr-08
Matrix: Soil

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Prepared by: [Signature]

Authorization: [Signature]

Queen's University

PREPARING LEADERS AND CITIZENS FOR A GLOBAL SOCIETY

126
### Analytical Services Unit
School of Environmental Studies, BioSciences Complex
Queen's University, Kingston, Ontario, Canada K7L 3N6
Tel 613 533-2602  Fax 613 533-2607

**Report of Analysis**

**ASU #** 11102 Q4.13

**Client:** Dr. Roper

**Dept. of Civil Engineering**

**Queen's University**

**Report ID:** Kaper-11102-TCE-2

**Date Submitted:** 1-July-08

**Date Tested:** 16-Aug-08

**Date Reported:** 17-Aug-08

**Matrix:** Soil

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Prepared by: **K. Mir**

Authorized: **Allison Rutter, PhD**

Director

**Queens University**

**Preparing Leaders and Citizens for a Global Society**

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Appendix C – Soil Saturation Calculation
The threshold concentration of TCE in the silica can be found by (Rucker, 2007):

\[
C_T = \frac{K_d C_w \rho_{bulk} + C_w \phi_w + C_w H_c \phi_a}{\rho_{bulk}}
\]  

(C-1)

Where \(K_d\) is the distribution coefficient, \(C_w\) is the chemical concentration in the pore water, \(\rho_{bulk}\) is the dry bulk density of the silica sand, \(\phi_w\) and \(\phi_a\) are the water and air filled porosities, respectively and \(H_c\) is Henry’s gas constant. Since silica sand was used assume \(\Phi_{oc} = 0\), therefore by the definition of \(K_d\) (Pankow and Cherry, 1996):

\[
K_d = K_{ao} \Phi_{oc}
\]  

(C-2)

\[
K_d = 126 \frac{ml}{g} \times 0
\]  

(C-3)

\[
K_d = 0
\]  

(C-4)

The air filled porosity of the soil is also equal to 0, so the total expression becomes:

\[
C_T = \frac{C_w \phi_w}{\rho_{bulk}}
\]  

(C-5)

Using the known values of \(C_w = 1100\) mg/l, \(\phi_w = 0.41\), and the measured \(\rho_{bulk}\) of the soil = 1.92 g/cm\(^3\). The calculated value of \(C_T\) is then 238.89 mg/kg.
Literature Cited
