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Contaminant mass transfer during boiling in fractured geologic media

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CONTAMINANT MASS TRANSFER DURING BOILING IN FRACTURED GEOLOGIC MEDIA

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Environmental Engineering and Science

by
Fei Chen
August 2011

Accepted by:
Dr. Ronald W. Falta, Committee Chair
Dr. Lawrence C. Murdoch
Dr. Fred J. Molz, III
Dr. David L. Freedman
ABSTRACT

Remediation of fractured geologic media contaminated with chlorinated volatile organic compounds that diffuse into the matrix is challenging using isothermal methods. Due to the low permeability of the matrix material and uncertainty of fracture networks, it is difficult to flush the system with any type of fluid or deliver remediation agents into the matrix. However, thermal methods have some promises. When the matrix is heated above water boiling temperature, depressurization in the fractures may trigger water boiling in the matrix, which, as a result, generates a large volumetric steam flow toward adjacent fractures, stripping the adsorbed or dissolved volatile contaminants from the matrix. This process has not been demonstrated in the laboratory or field, and the parameters that control the contaminant mass removal from the fractured geologic media at the scale of a single fracture and field application were not well understood. The objective of this study is to understand the contaminant mass transfer due to boiling in fractured geologic media.

Local-scale matrix boiling and contaminant mass transfer during the process were demonstrated using a sandstone core, where the unfractured core represents the matrix and an end the fracture. The core was contaminated by pumping water dissolved with 1,2-DCA and NaBr. When boiling occurred in the matrix, a temperature gradient toward the fracture was observed, indicating, under saturated vapor condition, a pressure gradient pushing the steam (water and vapor mixture) towards the fracture. When boiling occurred, 1,2-DCA was removed at a rate 6 times higher than before heating. The nonvolatile bromide concentration, as an indicator of the steam quality, showed a reverse
correlation with the volatile 1,2-DCA concentration, indicating that the majority of 1,2-DCA was removed by partitioning to the vapor phase.

To accurately predict the partitioning of contaminant between aqueous and gaseous phase at high temperature, Henry’s law constants were measured for 12 chlorinated solvents (tetrachloroethylene, trichloroethylene, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethane, dichloromethane, carbon tetrachloride, cis-1,2-dichloroethylene, chloromethane, chloroethane, and vinyl chloride) over temperatures from 8 to 93 °C. The measured results show that Henry’s law constant is strongly dependent on temperature, increasing by factors from 3 (chloromethane) to 30 fold (1,2-DCA) as temperature increases from 8 to 93 °C. The temperature dependency of Henry’s law constants was modeled with the Van’t Hoff equation. Better fitting is obtained by assuming the enthalpy of dissolution is a function of temperature, suggesting the inappropriateness of extrapolating the Henry’s law constant from measurements at low temperature using a linear function. Using measured data for solubility, a vapor pressure-solubility model gives a reasonable prediction of the Henry’s law constants. With improved data on Henry’s law constants at high temperatures for the 12 common CVOCs measured in this study, it will be possible to more accurately model subsurface remediation processes that operate near the boiling point of water.

The laboratory experiment was simulated with a 2-D multiphase numerical model using the TMVOC code. The simulated results are in reasonable agreement with the experiment, providing confidence for the TMVOC code in predicting the CVOC removal from fractured geologic media by boiling. A 1-D numerical model was further
used to demonstrate the contaminant mass transfer from a core without end effects. Similar to the experiment results, a temperature gradient was observed while pore water in the matrix was boiled. After opening to the atmosphere, a high proportion of steam vapor was produced, corresponding to a high removal rate of 1,2-DCA. All of the 1,2-DCA mass was removed after boiling out around 50 mL pore water. The contaminant removal from fractured geologic media at field scale was simulated using the MINC method. After about 35 days of treatment, 27.8% of the pore water (including both steam vapor and liquid water) was extracted, and essentially all the 1,2-DCA mass (more than 99%) was removed from the fractured site. The simulation shows boiling is an effective mechanism for CVOC removal from fractured geologic media.

Effects of chemicals, fracture spacing, fracture aperture, diameter of heating pattern, matrix permeability, extent of vacuum, and different operational strategies on the performance of thermal treatment of a fractured site were investigated. The simulation results show that, under the same boiling conditions, the contaminant removal rates vary for different chemicals, depending on their Henry’s law constants. The higher the Henry’s law constant for a chemical, the higher the contaminant removal rate. Variations of fracture properties (aperture and spacing), size of heating pattern, and the extent of extraction vacuum have larger effects on the system temperature than the matrix permeability due to the different percentages of heat extracted from the system. The contaminant removal is more sensitive to the matrix permeability. A higher percentages of contaminant are removed in the case of higher matrix permeability, where boiling occurs in both the matrix and fracture, while less is removed in the lower permeability
case (e.g. $1 \times 10^{-17} \text{ m}^2$), where boiling occurs primarily in the fracture. Further simulation based on a 3-D model that includes the effects of cold water shows that the cooling effect caused by the influx of cold ground water is significant. When the fracture network is permeable, the extraction wells pull a large amount of cold water into the treatment zone, which holds the majority of the treatment zone below the water boiling temperature, minimizing the performance of thermal remediation. Compared to the effect of water flow pulled by extraction, ground water flow caused by the regional hydraulic gradient is insignificant.
DEDICATION

To my dad, my wife, and my new born son, William W. Chen.

In memory of my mom
ACKNOWLEDGMENTS

I acknowledge the Strategic Environmental Research and Development Program (Project# ER-1553) for providing financial support to this work.

I would like to thank my advisor, Dr. Ronald W. Falta, for his guidance and encouragement during my studies and many aspects of this research. I appreciate him for providing me such an exciting opportunity working in this project and flexible research environment. Without his fully support, this work is not possible. I am highly indebted to my committee members: Dr. Lawrence C. Murdoch for providing guidance and support in the experimental part of this work, Dr. David L. Freedman for his instruction in the Henry’s law constant measurements, and Dr. Fred J. Molz III for his continuous support and valuable comments on this research. Thanks also go to Mr. Robert Teague for his assistance in Labview programming and data acquisition system installation. I would also thank James Henderson for introducing this project to me and providing help in the initial analytical method setup. Jan K. Young has provided tremendous help and support during my study at Clemson. I appreciate her for being there when I need a help.

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At last, I would like to thank my wife, He Wen, for her love, patience, and unconditional support.
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CHAPTER ONE

INTRODUCTION

Releases of chlorinated volatile organic compounds (CVOCs) into fractured geologic media may cause long-term groundwater contamination (Falta, 2005; Parker et al., 1997). As the dissolved contaminants or the dense non-aqueous phase liquids (DNAPLs) are released to a fractured site, they preferentially move and spread through the fractures (Kueper and McWhorter, 1991). These contaminants in the fractures diffuse rapidly into the matrix due to the sharp concentration contrast and a significant amount of contaminants will be stored in the matrix material (Kueper and McWhorter, 1991; Parker et al., 1997). After the contaminants in the fractures are removed by engineered or natural processes, the contaminants that are dissolved in the pore water and adsorbed in the matrix will diffuse back to the water flowing through the fractures, with the concentrations significantly above the regulatory limits for hundreds to thousands of years in the absence of decay (Falta, 2005; Reynolds and Kueper, 2002). Even with a moderate amount of chemical decay occurring in the matrix, this process would last for tens or hundreds of years (Falta, 2005).

Remediation of a fractured site is challenging using isothermal methods. Conventional isothermal remediation options include: 1) removing the contaminants by flushing the media with air, water, or other fluids, such as ethanol or surfactants; and 2) destroying the chemicals by delivering remediation agents such as chemical oxidants. Due to the low matrix permeability, it is difficult to flush the matrix material with any type of fluid. The effectiveness of the flushing methods is limited by the relatively low
flow rates through the fractures and the relatively slow mass transfer into the fractures from the matrix by diffusion (Falta, 2005). Besides, the fracture networks are usually difficult to characterize (Murdoch et al., 1990; National Research Council, 1994). The uncertainty of the fracture network makes it even more difficult to reliably deliver remediation agents into the matrix (Goldstein et al., 2004; Murdoch et al., 1990; National Research Council, 1994).

Thermal methods are promising in remediating fractured geologic media because thermal energy can be delivered to the matrix material by thermal conductive heating (Heron et al., 2009), steam enhanced extraction (Heron et al., 2005; Hodges et al., 2004; Ochs et al., 2003), electrical resistance heating (Gauglitz et al., 1994; Heron et al., 1998; Peurrung and Schalla, 1998), and radio-frequency heating (Kawala and Atamanczuk, 1998). As the matrix material is heated above the water boiling point, depressurization in the fracture may trigger boiling occur in the matrix material (Pruess, 1983). At atmospheric pressure, this phase change will cause a volume of water expand into 1600 volumes of vapor, and generate a large pressure gradient and volumetric steam flow towards the fractures. The portion of CVOCs that dissolve in the pore water and adsorb to the matrix materials will preferentially partition to the vapor phase due to the increased Henry’s law constant at steam temperature (Heron et al., 1998). The Henry’s law constants of CVOCs at steam temperature are approximately 10 times higher than those at groundwater temperature (Heron et al., 1998).

Boiling might be an extremely effective mechanism for contaminant removal. A thermodynamic analysis conducted by Udell (1996) and Heron et al. (1998) showed that,
under batch conditions, boiling 1% of the involved water will cause the reduction of the concentration of trichloroethylene (TCE) dissolved in the water by tens of orders of magnitude. Field (Gauglitz et al., 1994; Heron et al., 2005; Heron et al., 2009) and laboratory (Heron et al., 1998) studies of soil and clay remediation showed that the contaminant mass removal rate increased significantly as the temperature reached the water boiling point, suggesting that water boiling contributes to enhanced contaminant removal from soils and clay. For fractured geologic media, the effectiveness of contaminant removal by boiling has not been demonstrated in a laboratory or in a field study, and the contaminant mass transfer in this process is not well understood.

Contaminant mass transfer due to boiling in fractured porous media is a complex phenomenon. When boiling occurs in such media, there are strong couplings between heat transfer, thermodynamics, and multiphase flow. This makes it difficult to predict the detailed effects of boiling, for example, where the boiling occurs and how the vapor and liquid water phases flow. However, details of boiling are important for the contaminant mass transfer from the matrix material to the fracture because it is this phase change that strips the volatile contaminant dissolved in the pore water and adsorbed to the matrix material. For example, depending on conditions, the moving phase from the boiling location in the matrix to the fracture could be vapor, liquid, or both phases. The efficiency of contaminant removal may vary greatly depending on the presence or absence of the steam stripping effect. Due to a lack of knowledge about this process, the effects of thermal and hydraulic properties of the matrix material, distribution of the fractures, and heating patterns on contaminant removal while applying thermal
remediation are not known. This causes the difficulties in evaluation of the feasibility of thermal remediation, development of design and operational strategies for maximizing the efficiency of contaminant removal. This dissertation is devoted to furthering the understanding of contaminant mass transfer due to boiling in fractured geologic media. The following section presents a background and literature review associated with thermal remediation.

1 BACKGROUND AND LITERATURE REVIEW

1.1 Effects of temperature on physical and chemical properties of CVOCs

Some physical and chemical properties of CVOCs change as temperature increases (Baston and Kueper, 2009; Davis, 1997; Heron et al., 2005). At elevated temperature, the dense nonaqueous phase liquids (DNAPLs) of CVOCs tend to have lower viscosities, interfacial tensions, and organic carbon partition coefficients (Davis, 1997; Imhoff et al., 1997), but higher vapor pressures (Reid et al., 1987) and Henry’s law constants (Heron et al., 1998). These changes can be effectively exploited for the remediation purpose. For example, at high temperature, the decreased viscosity and interfacial tension increase the mobility of DNAPL, which, combined with conventional treatment methods such as pump and treat or vapor extraction, accelerates the treatment process and shortens the duration. Decreasing the organic partition coefficient results in an enhanced desorption from soils (Keyes and Silcox, 1994; Sleep and McClure, 2001). Increasing the vapor pressure (or the Henry’s law constant) can effectively enhance the DNAPL (or water)-air mass transfer (Heron et al., 1998; Udell, 1996). Chlorinated solvents may undergo chemical reactions such as aqueous oxidation and pyrolysis when
the temperature is raised, which destroys the contaminants in situ and lessen the need for further above-ground treatment (Baker and Kuhlman, 2002; Baston and Kueper, 2009; Costanza et al., 2005; Costanza and Pennell, 2007).

1.2 Heating methods

Depending on the means of energy delivery, the heating method can be categorized as steam enhanced extraction, electrical resistance heating, thermal conductive heating, and radio-frequency heating.

1.2.1 Steam enhanced extraction (SEE)

SEE exploits steam as an energy carrier to deliver thermal energy into the treatment zone. It was originally developed in the petroleum industry to achieve enhanced oil recovery (Nilsson et al., 2011). In the last three decades, it has been used to remediate contaminated sites (Baston and Kueper, 2009; Carrigan and Nitao, 2000; Heron et al., 2005; Ochs et al., 2003; Tse et al., 2006). Successful remediation tests have been conducted on the highly permeable soil (Baston and Kueper, 2009; Carrigan and Nitao, 2000; Heron et al., 2005; Ochs et al., 2003; Tse et al., 2006), and small low-permeability zone adjacent to high-permeability zones (Baston, 2008; Carrigan and Nitao, 2000; Gudbjerg et al., 2004). However, application of SEE is limited by the transmissivity of treatment zone. It was reported incapable of significantly raising the temperature of large or thick low-permeability zones (e.g. fractured limestone) due to the low transmissivity in the injection interval and sparsely spaced fractures (Baston, 2008; Carrigan and Nitao, 2000; Davis et al., 2005). Combined with hydraulic fracturing which creates highly-permeable avenues for the steam flow, it can be used for remediating low-
permeability unconsolidated media (Nilsson et al., 2011). Theoretical and experimental studies show SEE is effective for remediating volatile or semi-volatile chemicals from both saturated and unsaturated porous media (Falta et al., 1992; Hadim et al., 1993; Hunt et al., 1988a; Nilsson et al., 2011; Schmidt et al., 2002; Sleep and McClure, 2001). However, a concern for applying this method is the gravity-assisted downward migration of NAPL that occurs in the condensation front (Hunt et al., 1988b; Schmidt et al., 2002; Sleep and Ma, 1997). Contaminant that volatizes in the steam zone condenses at the heat front, where a pool of contaminant accumulates as NAPL. As it exceeds the residual saturation, it move downwards under the force of gravity (Hunt et al., 1988b; Schmidt et al., 2002). To avoid this from occurring, one could co-inject the steam with air or heat up the area below the contaminated zone (Hodges et al., 2004; Nilsson et al., 2011; Ochs et al., 2003).

1.2.2 Electrical resistance heating (ERH)

ERH is operated by placing an array of electrodes in the subsurface and passing alternate currents (power-line frequency of 50-60 Hz) throughout remediation area. Here, the electrodes are placed in boreholes with a horizontal spacing of 4-8 m. Current is conducted through the wet soil/rock that acts as a resistive heating element, generating Joule heating effect (Baston, 2008; Beyke and Fleming, 2005; Morgenstern et al., 2007). This technology was initially developed in the Pacific Northwest National Laboratory in the 1990s (Morgenstern et al., 2007). It can apply three-phase (Buettner and Daily, 1995) or six-phase electricity (Gauglitz et al., 1994). Both were demonstrated as robust techniques to raise the temperature of low-permeable treatment zone to about the water
boiling temperature in fractured or unfractured rock and in all soil types, regardless of the permeability of the material (Beyke and Fleming, 2005; Heron et al., 2008). The heating rate might differ between the near-electrode region and the center of the array (Carrigan and Nitao, 2000). The uniformity of heating could be improved by increasing the number of electrical phases employed in supplying current to the electrodes (Carrigan and Nitao, 2000), and the six-phase ERH has a more uniform heating pattern than the three-phase ERH (Carrigan and Nitao, 2000; Gauglitz et al., 1994). This technology is the most popularly used in situ thermal treatment technology, occupying more than half (57%) of the implementations at full scale since 2000 (Kingston et al., 2010). A limitation for this method is that the target temperature is below or at the water boiling temperature, and only a small portion of pore water can be boiled during heating because of its reliance of the connected pore water to conduct electrical current (Baston, 2008; Beyke and Fleming, 2005). With more and more water boiled, the electrical resistance of the soil/rock increases dramatically, resulting in less current passing through and much lower heating rate.

1.2.3 Radio frequency heating (RFH)

RFH can heat the treatment zone to more than 400 °C by transmitting radio wave at frequency typically ranging between 3-30 MHz (Buettner and Daily, 1995; Roland et al., 2008). Except for a larger penetration depth, the heating mechanism of RFH is similar to that of a microwave oven. Temperature increase is caused by the friction occurring in the reorientation of the molecular dipoles when the external electromagnetic field changes rapidly (Roland et al., 2008). Under careful control of the radio frequency
transmissions, heat can be imparted to all types of contaminated media, regardless of dry or humid conditions (Roland et al., 2008). It provides a steerable heating pattern. If the system is properly configured, the heating pattern of RFH can be controlled by varying the operating frequency, electrical phasings, and antenna length and position. This technology can be used for remediation of both volatile and semi-volatile compounds (Roland et al., 2010). A concern for this technology is that substantial capital costs are associated with the conversion of power-line frequency to the radio-frequency energy. Compared to other techniques such ERH and SEE, the RFH method is more expensive.

1.2.4 Thermal conductive heating (TCH)

TCH provides thermal energy to the treatment zone by utilizing resistance heating elements placed in the wells throughout the treatment zone (Baston and Kueper, 2009; Baston et al., 2010; Heron et al., 2008). Heat is generated in the resistive heating elements (heaters), and heat transfer is dominated by radiation at near the heaters, which typically operate at 800-900 °C (Stegemeier and Vinegar, 2001). At greater distances away from the heaters, heat transfer is governed by thermal conduction (Baston and Kueper, 2009; Stegemeier and Vinegar, 2001). Usually the heaters are placed in a spacing less than 6 m (Kingston et al., 2010). This method is capable of heating the target zone up to approximately 800 °C (Baston and Kueper, 2009; Heron et al., 2009). Fractured bedrock and low-permeability unconsolidated soils (e.g. thick clay layers) were reported to be heated to water boiling point using this method (Baston, 2008; Heron et al., 2008; Stegemeier and Vinegar, 2001). Field studies demonstrate it is effective for removing a
variety of chemicals such as polychlorinated biphenyls (PCBs), pesticides, chlorinated solvents, and heavy and light hydrocarbons (Stegemeier and Vinegar, 2001).

1.3 Water boiling

Water boiling is a phenomenon where liquid water absorbs latent heat and undergoes phase change into steam vapor at the water boiling temperature. The definition of water boiling temperature is correlated to the pressure at the location where boiling occurs. It is defined as the temperature where its vapor pressure equals the external pressure (Atkins and Paula, 2003). The vapor pressure of water as a function of temperature is described by the Clausium-Clapeyron equation (Atkins and Paula, 2003):

$$\frac{d\ln p}{dT} = \frac{\Delta_{vap} H}{RT^2}$$

(1.1)

where $p$ is the vapor pressure in Pa, $T$ is the temperature in K, $\Delta_{vap} H$ is the molar enthalpy change, $R$ is the gas constant.

1.4 Heat transfer in boiling porous media

Heat transfer in boiling porous media could be very complex. Many different mechanisms occur such as thermal conduction in solids and between solid and liquid, thermal convection, and the boiling/condensation effect, picking up the latent heat at one location and releasing it at other locations (Incropera et al., 2007). It differs from pool boiling on a plane surface in several ways. For example, the particles constituting the porous medium provide nucleation sites for boiling and enhance the surface area available for heat transfer (Dhir, 1994); the capillary pressure difference that exists in pores of different sizes provides an additional force for the movement of vapor and liquid (Dhir, 1994). Plus the fact that different boiling modes exist, this phenomenon is even
more difficult to characterize using analytical solutions. More information about the boiling in porous media can be found in the review by Dhir (1994).

1.5 Multiphase flow

The multiphase flow when boiling occurs in porous media is driven by the pressure gradient, the buoyancy force, and the capillary force. As mentioned before, when boiling occurs, a volume of water expands to more than 1600 volumes of vapor at atmospheric pressure (Heron et al., 1998). This volume expansion will provide high pressure gradients that drive fluids away from the boiling location. Buoyancy forces are caused by the density difference between liquid water and vapor.

Capillary pressure plays an important role in the distribution of immiscible fluids under static conditions and the movement of the fluids in the subsurface (Davis, 1994). It is a function of the physical and chemical properties of the fluids and the porous medium, such as pore size distribution, the interfacial tension between the wetting and nonwetting phase, and the contact angles between fluid-fluid interfaces and the grain surfaces of porous media (Davis, 1994; She and Sleep, 1998). The capillary pressure of a tube can be expressed as:

\[ P_c = \frac{2\gamma \cos \theta}{r} \]  

(1.2)

where \( P_c \) is capillary pressure; \( \gamma \) is the interfacial tension between wetting and nonwetting phase; \( \theta \) is the contact angle between the fluid interface and the solid surface; and \( r \) is the effective radius of the interface (Davis, 1994).

The capillary pressure varies at different saturation states. The relationship between the capillary pressure and water saturation is described by many models (Brooks
and Corey, 1966; Corey, 1954; Li and Horne, 2007; van Genuchten, 1980). Two of the frequently used models are van Genuchten and Brooks-Corey models. The van Genuchten model can be mathematically expressed as:

\[
S^* = \left[ \frac{1}{1 + (\alpha h)^n} \right]^m
\]

(1.3)

where \( S^* = \frac{(S - S_r)}{(S_s - S_r)} \), here the \( S \) is water saturation, \( S_r \) is the residual water saturation, and \( S_s \) is the maximum water saturation (van Genuchten, 1980). The Brooks-Corey model represents the capillary pressure as a power law function of the wetting-phase saturation:

\[
P_c = P_e (s)^{\frac{1}{\lambda}}
\]

(1.4)

where \( P_e \) is the entry capillary pressure and \( \lambda \) is the pore size distribution index (Brooks and Corey, 1966).

The multiphase flow could be described by extension of Darcy’s law considering the relative permeability of each phase (Falta et al., 1992). Relative permeability is defined as the ratio of effective permeability of a phase to the absolute permeability for a multiphase-flow system. It can be either obtained from direct measurement or derived from the capillary pressure-saturation curve. Many models have been proposed to obtain relative permeability from capillary pressure data (Brooks and Corey, 1966; Corey, 1954; Parker et al., 1987; Purcell, 1949; van Genuchten, 1980). It is difficult to measure relative permeability when the sample has low permeability or significant phase transformation and mass transfer between two phases as pressure changes occur in the fluid system (Li, 2010). Two measurements of steam relative permeability were conducted on unconsolidated sands and sandstone by Verma (1986) and Mahiya (1999), respectively.
Both of them found that the relative permeability of steam vapor phase is significantly higher than that of noncondensible gas such as air.

1.6 Contaminant removal due to boiling

1.6.1 Batch conditions

Volatile contaminant dissolved in the water is removed primarily by the passing steam generated by boiling. This partition of a chemical between the aqueous and gas phase at equilibrium is described by the Henry’s law. A thermodynamic analysis showing the reduction of volatile contaminant concentration by boiling under batch conditions was conducted by Udell (1996). In his analysis, the contaminant concentration after boiling was expressed as:

\[
\frac{C_{w,if}}{C_{w,i0}} = \left( \frac{m_{wf}}{m_{w0}} \right)^{\left( \frac{H \rho_l}{\rho_v} - 1 \right)}
\]

where \( C_{w,if} \) is concentration of contaminant \( i \) after boiling, \( C_{w,i0} \) is the initial contaminant concentration, \( m_{wf} \) is the mass of water after boiling, \( m_{w0} \) is the mass of water before boiling, \( H \) is Henry’s law’s constant of contaminant \( i \), \( \rho_l \) is the density of liquid water, \( \rho_v \) is the density of vapor. Assuming the vapor is an ideal gas, Heron et al. (1998) estimated the exponent \( \left( \frac{H \rho_l}{\rho_v} - 1 \right) \) for TCE to be 5640 at 99 °C. Therefore, boiling out 1% of the water would lead to a TCE concentration tens of orders of magnitude higher (Falta, 2005; Heron et al., 1998; Udell, 1996). This calculation shows that boiling is a very effective mechanism for removing dissolved contaminants under batch conditions.
1.6.2 Unfractured media

In porous media, the contaminant mass transfer by boiling might behave differently. This is because the boiling phase change and the multiphase flow in porous media are different from the batch conditions. The removal efficiency is expected to be no more than under the batch conditions, because the contaminant mass may not be stripped by the moving vapor phase or the moving phase may not be the liquid phase when boiling in porous media. The complex feature of the boiling in porous media causes it difficult to simply apply the above analytical equations in predicting the removal efficiency or providing guidance for the design and operation of thermal remediation.

A laboratory (Heron et al., 1998) study on silty clay showed increased contaminant fluxes as the temperature increased to the water boiling point. Heron et al. (1998) investigated removal of TCE dissolved in the low-permeable silty soil layer. The silty soils were heated up to 100 °C using electrical resistance heating. They observed that the TCE flux removed from the silty soil was 19 times higher than that in ambient temperature (Heron et al., 1998). Slightly decreasing the temperature, boiling ceased, caused the decreasing of TCE flux similarly (Heron et al., 1998).

Similar observation was made in several field studies. Heron et al. (Heron et al., 2005) reported heating a site contaminated with TCE, cis-1,2-DCE, methylene chloride, toluene, and petroleum hydrocarbons using a combination of steam injection and electrical resistance heating. The layer of highly permeable sand was heated by injecting steam and the layer of low-permeability clay and sand was heated using electrical resistance heating (Heron et al., 2005). Both vapor and water were captured at extraction
wells. When the target zone was heated to the water boiling temperature, the operation of pressure cycling caused the temperature in the layer of low-permeability clay changed at the same frequency as the pressure change, suggesting boiling was induced in the low-permeability clay layer. At the same time, the contaminant concentrations in vapor phase increased (Heron et al., 2005). Increased contaminant removal rate was also observed in a field study at the Savannah River Site (Gauglitz et al., 1994). The PCE flux removed from the clay increased by a factor 3 when the temperature reached 100 °C (Gauglitz et al., 1994). This is possibly due to the induced boiling in the clay.

Laboratory and field results have shown that boiling greatly increases the recovery rate of TCE from unfractured media. However, details of boiling such as boiling location and temperature gradient that corresponds to the pressure gradient that drives the steam flow were not documented, though the link between the details of boiling and contaminant removal are important for understanding the phenomenon.

1.6.3 Fractured media

There are limited studies conducted on the thermal remediation of fractured geologic media. Fractured rock behaves differently than unfractured material.

A study on steam enhanced remediation for recovery of volatile organic contaminants from fractured limestone was conducted at the former Loring Air Force Base (AFB) in limestone, Maine (Davis et al., 2005). The steam injection rate and the energy input rate were low due to the low transmissivities in the injection intervals and sparsely spaced fractures (Davis et al., 2005). The entire target zone for treatment was not
heated to the water boiling temperature. The highest recorded temperature away from the injection well was approximately 50 °C (Davis et al., 2005).

Heron et al. (2008) successfully heated a fractured site above the water boiling temperature using thermal conductive heating. The site was underlain by Fill (0-7.6 m), Saprolite (7.6-16.7 m), partially weathered bedrock (16.7-22.7 m), and fractured bedrock (below 22.7 m). The area of treatment zone was about 237 m². Their heater extended about 27 m below ground surface and the bottom 4.3 m of the treatment zone consisted of fractured gneiss. The effective permeability of the fractured rock is about $1 \times 10^{-14}$ m². This site was contaminated with TCE, with the amount of release unknown. Before the treatment, DNAPL was visually observed in soil and water samples. Arrays of heaters heated the treatment zone to 100 °C in approximately 100 days. After treatment the concentration of TCE in groundwater samples was reduced to less than 5 µg/L (from starting TCE concentrations at saturation levels, 1,100,000 µg/L). The mean TCE soil concentration for the entire treatment zone (including both above and below the water table) was 17 µg/kg. The amount of electrical energy used was about 239 kWh/m³. This study showed a good removal of TCE from a fractured gneiss rock site. However, the contaminant mass transfer from matrix to fracture by boiling was not demonstrated. Also, the key factors that affect the contaminant mass transfer are not known. (Heron et al., 2008)

1.7 Numerical simulation

The process of contaminant removal from porous media due to boiling has been simulated. Udell and Itamura (1998) simulated TCE removal at 100 °C from a partially
saturated (10%) porous media during a depressurization cycle. Their results showed an effective reduction of TCE concentration from near its solubility to below the drinking water standards in a high permeable porous media ($10^{-12}$ m$^2$). The time required for remediating porous media with lower permeability was longer than those of higher permeability using depressurization (Udell and Itamura, 1998). However, partially saturated porous media were considered, while many fractured porous media are below the water table. Similar results have been obtained by Carrigan and Nitao (2000). They simulated electrical resistance heating of a low-permeability clay layer. Their simulated results showed that high pressure of the vapor phase drove the contaminant into adjacent, high-permeability layers and the region between electrodes were swept clean owing to vaporization caused by ohmic heating (Carrigan and Nitao, 2000).

Flows and heat, water, and contaminants in fractured rock masses can be simulated in four ways. The first method is to use a uniform model with the equivalent permeability and average thermal properties. This approximation is capable of solving for total fluid Darcy velocities in a highly fractured system, but it cannot account for any fracture-matrix interactions. The second method is the dual porosity/permeability method. This method involves a special discretization that subdivides each normal gridblock into two volume fractions, representing the fracture and matrix, respectively. Volume fractions, permeability, capillary and relative permeability functions, porosity, and thermal properties are assigned to their domains. In the dual porosity method, the fracture volumes are globally connected in 3-D, and the matrix material is locally connected to the fracture elements. In the dual permeability method, both the fracture and
matrix blocks are globally connected. The dual porosity/dual permeability methods can simulate transient multiphase fluid, heat and mass flows between the fractures and the matrix (Pruess et al., 1999), but they may not accurately resolve heat and mass fluxes between the fracture and matrix in situations where temperature, saturation, pressure and concentration gradients in the matrix are variable with time and distance into the matrix, because the state variables in the matrix block (temperature, pressure, phase saturations, concentrations) are represented by single average values over the entire matrix, and the gradients are calculated using the single average nodal distance from the matrix centroid to the fracture.

The third simulation method is the multiple interacting continua (MINC) method. This method can resolve local transient gradient of temperature, pressure, saturation, and concentration in the matrix by extending the dual porosity method to include multiple nested matrix block elements (Pruess, 1983; Pruess and Narasimhan, 1985). It subdivides a normal 3-D gridblock into a fracture element, and multiple nested matrix elements. The fracture elements are connected globally in 3-D, while the matrix elements are only locally connected to each other, and ultimately to the fracture. The individual matrix element volumes and nodal distances are based on different conceptual models of the fracture orientation and spacing. With a 3-D set of orthogonal fractures, each nested matrix element has the shape of a hollow cube, the outer matrix element is connected to the fractures, and the inner matrix elements are connected to each other in 1-D. The nested matrix elements represent the average response of the matrix based on their distance from the nearest fracture. This method has been used to simulate energy
production and mass transfer in fractured reservoirs in geothermal studies (Pruess 1983; Pruess and Narasimhan 1985; Pruess 2002). However, it appears that this method has not previously been applied to simulate contaminant transport in a non-isothermal process.

The fourth simulation method is to model a fractured porous media with a discrete fracture-matrix model, where the fractures and matrix are fully discretized and connected in 3-D. This is the most accurate way to numerically represent a fractured porous media; however, the discretization must be limited to small domains for problems involving non-isothermal multiphase flow due to the high computational demands. Experience with these types of simulations shows that model meshes should be restricted to a few tens of thousands of gridblocks or less for reasonable run times.

1.8 Summary

Previous studies show that boiling may be an effective mechanism for contaminant removal from fractured geologic media. Boiling in fractured geologic media is anticipated to be more complex than in batch conditions. Details of boiling were not demonstrated in previous studies, which are believed to be important to understand the contaminant mass transfer due to boiling. The factors such as matrix/fracture permeability, fracture spacing and apertures, and other geologic or operational parameters that control the process are not known. The lack of knowledge of the mechanisms of contaminant mass transfer due to boiling causes difficulties in evaluation of the feasibility of thermal remediation, and in providing guidance for the design and operational strategy for maximizing contaminant removal while implementing thermal remediation at fractured sites.
References


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CHAPTER TWO
RESEARCH OBJECTIVES

This dissertation research is devoted to developing a better understanding of the coupled multiphase heat and mass transfer process that occur in fractured porous media when they are heated and depressurized by an adjacent fracture. It includes both laboratory and numerical analyses of the multiphase heat and mass transfer phenomenon. The specific objectives include:

1) Experimental Demonstration of Contaminant Removal from Fractured Rock by Boiling
   a) Development of an experimental system: This part of the research includes designing and fabricating sensors, a sample container and heater, pressurized vessel, data acquisition system, and fluid handling and sampling equipment associated with the experimental apparatus.
   b) Baseline flow experiment: This part includes a tracer test to check the flow of the system, reliability of the sampling collection system and analytical method.
   c) Contaminant transport experiment: This is to evaluate the transient recovery of a volatile contaminant (1,2-DCA) during depressurization boiling.

2) Henry’s Law Constants of Chlorinated Solvents at Elevated Temperatures
   a) Measurement of the Henry’s law constants of 12 chlorinated solvents from 8 to 93 °C.
b) Measurement of aqueous solubility of pure chlorinated solvents, and comparison of the calculated Henry’s law constants from vapor pressure-solubility model with the experimentally determined values.

3) Numerical Analysis of Contaminant Removal from Fractured Rock by Boiling
   a) Simulation of the laboratory experiment (from objective 1) with the TMVOC code.
   b) Simulation of contaminant mass and heat transfer during boiling without end effects.
   c) A field scale simulation of the thermal remediation of a contaminant in fractured geologic media.

4) Multiphase Numerical Analysis of Thermal Remediation in a 3-D, Field Scale, Fractured Geologic Media
   a) Sensitivity analysis over chemical property of contaminant, fracture and matrix properties, operational and design strategies.
   b) Numerical analysis of the impact of cold water present in the field (considering both flat and dipped water tables) on the performance of thermal remediation.
CHAPTER THREE

EXPERIMENTAL DEMONSTRATION OF CONTAMINANT REMOVAL FROM FRACTURED ROCK BY BOILING

This chapter is the 2010 paper “Experimental demonstration of contaminant removal from fractured rock by boiling” by F. Chen, X. Liu, R. Falta, and L. Murdoch that was published in Environmental Science & Technology, vol 44, no. 16, 6437–6442. Xiaoling Liu has partially contributed in the analytical methods and experimental system setup. It describes a set of experiments that demonstrate the removal of dissolved 1,2-DCA from fractured rock (using a unfractured sandstone core to represent the matrix and the end to represent the fracture) by partitioning to the steam vapor flow generated by boiling.

Abstract

This study was conducted to experimentally demonstrate removal of a chlorinated volatile organic compound from fractured rock by boiling. A Berea sandstone core was contaminated by injecting water containing dissolved 1,2-DCA (253 mg/L) and sodium bromide (144 mg/L). During heating, the core was sealed except for one end, which was open to the atmosphere to simulate an open fracture. A temperature gradient towards the outlet was observed when boiling occurred in the core. This indicates that steam was generated and a pressure gradient developed towards the outlet, pushing steam vapor and liquid water toward the outlet. As boiling occurred, the concentration of 1,2-DCA in the condensed effluent peaked up to 6.1 times higher than the injected concentration. When 38% of the pore volume of condensate was produced, essentially 100% of the 1,2-DCA
was recovered. Non-volatile bromide concentration in the condensate was used as an indicator of the produced steam quality (vapor mass fraction) because it can only be removed as a solute, and not as a vapor. A higher produced steam quality corresponds to more concentrated 1,2-DCA removal from the core, demonstrating that the chlorinated volatile compound is primarily removed by partitioning into vapor phase flow. This study has experimentally demonstrated that boiling is an effective mechanism for CVOC removal from the rock matrix.

1 INTRODUCTION

Chlorinated volatile organic compounds (CVOCs) that diffuse into low permeability matrix in a fractured rock site may cause long-term groundwater pollution and difficulties in cleanup. When CVOCs are released, and the dissolved CVOCs and dense nonaqueous phase liquids (DNAPLs) move through fractures, the sharp concentration distinction between the fracture and matrix will result in rapid diffusion of CVOCs into the low permeability rock matrix (Espositio and Thomson, 1999; Falta, 2005; O'Hara et al., 2000; Parker et al., 1994; Parker et al., 1997; Reynolds and Kueper, 2001; Reynolds and Kueper, 2002; Ross and Lu, 1999; Slough et al., 1999). A significant amount of dissolved and adsorbed contaminant mass will be stored in the matrix over time, serving as a reservoir of contaminants. When the contaminants in fractures are removed by engineered or natural processes, contaminants in the matrix continuously diffuse back into the water flowing through the fractures. This may result in aqueous contaminant concentrations several orders of magnitude higher than maximum contaminant levels (MCLs) (Falta, 2005; Parker et al., 1997; Reynolds and Kueper, 2002;
Without treatment, this process could last for hundreds of years (Falta, 2005; Parker et al., 1997; Reynolds and Kueper, 2002; Slough et al., 1999), serving as a long-term source for groundwater contamination. Remediation of fractured sites is challenging using isothermal methods such as air sparging, pump and treat, and chemical oxidation. Due to the low matrix permeability, it is difficult to flush the system with any type of fluid (Baston, 2008; Falta, 2005). The uncertainty of fracture network configurations makes it even more difficult to reliably deliver remediation agents into the matrix (Goldstein et al., 2004; Mundle et al., 2007; National Research Council, 1994).

Figure 3.1 Schematic of experimental design: (a) a 3-D fractured rock block where boiling occurs in the matrix; (b) enlarged view of a fracture-matrix set; (c) a cylindrical core where the unfractured core represents the rock matrix and the end represents the fracture adjacent to the matrix.

Thermal methods hold promise for remediating fractured geologic media. Heat can be successfully transferred to the rock matrix by thermal conduction (Gudbjerg et al., 2004; Heron et al., 2009; Ochs et al., 2003), electrical resistive heating (Gauglitz et al., 1994; Heron et al., 2005) or radio-frequency heating (Kawala and Atamanczuk, 1998; Roland et al., 2008). As fractured rock or soil is heated above the water boiling point, subsequent depressurization will induce boiling in the matrix (Figure 3.1a). When boiling
occurs, one volume of liquid water turns into about 1600 volumes of steam vapor at atmospheric pressure, resulting in high pressure gradients and steam volumetric flux. The portion of volatile contaminant dissolved in water in the matrix will preferentially partition into the steam due to the increased Henry’s law constant at steam temperature, which is approximately 20 times higher than at ground water temperature for trichloroethylene (TCE) (Heron et al., 1998a). This in situ boiling may be an extremely effective mechanism for CVOCs removal. Assuming batch conditions, Udell (1996) and Heron et al. (1998b) calculated that boiling away one percent of the water mass could theoretically lead to a decrease of dissolved (TCE) concentration by tens of orders of magnitude.

Contaminant mass transfer in fractured media due to in situ boiling is not well understood. Some previous field studies showed increased removal rates when heating to above the water boiling temperature (Gauglitz et al., 1994; Heron et al., 2005). Heron et al. (1998b) examined TCE removal from a partially saturated (water saturation of 0.90) unfractured low permeability silt in the laboratory. When the temperature in the tank reached 99 °C, boiling started, and the TCE removal rate was about 20 times higher than the initial removal rate (Heron et al., 1998b). At the termination of the experiment, about 99.8% of the initial TCE mass was removed from the silt (Heron et al., 1998b). However, it is unclear where the boiling occurred in this study, though the removal of contaminant was linked to the in situ boiling that was induced.

The contaminant mass transfer in fractured media due to boiling is anticipated to be a complex phenomenon. When boiling occurs in fractured media, there are strong
couplings between convective and conductive heat transfer, multiphase flow and thermodynamics. Recently, Baston et al. (2010) found that fracture and rock matrix properties have significant influence on the heating time to remove all liquid water in the treatment zone. The details of boiling phase change are important for contaminant mass transfer during this process because it is this phase change that strips the volatile contaminant from the liquid phase. Depending on conditions, the majority of boiling phase change could occur near fractures, or in the matrix. Some early studies on geothermal reservoirs showed that boiling could be induced in the matrix provided that matrix permeability is larger than about $1\times10^{-17}$ m$^2$ (Pruess, 1983). When this is the case, the vapor phase moves from boiling locations in the matrix to the fracture. When the permeability less than about $1\times10^{-17}$ m$^2$, the liquid phase moves from the matrix to the fracture and boiling occurs mainly in the fracture (Pruess, 1983). The efficiency of contaminant removal in these two scenarios would vary greatly due to the presence or absence of steam stripping by the vapor phase in the matrix. Understanding the mechanism of mass transfer due to in situ boiling in fractured porous media helps to evaluate remediation feasibility, and develop design and operational strategies for maximizing the effectiveness of thermal remediation in fractured media. The purpose of this study was to demonstrate removal of CVOCs due to in situ boiling in fractured geologic media.
2 EXPERIMENTAL SECTION

2.1 Apparatus

The apparatus (Figure 3.2) is primarily composed of a core assembly, pressurized vessel, condenser, circulation system, temperature control and data acquisition systems.

2.1.1 Core preparation

The core assembly is made up of a cylindrical unfractured rock sample (5.08×30.48 cm), two aluminum endcaps, porous disks, a Teflon shrink tube, thermistors, resistive temperature detectors (RTDs), heaters and an insulation layer. A Berea sandstone core with a hydraulic permeability of $1.5\times10^{-13}$ m$^2$ and porosity of 0.174 (pore volume: 104 mL) was obtained from Cleveland, Ohio. This rock core is used to represent the rock matrix with the top end representing the fracture adjacent to matrix (Figure 3.1).
The system is designed so that the core may be contaminated by water circulation at high pressure. During heating tests, the top end of the core is open, to simulate a depressurized fracture.

The sample combined with porous disks at each end is sealed with a Teflon shrink tube (diameter less than 5.08 cm after heating) and two aluminum endcaps. Water is introduced and removed from the core through the channels in endcaps, connected with copper (OD: 0.635 cm) and brass (OD: 0.3175 cm) tubes through Yor-Lok brass compression fittings (McMaster-Carr) at the inlet and outlet ends, respectively. A pressure gauge is connected to the top of the core. The assembly is then wrapped with a strip heater (SRT051-120, OMEGALUX). A series of thermistors (10KcMCD1, Betatherm) are embedded 2.54 cm deep, along the axis of the core to monitor the core temperature. Between the strip heater and Teflon shrink tube, a series of RTDs (SA1-RTD, Omega Engineering) are placed to monitor surface temperature. An insulation layer is added around the strip heater to reduce heat dissipation from the core. Two Teflon plates embedded with cartridge heaters sets (CSS-01115, Omega Engineering) are used to hold the assembly at each end of the core, and are attached to the flange of a pressurized steel vessel.

2.2 Pressurized vessel, condenser and circulation system

A steel pressurized vessel is used to provide confining pressure to the core. An air compressor is connected and used to pressurize the vessel to 1.72×10^5 Pa, gauge pressure. A confining pressure of 1.72×10^5 Pa is necessary to keep the Teflon shrink tube tight enough to prevent water from flowing between the shrink tube and rock sample. Copper
tubes (OD: 0.635 cm), and 3-way valve and brass compression fittings are used to connect the inlet endcap of the core with the water and contaminant reservoirs. Water/contaminant is introduced from the bottom of the core. A 3-way valve is used to control whether water or contaminant or neither is introduced. Below the 3-way valve, a sampling port made up of a brass Yor-Lok tube fitting Tee sealed with Teflon-backed septa allows for influent sampling. The outlet endcap connects to a heat exchanger through brass tubes (OD: 0.3175 cm), compression fittings and a valve. The heat exchanger is made by placing a segment of brass tube with a bigger diameter (1.27 cm in OD) around the outlet brass tube and connecting it with a source of cold water. During heating tests, hot vapor and liquid produced from the core flows through the outlet brass tube while cold water is pumped counter-currently through the annular space between the tubes. A needle is placed at the end of the heat exchanger via a Luer-Lok coupling (VWR International) for sampling and collecting the liquid condensate.

2.2.1 Temperature control and data acquisition system

Temperatures along the core are monitored by connecting the temperature sensors with a data acquisition system. The data acquisition system is comprised of a temperature module (NI-1305, National Instruments), a terminal block (NI-1306, National Instruments), a chassis (SCXI-1000, National Instruments), a data acquisition board (PCI-6220, National Instruments) and a computer. Ends of RTDs are connected with the terminal block via an Integrated Drive Electronics (IDE) cable. A program in Labview is used to automatically sample temperature data every second.
The temperature control system consists of the data acquisition system as described above, a counter output (PCI-6602, National Instruments), and a digital solid state relay (SSRL240DC25, Omega). Three heaters are used: one strip heater and two cartridge heaters. The strip heater (SRT051-120, Omegalux) is wrapped around the Teflon core sleeve. Two sets of cartridge heaters (CSS-01115, Omega Engineering) used to counteract the heat loss at ends, along with two RTDs, are placed in the Teflon plates at both ends. The heating rate is controlled by adjusting the proportion of heating time in a cycle (duty cycle) in a Labview program.

2.3 Chemicals, sample collection and analytical techniques

Chemicals used in this test are 1,2-dichloroethane (1,2-DCA) (Analytical grade, Mallinckrodt), and sodium bromide (NaBr) (Analytical grade, Mallinckrodt). The choice of 1,2-DCA as the model compound was because it was frequently found in contamination sites (Henderson et al., 2008); and, it has similar physical properties to other chlorinated solvents such as TCE, but relatively with high solubility, which minimizes losses from evaporation during the experiment. NaBr was used as a tracer because it is non-volatile and conservative.

Effluent samples were collected at the end of the heat exchanger using 10-mL glass vials sealed with Teflon-backed septa. About 2 mL of air was pre-extracted from each vial using a graduated syringe to reduce pressure buildup during sampling. The weight of the sealed vial is recorded as $W_1$. The sample is taken by plugging the sealed vial to the outlet needle and pulling out the vial after about 2 mL of sample is collected. The weight of the vial with sample is recorded as $W_2$. The mass of sample ($W_s$) was
calculated as $W_i = W_2 - W_1$. Influent samples were collected at the sampling port below the 3-way valve. About 2 mL of influent sample was collected with a graduated syringe and transferred to a partially vacuumed vial. The mass of sample was obtained by weighing the vial with and without sample.

The aqueous concentration of 1,2-DCA was quantified by head space analysis using a 5890 series II Plus Hewlett-Packard gas chromatograph (GC), equipped with a flame ionization detector (FID). The detection limit for this method is 0.016 mg/L. Samples were filtered with 0.2-μm-pore-size PTFE syringe filters (VWR International). Bromide was measured from filtered samples with a Dionex ion chromatograph (IC) with an AS11/AG11 column and the concentration was referred as NaBr. The eluant for bromide determination is sodium carbonate (4.5mM) and sodium bicarbonate (0.8mM). The detection limit for this method is 0.01 mg/L.

2.4 Experimental procedures

2.4.1 Saturating the sample

The rock sample was saturated with water by first circulating CO$_2$ gas at a low rate to remove air from the core. De-aired water was then pumped through the core from bottom to top at 6.89×10$^4$ Pa (gauge pressure), until the inlet flow rate equaled to the outlet flow rate.

2.4.2 Dissolved tracer test

A tracer test was conducted after the core was water saturated. A 132 mL solution containing 108 mg/L NaBr, and 255 mg/L 1,2-DCA was injected. The tracer solution was followed by 629 mL of clean water. Samples were collected at the outlet, and the volume
of effluent produced was recorded. Concentrations of 1,2-DCA and bromide were measured using gas chromatography (GC) and ion chromatography (IC), respectively.

2.4.3 Heating Test

The water saturated rock sample was contaminated by injecting an aqueous solution containing 1,2-DCA (253 mg/L), and NaBr (144 mg/L) through the sample. Both the influent and the effluent concentrations, and the volume of water circulated were monitored. Both inlet and outlet valves were closed when the effluent 1,2-DCA and bromide concentrations stabilized. The amounts of 1,2-DCA and bromide mass remaining in the core are calculated by substracting the mass removed from the core from the mass injected.

A constant power input of 31.3 W was applied with the strip heater. The power inputs of cartridge heaters at each end were adjusted to counteract the heat loss at the ends, ranging from 1.2 W to 15 W. Due to thermal expansion of fluid and possible noncondensible gases dissolved in the pore, the core pressure increased during the heating process prior to boiling. It was released by quickly opening and shutting the outlet valve as the gauge pressure exceeded about $1.03 \times 10^5$ Pa.

The outlet valve was opened when the surface temperature exceeded 100 °C. Steam generated from boiling was condensed to liquid in the heat changer. The condensate was collected at the outlet by plugging in the sealed and partially vacuumed vials. The volume of condensate produced was recorded, and concentrations of 1,2-DCA and bromide in the condensate were measured by GC and IC analysis, respectively.
RESULTS AND DISCUSSION

3.1 Tracer Test

The tracer test was conducted by injecting a pulse of 132 mL of water with NaBr at 108 mg/L, and 1,2-DCA at 255 mg/L followed by water. The influent and effluent concentrations of 1,2-DCA, and bromide (referred as NaBr) were plotted as a function of water produced from the core (Figure 3.3). Bromide was produced after circulating approximately one pore volume of pore (104 mL), indicating that water flows axially through the core without short circuiting. 1,2-DCA breakthrough follows the bromide, flowing out after circulating 118 mL of water, indicating only slight adsorption of the 1,2-DCA. This is consistent with its low K_{oc} of 33 (EPA, 1995).
A mass balance on the tracer test was conducted by integrating the area under the curves in Figure 3.3. The ratio of cumulative effluent mass to the total mass injected is presented in Figure 3.4. The recovery of 1,2-DCA and bromide in this tracer test were 98% and 93%, respectively. The high recovery of mass suggests that there is little leakage or other source of mass loss from the system during sampling and analysis.

### 3.2 Contamination of the Core

Before the heating test, the core was contaminated by injecting 1,2-DCA and NaBr dissolved in water. To uniformly contaminate the core, 350 mL of 1,2-DCA (253 mg/L), and NaBr (144 mg/L) were injected under high pressure \( (6.89 \times 10^4 \text{ Pa, gauge}) \). Both inlet and outlet concentrations were monitored, and the results are shown in Figure 3.5. Initially, the 1,2-DCA and bromide concentrations in the core were nearly zero. After injecting 350 mL of solution, effluent concentrations stabilized and both inlet and outlet...
valves were then closed. The masses of 1,2-DCA and bromide (referred as NaBr) remaining in the core were 26.9 mg and 15.3 mg, respectively.

Figure 3.5 Contamination of rock core by high pressure injection of an aqueous solution

3.3 Temperature Profile and Condensate Flow during Heating

After the core was uniformly contaminated, both inlet and outlet valves were closed, and the heaters were turned on. Condensate samples were collected over time until no more condensate was produced. The heaters were shut off after the core started drying out.
Figure 3.6 Temperature and condensate production during heating: (a) locations of temperature sensors; the distances of sensors #1, #2, #3, #4, #5, #6, and #7 from the top of the core are 0, 2.54, 5.08, 10.16, 15.24, 20.32, and 25.4 cm, respectively; (b) temperature profile; (c) condensate flow rate

Core temperatures were monitored using sensors embedded 2.54 cm deep in the core (Figure 3.6a). The distances away from the top (outlet) end the core are 0, 2.54, 5.08, 10.16, 15.24, 20.32, and 25.4 cm. From top to bottom, they are labeled as #1, #2, #3, #4, #5, #6 and #7. Before the outlet valve was opened, the core was uniformly heated
and the temperature increased gradually; when the temperature exceeded 100 °C, the outlet valve was opened. The temperature at the outlet (#1) dropped immediately, subsequently followed by temperature drops at #2, #3, #4, #5, #6, and #7. When boiling occurs, thermal energy is taken from the surrounding due to the phase change. The immediate temperature drop at the outlet end indicates that boiling was initiated at the outlet, and this temperature corresponds to the pressure at that location. As boiling in the core occurred, a temperature gradient was observed from bottom to top. This is explained by the fact that as steam was generated, a pressure gradient developed towards the outlet, pushing steam vapor and liquid water toward outlet end. A higher pressure corresponds to a higher boiling temperature under these saturated vapor conditions. Over time, the temperature gradient gradually decreases. This is due to the decreasing water saturation, which results in an increase in the relative permeability of gas phase. As a result, the pressure and hence the temperature gradient toward the outlet decreased with time. Some small spikes in temperature curves were observed due to sampling. Since the condensate was sampled with sealed and partially vacuumed vials, the outlet pressure decreased as the vial was plugged in, and increased when more and more condensate was collected, returning to atmospheric pressure when the vial was unplugged. The temperature at the outlet (#1) is the most sensitive to the outlet pressure change caused by sampling. Sensors at deeper locations were less influenced by the small outlet pressure changes due to dampening of the pressure waves as they travelled through the core (Roberts, 2002).

At later times, the outlet (#1) temperature began to increase as the liquid water boiled away, and superheated vapor conditions prevailed. Subsequently the temperatures
at locations #2, #3, #4, #5, #6, and #7 increased as these zones dried out. After approximately 6.3 hours, the heater was turned off and the temperature started decreasing.

Steam (a mixture of liquid and vapor) coming out of the core was condensed and the condensate flow rate with time was plotted (Figure 3.6b). A large amount of condensate was generated right after the valve was opened, but as will be explained, some of this exited the core as a liquid phase. The flow rate increased to 108.6 mL/h, and gradually dropped to about 14.79 mL/h. After about 5.56 hours of heating, the core dried out, which corresponds to the temperature increases at the bottom of the core.

3.4 Contaminant Removal Due to Boiling

3.4.1 Contaminant Removal

The contaminant concentrations removed from the core by in situ boiling were monitored, and are shown as a function of condensate production (Figure 3.6). During heating the core to 100°C, pressure build-up due to fluid expansion was released by quickly opening and shutting the valve as it reached 1.03×10^5 Pa, gauge pressure. During this initial heating, 11 mL of fluid was pushed out when the valve was opened and shut to release increased core pressure. Before the outlet valve was completely opened, the effluent concentration of 1,2-DCA was 632.5 mg/L. As temperature exceeded 100 °C, the outlet valve was opened, and left open to the atmosphere. The pressure drop induced boiling. Steam coming out of the core was condensed to ambient temperature. Since a small amount of fluid (8 mL) resides in the condenser, samples taken at the start of the heating experiment actually represent the contaminant concentration in the condenser,
instead of the concentrations from the core. To better present the contaminant removal from the core, the volume of fluid that remained in the condenser was subtracted from the total volume of fluid coming out of the core, and is shown as negative values in Figure 3.8.

![Figure 3.7 Relative concentration of 1,2-DCA and bromide in condensate produced during heating experiment](image-url)

After opening the valve for good, the effluent contaminant concentrations increased dramatically, reaching 1555 mg/l for 1,2-DCA, about 6.13 times higher than its concentrations before heating. Then a fluctuation of the 1,2-DCA concentration was
observed, while at the same time the bromide concentration increased, indicating production of some liquid water. After 18.2 mL of condensate was produced, the effluent concentrations of 1,2-DCA dropped quickly. After 36.9 mL of condensate, the effluent concentration of 1,2-DCA dropped to 16.9mg/L, which is less than 9% of the concentration before heating. Contaminant mass removed from the core was plotted in Figure 3.8. The results show that up to 99% of 1,2-DCA mass was removed from the core with the production of 40 mL of condensate, which is about 38% of the core pore volume.

Effluent bromide concentration is a good indicator of the steam quality in this heating test. Since bromide is nonvolatile, it will not be removed by partitioning to the steam vapor. However, it can be removed as a result of liquid water being pushed out of the core. The condensed effluent could be either from the steam vapor generated by boiling, from the pore water pushed out by the pressure gradient, or from combined sources. When the valve was opened for good, the bromide concentration (referred as NaBr) in the condensate dropped. The percentage of bromide concentration in effluent samples is inversely related to the percentage of water coming out as vapor. From Figure 3.7, one can see that the bromide concentration dropped greatly after the valve was opened, which as a result corresponds to a period of high contaminant removal. Then an increase of the percentage of bromide corresponds to the decrease of contaminant concentration removed from the core. Further decrease of the bromide concentration corresponds to another peak of contaminant concentration. Bromide concentration
approached zero when approximately 50 mL condensate (about 48% pore volume) was produced, indicating that the condensate was 100% vapor when it left the core.

Figure 3.8 Contaminant mass recovery during heating

4 SUMMARY

Thermal removal of chlorinated solvents from a sandstone rock matrix was experimentally demonstrated in the laboratory. After the core was contaminated with 1,2-DCA, heating the core above 100 °C and subsequently opening one end of the core to the atmosphere induced boiling in the core. As boiling occurred in the core, a temperature gradient towards the outlet was observed, indicating that steam was generated and a pressure gradient developed towards the outlet, pushing steam vapor and liquid water out of the core. As boiling occurred, the effluent concentration of 1,2-DCA peaked up to 6.1 times higher than before being heated. The 1,2-DCA was quickly removed from the matrix due to in situ boiling. When 38% of the pore volume of condensate was produced, nearly 100% of the 1,2-DCA was recovered. Non-volatile bromide concentration in
condensate is a good indicator of the percentage of water coming out as liquid water. Combined with the 1,2-DCA concentration curve, it shows that a higher percentage of condensate coming out as vapor corresponds to more concentrated 1,2-DCA removal from the core. This demonstrates that the chlorinated volatile compound is primarily removed by partitioning to vapor phase flow. This study provides a platform for further understanding the key factors that control contaminant mass transfer from heated fractured rock by boiling.
References


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CHAPTER FOUR

HENRY’S LAW CONSTANTS OF CHLORINATED SOLVENTS AT ELEVATED TEMPERATURES

This chapter describes the measurement of Henry’s law constant of 12 chlorinated volatile organic compounds from 8 to 93 °C. These data are helpful for accurate modeling of subsurface remediation processes that operate near the boiling point of water.

Abstract

Henry’s law constants for 12 chlorinated volatile organic compounds (CVOCs) were measured as a function of temperature ranging from 8 to 93°C, using the modified equilibrium partitioning in closed system (EPICS) method. The chlorinated compounds include tetrachloroethylene, trichloroethylene, cis-1,2-dichloroethylene, vinyl chloride, 1,1,1-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, chloroethane, carbon tetrachloride, chloroform, dichloromethane, and chloromethane. The variation in Henry’s constants for these compounds as a function of temperature ranged from around 3-fold (chloroethane) to 30-fold (1,2-dichloroethane). Aqueous solubilities of the pure compounds were measured over the temperature range of 8 to 75°C. The temperature dependence of Henry’s constant was predicted using the ratio of pure vapor pressure to aqueous solubility, both of which are functions of temperature. The calculated Henry’s constants are in a reasonable agreement with the measured results. With the improved data on Henry’s law constants at high temperatures measured in this study, it will be possible to more accurately model subsurface remediation processes that operate near the boiling point of water.

1 INTRODUCTION

Henry’s law constant determines the tendency of a compound to partition between the aqueous phase and gaseous phase at equilibrium. Its values are required by multiphase flow
contaminant transport models and they are used in design and performance models of remediation processes such as air-stripping and thermal enhanced remediation (Gossett, 1987; Heron et al., 1998a). Many studies have been conducted to determine Henry’s law constant at ambient temperatures (Ashworth et al., 1988; Gossett, 1987), and the values are available usually at temperatures below 40°C (Brennan et al., 1998; Mackay and Shiu, 1981; Staudinger and Roberts, 2001). Henry’s law constant data at higher temperatures are limited.

Thermal methods have been used as an alternative means of removing contaminants from geologic media due to the increased contaminant mass transfer at higher temperatures. Electrical resistance heating, steam enhanced extraction, thermal conductive heating, and radio-frequency heating can increase the subsurface temperature to above the water boiling temperature. As boiling occurs, volatile compounds partition to and are removed by the moving vapor phase. This process effectively removes dissolved contaminants from soils and fractured rocks (Beyke and Fleming, 2005; Chen et al., 2010; Gauglitz et al., 1994; Gudbjerg et al., 2004; Heron et al., 1998b; Heron et al., 2009; Hodges et al., 2004; Ochs et al., 2003). Knowing the Henry’s law constants of CVOCs that are frequently encountered at contaminated sites at higher temperatures is important for understanding the process of contaminant removal and for predicting the performance of thermal remediation.

Efforts to extrapolate Henry’s law constant data from the available data measured at ambient temperatures are complicated by the fact that the enthalpy of dissolution is a function of temperature over wide temperature ranges (Heron et al., 1998a). Different models have been proposed to predict Henry’s law constants at higher temperature ranges (Abraham and Acree, 2007; Brennan et al., 1998; Gorgenyi et al., 2002; Lau et al., 2010; Mackay and Shiu, 1981; Plyasunov and Shock, 2003). However, for most compounds, these models have not been
validated due to the lack of direct measurements at high temperatures (Brennan et al., 1998). In this study, we measured the Henry’s law constants for 12 CVOCs at temperatures from 8 to 93°C. Our data are compared to previously measured and estimated values on the temperature dependency of Henry’s law constants.

2 THERMODYNAMIC BACKGROUND

Henry’s law constant is defined as the ratio of the gaseous and aqueous concentrations of a compound at equilibrium. Depending on the expression of abundance of contaminant in the gaseous phase, two forms are typically used: if the gaseous ($C_g$) and aqueous ($C_w$) concentrations are expressed in molar concentration (mol/m$^3$), a dimensionless form of Henry’s constant ($H$) is obtained (Heron et al., 1998a; Reid et al., 1987; Schwarzenbach et al., 1993):

$$H = \frac{C_g}{C_w}$$

(4.1)

If the partial pressure ($p_i$ in atm) of a contaminant is used, the Henry’s constant ($H_c$) has the unit of atm·m$^3$/mol (Heron et al., 1998a; Reid et al., 1987; Schwarzenbach et al., 1993):

$$H_c = \frac{p_i}{C_w}$$

(4.2)

The temperature dependence of Henry’s law constant can be described with the Van’t Hoff equation formulated for water-gas equilibrium (Heron et al., 1998a):

$$\frac{d\ln H_c}{dT} = \frac{\Delta H_{dis}}{RT^2}$$

(4.3)

where $\Delta H_{dis}$ is the enthalpy of dissolution of the gaseous contaminant into water (J/mol), $R$ is the gas constant, and $T$ is absolute temperature (K). If the enthalpy of dissolution is constant in a temperature interval from $T_0$ to $T$, it yields:

$$\ln H_c(T) = \ln H_c(T_0) - \frac{\Delta H_{dis}}{R \left( \frac{1}{T} - \frac{1}{T_0} \right)}$$

(4.4)
where $H_e(T)$ and $H_e(T_0)$ are the Henry’s law constants at temperatures $T$ and $T_0$, respectively. This equation can be further simplified by combining the thermodynamic quantities into parameters $A$ and $B$ as:

$$\ln(H_e) = A - \frac{B}{T}$$  \hspace{1cm} (4.5)

where a linear relation exists between $\ln(H_e)$ and $1/T$. Parameters $A$ and $B$ can be obtained by linear regression of the experimental data from plotting $\ln(H_e)$ versus $1/T$. This method has been applied in many previous studies (Ashworth et al., 1988; Gossett, 1987). However, the assumption of constant enthalpy of dissolution can be inappropriate over a wider temperature range. Heron et al. (1998a) found that the enthalpy of dissolution for trichloroethylene varies by about 40% when the temperature ranges from 0 to 80°C. They proposed to model the temperature dependency of the enthalpy of dissolution with a linear function (e.g. $\Delta H_{dis} = aT + b$). With such an assumption, the integration of equation 4.1. yields (Heron et al., 1998a):

$$\ln\left(\frac{H_e}{H_e(T_0)}\right) = \frac{a}{R\ln(T/T_0)} - \frac{b}{R\left(\frac{1}{T} - \frac{1}{T_0}\right)}$$  \hspace{1cm} (4.6)

It can be further simplified as (Heron et al., 1998a):

$$\ln(H_e) = A - \frac{B}{T} + ClnT$$  \hspace{1cm} (4.7)

3 MATERIALS AND METHODS

3.1 Chemicals and stock solutions

The following chlorinated volatile organic compounds were selected for study: tetrachloroethylene (99%, ACROS ORGANICS), trichloroethylene (99.5%, Aldrich Chemical), chloroform (molecular biology certified, Shelton Scientific), 1,1,1-trichloroethane (Fisher scientific), 1,1-dichloroethane (TCI), dichloromethane (Burdick & Jackson), carbon tetrachloride
(99.9%, Sigma-Aldrich), vinyl chloride (Matheson Gas Products), chloroethane (Sigma-Aldrich), chloromethane (Holox), cis-1,2-dichloroethylene (TCI), and 1,2-dichloroethane (Analytical agent, Mallinckrodt).

For analytical convenience, three mixtures of compounds were prepared. Mixture A contained methanol (0.900 g/g), tetrachloroethylene (0.0194 g/g), 1,1,1-trichloroethane (0.0156 g/g), trichloroethylene (0.0175 g/g), chloroform (0.0174 g/g), dichloromethane (0.0156 g/g), and 1,1-dichloroethane (0.0141 g/g). Mixture B contained methanol (0.963 g/g), carbon tetrachloride (0.0212 g/g) and 1,2-dichloroethane (0.0158 g/g). Mixture C contained methanol (0.982 g/g), chloromethane (3.65×10^-4 g/g), vinyl chloride (3.54×10^-4 g/g), chloroethane (2.86×10^-4 g/g), and cis-1,2-dichloroethylene (0.0172 g/g).

3.2 EPICS procedure

The original EPICS procedure was based on addition of equal amounts of volatile solute to two closed systems with different solvent volumes (Gossett, 1987). The gaseous concentrations of the two systems at equilibrium were measured and used to compute the dimensionless Henry’s law constant using the combined mass balance equations. However, this procedure has a low level of precision due to the constraint of delivering equal masses of solute to the systems (Lincoff and Gossett, 1984). To improve on the precision, Gossett (1987) modified the EPICS procedure by using the mass ratio of added solute in the calculation of Henry’s law constant. This study follows the modified EPICS procedure. For each aqueous mixture at each temperature, six 160-mL serum bottles were used: three containing 100 mL distilled deionized (DDI) water and three containing 25 mL DDI water. Before the bottles were sealed with Teflon-lined red rubber septa and crimp caps, they were placed at the desired temperature for 5 minutes to equilibrate the pressure. Approximately 20 µL stock solution was
then added to each sealed bottle. The exact amount of stock solution added was determined gravimetrically. For measurements at temperatures from 38 °C to 93 °C, the six EPICS serum bottles were submerged in a water bath at the desired temperatures for 3 hours. They were taken out and shaken every 15 minutes. For measurements at 21 °C, the bottles were placed on a shaker table overnight. For measurements at 8 °C, the bottles were incubated for more than 24 hours in a water bath that was kept in a refrigerator.

3.3 Headspace analysis of volatile compounds

Headspace concentrations at equilibrium were measured with a gas chromatograph (Hewlett Packard, 5890 Series II) equipped with a flame ionization detector, using the same temperature program described by Gossett (1987). The retention times of the studied chemicals ranged from 1.6 (chloromethane) to 14.5 min (tetrachloroethylene). Dimensionless Henry’s law constants were calculated with the following the equation (2):

\[
H = \frac{V_{w2} - \left[\frac{(C_{g1}/M_1)/(C_{g2}/M_2)}{(C_{g1}/M_1)/(C_{g2}/M_2)}\right]V_{w1}}{\left[\frac{(C_{g1}/M_1)/(C_{g2}/M_2)}{(C_{g1}/M_1)/(C_{g2}/M_2)}\right]V_{g1} - V_{g2}}
\]

(4.8)

where \(V_w\) and \(V_g\) refer to the volumes of water and gas in serum bottles, \(M\) refers to the mass of solute added to the bottles, \(C_g\) is the mass concentration of volatile compound in the gas phase, and subscripts 1 and 2 denote the serum bottles with different volumes of water. The calculation was repeated for every possible pair of bottles with differing volumes of water. The average and standard deviation were calculated based on the 9 values of \(H\).

3.4 Measurement of aqueous solubility

Pure aqueous solubilities were measured for nine of the CVOCs using water-saturated solutions, as follows: For each chemical, a sufficient amount of neat liquid was added to a 160 mL serum bottle containing 150 mL of DDI water, such that a nonaqueous phase of the chemical was present. The serum bottles were sealed with Teflon-faced septa and incubated at the desired
temperature for one week. The concentration of the CVOC in the aqueous phase was determined by removing less than 1 mL of the aqueous phase from each bottle and injecting it into a sealed serum bottle containing DDI water; the amount of DDI water was adjusted so that the total liquid volume present after adding the CVOC samples was 100 mL. Triplicate samples were taken for each compound. For analytical convenience, aqueous samples of different chemicals were mixed in the same combination used to measure Henry’s law constants (i.e., mixtures A, B, and C). These mixtures were placed on a shaker table at room temperature overnight before measuring the headspace concentrations by GC. Using externally prepared standards for each compound, the total amount of each compound present in the bottles was determined. This amount was divided by the volume of saturated water added to provide the saturation concentration.

4 RESULTS AND DISCUSSION

4.1 Effect of temperature on Henry’s law constant

Measured values and standard deviations for Henry’s constants at different temperatures are presented in Table 4.1. As expected, the Henry’s law constant is strongly dependent on temperature. For example, the Henry’s constant for tetrachloroethylene increases by a factor of around 24 from 8 to 91°C. Henry’s constants for trichloroethylene, chloroform, and 1,2-dichloroethane increase by 24-, 17-, and 30-fold from 8 to 93°C, respectively. Smaller variations were observed for 1,1,1-trichloroethane (8-fold), 1,1-dichloroethane (11-fold), dichloromethane (7-fold), carbon tetrachloride (9-fold), cis-1,2-dichloroethylene (13-fold), chloromethane (3-fold), chloroethane (6-fold), and vinyl chloride (10-fold).
Table 4.1 Measured Henry’s law constants at various temperatures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>$H$ (dimensionless)</th>
<th>$H_c$ (m$^3$·atm·mol$^{-1}$)</th>
<th>% SD$^a$</th>
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$^a$ Percent standard deviation = 100(SD/mean).
The measured values of Henry’s law constants were compared with literature values. Generally, the measured values below 40 °C are close to the results reported by Gossett (1987) and the standard deviations of the data are of the same magnitude. The compound 1,2-dichloroethane was not included in the study by Gossett (1987). The $H$ measurement for 1,2-dichloroethane at 8°C has a high standard deviation. Values of Henry’s constant at other temperatures are close to the values reported by Ashworth et al. (1988). Görgényi et al. (2002) measured Henry’s law constants for chloroform, 1,1-dichloroethane, trichloroethylene, and several other chemicals using the EPICS-SPME technique (equilibrium partitioning in closed systems-solid phase microextraction) in the temperature range from 2 to 70°C. Our results for chloroform, 1,1-dichloroethane, and trichloroethylene in this temperature range are close to their reported values. Henry’s constants above 70°C are only available in the literature for trichloroethylene (Heron et al., 1998a). Heron et al. (1998a) reported dimensionless Henry’s constants for trichloroethylene of 0.2, 0.4, 1.0, 1.2, 2.5, 3.7, and 4.6 at 10, 21, 50, 58, 81, 90, and 95°C, respectively. Similar results were obtained below 80°C in the present study. For measurements higher than 80°C, the values from this study are about 30% lower than theirs. However, the standard deviations of measurements in this temperature range are larger than at ambient temperatures, with coefficients of variation (i.e., standard deviation/average) ranging from 7% to 36% in this study and about 30% or more in their study.
Figure 4.1 Temperature regression of Henry’s law constants
Figure 4.1 Temperature regression of Henry’s law constants (continued)
The modified EPICS method had good precision in the temperature range between 24 and 58°C. Except for a few compounds, coefficients of variation were within 10%. Increasing standard deviations were observed for measurements at temperatures higher than 78°C. Similar behavior was observed by Heron et al. (1998a). It appears that the EPICS method becomes less precise as the Henry’s law constant exceeds 3. Errors for measurements of chloroform (48%), dichloromethane (32%), and 1,2-dichloroethane (112%) were also relatively high at 8°C, perhaps due to the very low value of the Henry’s constants for these CVOCs at this temperature.

Table 4.2 Temperature regressions of Henry’s law constants

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<th>$H_c = \exp(A-B/T)$</th>
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<td>161.6</td>
<td>10,739</td>
</tr>
<tr>
<td>chloromethane</td>
<td>13.35</td>
<td>2,509</td>
</tr>
<tr>
<td>chloroethane</td>
<td>252.6</td>
<td>14,112</td>
</tr>
<tr>
<td>vinyl chloride</td>
<td>-132.4</td>
<td>-3775</td>
</tr>
</tbody>
</table>

The temperature dependency of Henry’s law constants has been widely modeled with the Van’t Hoff equation (Ashworth et al., 1988; Gossett, 1987; Heron et al., 1998a). Based on different assumptions used with respect to enthalpy of dissolution, equations 4.5 and 4.7 are used to empirically model Henry’s law constants (Ashworth et al., 1988; Gossett, 1987; Heron et al., 1998a). The difference between equations 4.5 and 4.7 is that equation 4.5 assumes a constant enthalpy of dissolution (Ashworth et al., 1988; Gossett, 1987), while equation 4.7 assumes that the enthalpy is a linear function of temperature (Heron et al., 1998a). Results from both linear
and nonlinear regression of lnHc versus 1/T are shown in Table 4.2 and Figure 4.1. From the r² values and the graphs, it is apparent that equation 4.7. fits the data better. The overall slopes obtained in this study were compared with previous findings based on measurements at low temperatures. The slopes obtained in this study using linear regression (equation 4.5.) are about one-third to two-thirds lower than those of Gossett (1987). This supports the conclusion from Heron et al. (1998a) that it may not be appropriate to extrapolate the data from measurements at low temperature by assuming that the enthalpy of dissolution is constant.

4.2 Effect of temperature on aqueous solubility

The aqueous solubilities of tetrachloroethylene, trichloroethylene, chloroform, 1,1,1-trichloroethane, 1,1-dichloroethane, dichloromethane, carbon tetrachloride, 1,2-dichloroethane, and cis-1,2-dichloroethylene were measured between 8 and 75°C. The measured values are presented in Table 4.3 and Figure 4.2. Except for tetrachloroethylene at 21°C, the standard deviations at temperatures above 20°C are within 4%. Standard deviations at 8°C range from 0.90% to 10.7%. Different chemicals showed different patterns of temperature dependency of solubility. For trichloroethylene, solubility increased from 1223 mg/L at 8 °C to 1503 mg/L at 75°C. Similar patterns were seen for tetrachloroethylene and 1,2-dichloroethane. The solubility of 1,1,1-trichloroethane fluctuated in the range of 1008-1354 mg/L at temperatures from 8 to 60°C and decreased to 719 mg/L at 75°C. The solubility of chloroform decreased from 8424 mg/L at 8°C to 7422 mg/L at 35°C, and increased to 7902 at 75°C. The solubility of cis-1,2-dichloroethylene and 1,1-dichloroethane changed little with temperature.
Table 4.3 Aqueous solubilities of chlorinated volatile compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Temperature (°C)</th>
<th>Solubility (mg/L)</th>
<th>% SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrachloroethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>209</td>
<td>6.51</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>197</td>
<td>8.64</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>236</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>256</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>320</td>
<td>2.37</td>
<td></td>
</tr>
<tr>
<td>trichloroethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1,223</td>
<td>5.201</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1,338</td>
<td>2.68</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1,310</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1,384</td>
<td>1.88</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>1,503</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1,354</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>1,059</td>
<td>2.74</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>1,313</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1,008</td>
<td>2.82</td>
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</tr>
<tr>
<td>75</td>
<td>719</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>chloroform</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8,424</td>
<td>3.24</td>
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</tr>
<tr>
<td>21</td>
<td>8,416</td>
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<td></td>
</tr>
<tr>
<td>35</td>
<td>7,422</td>
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</tr>
<tr>
<td>60</td>
<td>7,454</td>
<td>2.78</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>7,902</td>
<td>2.41</td>
<td></td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5,403</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>5,490</td>
<td>2.65</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>5,265</td>
<td>2.92</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>5,434</td>
<td>3.47</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>5,471</td>
<td>3.85</td>
<td></td>
</tr>
<tr>
<td>dichloromethane</td>
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<td></td>
</tr>
<tr>
<td>8</td>
<td>9,760</td>
<td>8.14</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>18,842</td>
<td>3.44</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>19,391</td>
<td>2.84</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>871</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>559</td>
<td>7.08</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>765</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>839</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>849</td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8,073</td>
<td>5.14</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>8,912</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>8,975</td>
<td>0.12</td>
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<td>60</td>
<td>9,679</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>10,305</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>cis-1,2-dichloroethylene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>6,954</td>
<td>3.71</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>7,026</td>
<td>1.99</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>7,044</td>
<td>3.36</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>6,937</td>
<td>2.19</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>7,178</td>
<td>0.82</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.2 Temperature regression of solubility data using equation 4.12
Heron et al. (1998a) measured the solubility of trichloroethylene between 9 and 71°C using a column generator technique. Their measured values range between 1300 mg/L and 1500 mg/L, with a minimum value around 30°C (Heron et al., 1998a). This is close to what we measured. Knauss et al. (2000) reported solubilities for trichloroethylene in the range of 1417 mg/L (21°C) to 1878 mg/L (75°C) and for tetrachloroethylene in the range of 200 mg/L at 21°C to around 300 mg/L at 75°C (Knauss et al., 2000). The solubilities of trichloroethylene measured in this study are lower than their results, but the results for tetrachloroethylene are similar.

4.3 Vapor pressure-solubility model

One predictive method for estimating Henry’s constants at high temperature is to divide the vapor pressure by the aqueous solubility (Brennan et al., 1998; Mackay and Shiu, 1981).

\[ H_c = \frac{P_{vp}}{S} \]  \hspace{1cm} (4.9)

where \( P_{vp} \) is pure vapor pressure, and \( S \) is aqueous solubility.

The values of pure vapor pressure were calculated with the Frost-Kalkwarf-Thodos equation (Reid et al., 1987) for 1,1-dichloroethane

\[ \ln P_{vp} = VPA - \frac{VPB}{T} + (VPC)\ln T + \frac{(VPD)(P_{vp})}{T^2} \]  \hspace{1cm} (4.10)

and the Wagner equation (Reid et al., 1987) for the rest of compounds

\[ \ln \left( \frac{P_{vp}}{P_c} \right) = (1 - x)^{-1}[(VPA)x + (VPB)x^{1.5} + (VPC)x^3 + (VPD)x^6] \]  \hspace{1cm} (4.11)

where \( x = 1 - T/T_c \), \( T \) is absolute temperature (K), \( T_c \) is critical temperature (K), \( P_{vp} \) is vapor pressure (bar), \( P_c \) is critical pressure (bar), \( VPA, VPB, VPC, \) and \( VPD \) are constants specific for each pure compound. These values were obtained from Reid et al. (1987).
Figure 4.3 Prediction of Henry’s law constant with the ratio of vapor pressure to solubility, using equation 4.9
Regression of the aqueous solubility data as a function of temperature was conducted with the following equation (Knauss et al., 2000):

\[ R\ln K = D + \frac{E}{T} + F\ln T \]  

(4.12)

where \( K \) is the solubility in mole fraction, \( T \) is the absolute temperature in Kelvin, \( R \) is the universal gas constant, and \( D, E \) and \( F \) are curve fitting parameters. The values of these parameters as well as the \( r^2 \) values are shown in Table 4.4; the model fit to the data are shown in Figure 4.2 (except for dichloromethane). The calculated value of solubility using this equation as a function of temperature is further used for the calculation of Henry’s law constant, as shown in Figure 4.3. Overall, there is good agreement between the estimated and measured Henry’s law constants. For temperatures higher than 75°C, the predicted values are sometimes higher than the measured values. A possible reason for this is the underestimation of the aqueous solubility of the compounds at these higher temperatures. Knauss et al. (2000) measured the aqueous solubilities of TCE and PCE over a wider range of temperature (21-161°C). They found that the solubility of TCE and PCE increases at a higher rate at higher temperatures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethane</td>
<td>-6.76571</td>
<td>-4,417</td>
<td>-5.60996</td>
<td>0.952</td>
</tr>
<tr>
<td>tetrachloroethylene</td>
<td>-1313.04</td>
<td>52,334</td>
<td>184.0563</td>
<td>0.932</td>
</tr>
<tr>
<td>trichloroethylene</td>
<td>-220.293</td>
<td>5,136</td>
<td>23.03885</td>
<td>0.862</td>
</tr>
<tr>
<td>chloroform</td>
<td>-835.754</td>
<td>37,099</td>
<td>115.0121</td>
<td>0.717</td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>1863.286</td>
<td>-84,438</td>
<td>-289.987</td>
<td>0.790</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>-2039.44</td>
<td>89,308</td>
<td>291.6319</td>
<td>0.344</td>
</tr>
<tr>
<td>cis-1,2-dichloroethylene</td>
<td>-125.696</td>
<td>3,082</td>
<td>10.54612</td>
<td>0.339</td>
</tr>
<tr>
<td>1,1-dichloroethane</td>
<td>-241.997</td>
<td>8,465</td>
<td>27.37585</td>
<td>0.283</td>
</tr>
</tbody>
</table>
The results of this study indicate a strong effect of temperature on Henry’s law constants, with increases between 3-fold (chloroethane) and 30-fold (1,2-dichloroethane) as temperature increased from 8 to 93°C. Because the enthalpy of dissolution is a function of temperature, it may not be appropriate to extrapolate the Henry’s law constant from measurements at low temperature using a linear function. The nonlinear function proposed by Heron et al. (1998a) that incorporates a temperature dependent enthalpy provides a better fit to the experimental data. Using measured data for solubility, the vapor pressure-solubility model gives a reasonable prediction of the Henry’s law constants. With improved data on Henry’s law constants at high temperatures for the 12 common CVOCs measured in this study, it will be possible to more accurately model subsurface remediation processes that operate near the boiling point of water.
References


CHAPTER FIVE
NUMERICAL ANALYSIS OF CONTAMINANT REMOVAL FROM FRACTURED ROCK BY BOILING

Presented in this chapter are simulations of the experimental results described in chapter 3. By comparing the simulated and experimentally determined results, confidence was established for the TMVOC code in predicting contaminant mass transfer in boiling fractured porous media. The numerical analysis helps to understand the coupled multiphase mass and heat transfer process when boiling occurs in fractured geologic media.

Abstract

A multiphase heat transfer numerical model is used to simulate a laboratory experiment of contaminant removal from fractured rock by boiling. The simulated results such as temperature, condensate production, contaminant and NaBr concentrations are in reasonable agreement with the experimental data. Further simulation is conducted using a 1-D geometry to illustrate the contaminant mass and heat transfer from fractured rock without experimental end effects. Without considering the heat loss from the ends, higher temperature gradients and steam flow rate are observed. However, the pattern of contaminant removal is similar with and without heat loss. After boiling out 50 mL of pore water (1/2 pore volume), approximately 100% 1,2-DCA is removed. Finally, a field-scale simulation is conducted to illustrate the possible field application of thermal remediation of fractured geologic media using the Multiple Interacting Continua numerical method (MINC). The simulation results demonstrate that thermal remediation
could be effective in treating fractured porous media at the field scale. After about 35
days of treatment, 27.8% of the pore water (including both steam vapor and liquid water)
was extracted, and essentially all the 1,2-DCA mass (more than 99%) was removed from
the fractured site.

1 INTRODUCTION

Remediation of fractured low-permeability geologic media is of environmental
concern. As chlorinated volatile organic compounds are released at a fractured site, they
flow preferentially through the fracture network, and a significant amount of
contaminants diffuse into the matrix due to the contrast of concentration (Parker et al.,
1994; Parker et al., 1997; Reynolds and Kueper, 2001; Reynolds and Kueper, 2002; Ross
and Lu, 1999). When the fractures are cleaned by natural or engineered processes, the
contaminants in the matrix slowly diffuse back into the fractures, serving as a long-term
groundwater contamination source (Parker et al., 1994; Parker et al., 1997; Reynolds and
Kueper, 2001; Reynolds and Kueper, 2002; Ross and Lu, 1999).

Thermal methods have promise for remediating fractured geologic media (Chen et
al., 2010; Heron et al., 1998b; Udell and Itamura, 1998). Thermal methods such as
electrical resistance heating (Gauglitz et al., 1994), thermal conductive heating (Heron et
al., 2009), and radio-frequency heating (Roland et al., 2008; Roland et al., 2010) can heat
the fractured media to the water boiling temperature. As the temperature approaches the
water boiling temperature, depressurization of the fractures may trigger water boiling in
the matrix (Pruess, 2002; Udell and Itamura, 1998). The phase transition and the
associated volume change produce a steam vapor flow, stripping the volatile
contaminants out of the matrix (Chen et al., 2010; Heron et al., 1998b; Udell and Itamura, 1998). The effectiveness of the stripping effect is enhanced at high temperature due to the increased Henry’s law constant of contaminants (Heron et al., 1998a). At steam temperatures, the Henry’s law constants of chlorinated volatile organic compounds (CVOCs) increase by 3- to 30-fold (Heron et al., 1998a).

Contaminant removal from fractured rock by boiling has recently been demonstrated in a laboratory experiment (Chen et al., 2010). After boiling away about 1/3 of the pore volume of water from a contaminated sandstone core, approximately 100% recovery of 1,2-dichloroethane (1,2-DCA) was achieved (Chen et al., 2010). However, the phenomenon of contaminant mass transfer from fractured geologic media during boiling is complex due to the strong coupling among heat transfer, multiphase flow, and thermodynamics. To investigate such a phenomenon, numerical simulation is helpful to better understand the coupled mass and heat transfer during the boiling process.

The T2VOC and TMVOC codes have been widely used for simulation of multiphase flow with single and multiple volatile organic chemical(s) (Falta et al., 1995; Pruess and Battistelli, 2003; Tse et al., 2006). They were validated with experimental results for a variety of isothermal and non-isothermal problems (Adenekan, 1992; Adenekan et al., 1993; Falta et al., 1992b; Gudbjerg et al., 2004; Ochs et al., 2003). However, contaminant mass transfer between matrix blocks and fractures due to boiling has received limited attention, and it is helpful to establish the reliability of the codes in predicting such experimental results.
In this chapter, the TMVOC code is used to simulate a laboratory experiment for contaminant removal from fractured rock by boiling. Next, the 1-D contaminant mass removal from the fractured rock by boiling is numerically analyzed without experimental end effects. Finally, simulation of field-scale application of thermal remediation is conducted, using a special discretization that can resolve local fracture-matrix interactions.

2 TMVOC SIMULATOR

For a multiphase system the governing equations consist of several mass balance equations and an energy balance equation that sum over the fluid and rock phases. The mass components can be H$_2$O, multiple volatile organic compounds (VOCs), and a noncondensible gas. In this study, the components are H$_2$O, 1,2-DCA, NaBr, and air. The TMVOC code is capable of modeling 3-phase flow of NAPL, liquid water, and gas using multiphase extension of Darcy’s law. Since dissolved 1,2-DCA was used in the experiment and no NAPL phase was involved, two-phase flow (gas and liquid water) is considered here. The multiphase Darcy’s law includes relative permeability effects, which are calculated using standard 2-phase functions of the phase saturations (van Genuchten, 1980; Verma, 1986). The fluid flow is driven by the phase pressure gradient with capillary pressure, and a gravity term depending on the phase density. Capillary pressure is computed as a function of phase saturation using various functions (van Genuchten, 1980). The transport of mass components in each fluid phase considers advection, and diffusion including temperature and pressure dependent diffusion coefficients, and phase saturation dependent tortuosities. Linear equilibrium adsorption to
the rock or soil is taken into account for the contaminant component. Heat transfer considers multiphase convection including both latent and sensible heat, and thermal conduction. The thermal conductivity is treated as a nonlinear function of liquid saturation. Both thermal and flow properties of the rock or soil can be heterogeneous.

The thermodynamic properties of water are built into the code, and the thermodynamic properties of CVOCs are calculated using the corresponding states method (Falta et al., 1995; Falta et al., 1992a; Pruess and Battistelli, 2002). The treatment of the heat transfer and thermodynamics allows for rigorous consideration of boiling and condensation of multicomponent mixtures, including noncondensible gas effects. The nonlinear coupled mass and energy balance equations are linearized using an implicit residual-based Newton-Raphson iterative technique, and solved using a selection of direct and iterative matrix solvers (Pruess and Battistelli, 2002).

3 SIMULATION OF THE EXPERIMENT

3.1 Heating Experiment

As described in the chapter 3, a laboratory study has been conducted on the demonstration of CVOC removal from fractured rock by boiling (Chen et al., 2010). The experimental system used in the study is as shown in Figure 3.2. An unfractured Berea sandstone core was used to represent the material while the end to represent the fracture. The core has an intrinsic permeability of $1.5 \times 10^{-13} \text{ m}^2$ and a porosity of 0.174. It was sealed with Teflon shrink tube and aluminum end-caps, and wrapped with a strip heater and an insulation layer. A set of cartridge heaters was placed in each Teflon plate to heat the ends of the core. The core assembly was placed in a pressurized vessel to keep the
Teflon tube in contact with the core. The effluent from the core was routed to a condenser, and the generated steam was condensed before it was collected in partially vacuumed sealed vials. Headspace samples were analyzed with gas chromatography and liquid samples were analyzed with ion chromatography (Chen et al., 2010).

Temperature was measured with the micro-thermistors embedded at 0, 2.54, 5.08, 10.16, 15.24, 20.32, 25.40 cm from the top of the core. Additional details are given by Chen et al. (2010).

![Diagram of experimental setup](image)

Figure 5.1 Model geometry to simulate the experimental setup

The experiment was conducted as follows. The core was first contaminated with 1,2-DCA and NaBr. Water containing 1,2-DCA (253 mg/L) and NaBr (144 mg/L) was injected under a gauge pressure of 6.89×10⁴ Pa. Both the inlet and outlet concentrations were monitored. After injecting 350 mL solution, the effluent concentrations stabilized at
a value equal to inlet concentrations. Then the core was heated with both the inlet and outlet valves closed. A constant power of 31.3 W was delivered by the strip heater. The power inputs by the cartridge heaters at the ends of the core were adjusted from 1.2 to 15 W, depending on the heat loss at ends. During the heating process prior to boiling, the core pressure built up due to thermal expansion of fluid and possible noncondensable gases dissolved in the pores. As the gauge pressure exceeded about 1 bar, the outlet valve was quickly opened and shut off to release the pressure build-up. When the temperature exceeded 100 °C, the outlet valve was opened to the atmosphere. The power inputs from the cartridge heaters remained constant during this time. The volume of condensate produced, concentrations of 1,2-DCA, and bromide in the condensate were measured. (Chen et al., 2010)

3.2 Model Development

Table 5.1 Values of material properties used in the simulation

<table>
<thead>
<tr>
<th>Subdomain</th>
<th>Porosity</th>
<th>Permeability (m²)</th>
<th>Density (kg/m³)</th>
<th>Thermal conductivity (W/m°C)</th>
<th>Specific heat (J/kg°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berea sandstone</td>
<td>0.167</td>
<td>1.5×10⁻¹³</td>
<td>2491</td>
<td>3.57 (wet)</td>
<td>1680</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.75 (dry)</td>
<td></td>
</tr>
<tr>
<td>Heater</td>
<td>0.001</td>
<td>1.0×10⁻¹⁸</td>
<td>501.2</td>
<td>1.07</td>
<td>1029</td>
</tr>
<tr>
<td>Porous disk</td>
<td>0.16</td>
<td>1.0×10⁻¹⁰</td>
<td>3950.0</td>
<td>41.22</td>
<td>1356.5</td>
</tr>
<tr>
<td>Aluminum end-cap</td>
<td>0.001</td>
<td>1.0×10⁻¹⁸</td>
<td>2702</td>
<td>237</td>
<td>903</td>
</tr>
<tr>
<td>Outlet tube</td>
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<td>1.46×10⁻¹⁰</td>
<td>8730</td>
<td>60</td>
<td>427</td>
</tr>
<tr>
<td>Condenser</td>
<td>0.0559</td>
<td>1.46×10⁻¹⁰</td>
<td>1.0×10¹⁰</td>
<td>60</td>
<td>10001.0</td>
</tr>
<tr>
<td>Inlet Tube</td>
<td>0.14</td>
<td>3.15×10⁻¹⁰</td>
<td>8940</td>
<td>400</td>
<td>427.8</td>
</tr>
<tr>
<td>Teflon Plate</td>
<td>0.001</td>
<td>1.0×10⁻¹⁸</td>
<td>2200</td>
<td>0.5</td>
<td>1001.0</td>
</tr>
<tr>
<td>Insulation Layer</td>
<td>0.01</td>
<td>1.0×10⁻¹⁸</td>
<td>100</td>
<td>0.28</td>
<td>844.0</td>
</tr>
<tr>
<td>Air in the vessel</td>
<td>0.99</td>
<td>1.0×10⁻¹⁸</td>
<td>1.09×10⁵</td>
<td>0.2</td>
<td>1009.0</td>
</tr>
<tr>
<td>Air out of the vessel</td>
<td>0.99</td>
<td>1.0×10⁻¹⁸</td>
<td>1.2×10¹⁰</td>
<td>0.2</td>
<td>10001.0</td>
</tr>
</tbody>
</table>
The experiment was simulated using a two-dimensional radially symmetric mesh consisting of 78×13 elements (Figure 5.1). The subdomain used to simulate Berea sandstone core is composed of 48×6 elements, while the remaining elements represent various parts of the experimental apparatus.

Properties for the core are assigned with the experimentally determined values (Table 5.1). A small porosity (0.001) and an extremely low permeability (1.0×10^{-18} m²) are used for the heater and aluminum caps in the model to simulate the sealed condition of the core (no fluid flow from the core through heater or aluminum cap). Typical values of the materials are used for the density, thermal conductivity, and specific heat. During the heating experiment, the air temperature increased to 36°C in the vessel. Thus, a high value (1.09×10^5 kg/m³) is given to the air density of the air in the vessel to simulate the temperature increase during the heating experiment. A constant temperature boundary is applied to the air outside of the vessel and condenser subdomains by assigning extremely high values of density and specific heat (Table 5.1). The density and specific heat for the air out of the vessel are assigned with 10001.0 J/kg°C and 1.2×10^{10} kg/m³, respectively. The condenser represented by 2 cells with a density of 1×10^{10} kg/m³ and a specific heat of 10001.0 J/kg°C to maintain the temperature at constant 5 °C.

3.3 Thermal Conductivity and Specific Heat

The thermal conductivity and specific heat of the saturated core were measured using the dual-probe heat-pulse method. This in-situ transient method has been used in the determination of thermal properties of soil and rock samples in many previous studies (Bachmann et al., 2001; Bristow et al., 1994; Carslaw and Jaeger, 1959; de Vries, 1952;
Kluitenbergen, 1993; Knight et al., 2007; Kubičár et al., 2006; Lewis et al., 1993; Lu et al., 2007; Muñoz et al., 2009; Tarara and Ham, 1997; Welch et al., 1996). This in situ transient method was developed based on the analytical solution for temperature distribution around an instantaneously heated infinite line source (Carslaw and Jaeger, 1959):

\[ T(r, t) = \left( \frac{Q}{4\pi \alpha t} \right) e^{-\frac{r^2}{4\alpha t}} \]  \hspace{1cm} (5.1)

where \( T \) is temperature (°C), \( r \) is radial distance from the line source (m), \( t \) is time (s), \( \alpha \) is the thermal diffusivity (m\(^2\)/s) of the medium surrounding the heater, \( Q \) is the finite quantity of heat liberated by the line source, which is calculated with:

\[ Q = \frac{q}{\rho c} \]  \hspace{1cm} (5.2)

Here, \( q \) is the quantity of the heat liberated per unit length of heater, \( \rho c \) is the volumetric heat capacity of the medium.

The thermal diffusivity and volumetric capacity are obtained by taking the derivative of the equation 5.1 in terms of time. At the peak of the temperature profile \((t = t_m)\), the first derivative of equation 5.1 is equal to zero. The thermal diffusivity and volumetric capacity are expressed as (Bristow et al., 1994; Campbell et al., 1991; Jaeger, 1965; Lubimova et al., 1961):

\[ \alpha = \frac{r^2}{4t_m} \]  \hspace{1cm} (5.3)

and

\[ \rho c = \frac{q}{e^{\pi r^2} \Delta T_m} \]  \hspace{1cm} (5.4)
where $e$ is the natural exponent, and $\Delta T_m$ is maximum temperature change.

Considering the duration of the heat pulse ($t_0$), thermal diffusivity can be calculated with the following modified equation (Bristow et al., 1994; Lubimova et al., 1961):

$$\alpha = \left( \frac{r^2}{4} \right) \left\{ \frac{1}{(t_m - t_0)} - \frac{1}{t_m} \right\} \ln \left[ \frac{t_m}{t_m - t_0} \right] \quad (5.5)$$

Knowing the thermal diffusivity and volumetric capacity, one can calculate the thermal conductivity as:

$$\lambda = \alpha \rho c \quad (5.6)$$

The measurement was conducted as follows: a rock sample (7.62 cm long, 5.08 cm in diameter) was cut from the sandstone core used in the experiment. Two parallel holes (6mm apart, 2.54 cm deep) were drilled in the core, embedded with a microheater and a thermistor. The microheater consists of a stainless steel tube (3.575 cm, O.D.) and a 10-cm-long enamed Evanohm wire (Pelican Wire Co., Naples, FL), twice doubly folded in the tube. The thermistor was connected to a data acquisition system for temperature measurement.

The microheater was connected to a 9V power supply (HQ Power, Fort Worth, TX) through a transistor board and a 10 $\Omega$ resistor (Figure 5.2). The transistor board functions as a switch, turning on and off the microheater, according to the digital signals from an I/O unit (NI-6008) that is controlled by a Labview program. A heat pulse was generated by turning on the microheater for 10 seconds, while the temperature was monitored every second.
Figure 5.2 Experimental setup for thermal property measurement

This dual-probe heat-pulse method was calibrated with gelled water. It was prepared by mixing 1% (w/w) agar powder (Becton, Dickinson, MD) in boiling water. Cooling down to about 70 °C, the mixture was poured to a cylindrical container that has inner diameter of 5.08 cm. After aging for 8 hours, the cylindrical gel was ready for thermal property measurement (Zhu et al., 2007). Due to the high percentage of liquid water, this immobile water has almost the same thermal conductivity of liquid water. Moreover, it eliminates the possible measurement error caused by heat transfer by convection. The thermal conductivity and specific heat of water are well known. Thus the measured values of gelled water can be used for calibration of the dual-probe method.

The measured thermal conductivities of the Berea sandstone core at both wet and dry conditions are 3.57 W/m K and 1.75 W/m K, respectively. The partially saturated porous media thermal conductivity λ is computed in the model using (Pruess and Battistelli, 2002)
\[ \lambda = \lambda_D + \sqrt{S_w \left( \lambda_w - \lambda_D \right)}, \]  

where \( \lambda_D \) is the dry porous media thermal conductivity, \( \lambda_w \) is the water-saturated porous media thermal conductivity. The measured rock grain specific heat is 1680 J/kg°C.

### 3.4 Relative Permeability and Capillary Pressure

The data of air relative permeability and capillary pressure as functions of water saturation were collected from two pieces of 3-inch core cut from the core used in the experiment. Measurements were conducted by Daniel B. Stephens & Associates, Inc.

![Capillary pressure curve of the Berea sandstone core](image)

Figure 5.3 Capillary pressure curve of the Berea sandstone core

The gas-water capillary pressures at different water saturation were fit with the *van Genuchten* equation (Parker et al., 1987; van Genuchten, 1980).

\[
P_{c_{gw}} = -\rho_g g \left( \frac{1}{\alpha_{gn}} + \frac{1}{\alpha_{nw}} \right) \left[ \left( \frac{S_w - S_{wr}}{1 - S_{wr}} \right) \frac{1}{m} - 1 \right]^{\frac{1}{m}} 
\]

\[ (5.8) \]
where \( m = 1 - 1/n \), \( S_{wr} \) is the residual water saturation, \( \alpha_{gn} \), \( \alpha_{nw} \), and \( n \) are curve shape parameters. They are adjusted to fit the experimental data (Figure 5.3), yielding \( \alpha_{nw} = \alpha_{gn} = 2.22 \), \( n = 1.56 \), and \( S_{wr} = 0.051 \), respectively.

![Relative permeability curve](image)

Figure 5.4 Relative permeability curve

The function used to model the gas relative permeability at different saturation was modified from the one used by Verma (1986) for steam-liquid systems:

\[
k_{rg} = A + B S S^* + C (S S^*)^2 + D (S S^*)^4
\]  \hspace{1cm} (5.9)

with

\[
S S^* = \frac{S_w - S_{wr} - 0.22873}{S_{ws} - S_{wr} - 0.22873}
\]  \hspace{1cm} (5.10)

where \( S_w \) is water saturation, \( S_{wr} \) is residual water saturation, \( S_{ws} \) is the maximum water saturation. This equation was developed for the steam-water relative permeability and has a good fit with the experimental measurements (Verma and Pruess, 1986; Verma, 1986).
Parameters A, B, C and D are adjusted to fit the data from the experiment (A=0.931, B=-2.87, C=2.59, D=-0.651). The relative permeability curves are shown in Figure 5.4.

The function used to simulate the aqueous phase relative permeability curve is the van Genuchten formulation (van Genuchten 1980):

\[ k_{rw} = \sqrt{S^*} \left\{ 1 - \left[ 1 - (S^*)^{(1/m)} \right]^2 \right\} \]  

(5.11)

where

\[ S^* = \frac{S_w - S_{wr}}{1 - S_{wr}}. \]  

(5.12)

The values of \( S_{wr} \) and \( m \) are equal to those measured in the capillary pressure curve.

3.5 Initial and boundary conditions

The initial conditions for the simulation are as follows: the subdomains of Berea sandstone core, porous disks, outlet and inlet tubes and condenser are saturated with water, where the concentrations of 1,2-DCA and NaBr are 253 mg/L and 144 mg/L, respectively, others have water saturation of 0. In the experiment, bromide was used as a tracer to indicate the steam quality due to its non-volatility. The behavior of bromide is simulated in TMVOC by assigning high solubility (0.1 in mole fraction) to a compound with low vapor pressure. The initial temperature for all subdomains is 20 °C except for the condenser at outlet (5°C). At the outlet end of the tube, the boundary condition of constant pressure was applied using a deliverability model. The production rate of phase \( \beta \) is calculated as:

\[ q_\beta = \frac{k_{\gamma \beta}}{\mu_\beta} \rho_\beta PL(\rho_\beta - P_{wb}). \]  

(5.13)
where $P_\beta$ is the pressure of phase $\beta$ at the center of the producing element, $P_{wb}$ is the specified outlet pressure, $k_{r\beta}$ is the relative permeability of phase $\beta$, $\mu_\beta$ is the $\beta$ phase viscosity in the element, $PI$ is productivity index ($PI = 1 \times 10^{-10} m^3$). The $P_{wb}$ is assigned with a value of $2.04746 \times 10^5$ Pa for the scenario that the outlet valve is closed and $1.01325 \times 10^5$ Pa when the outlet valve is open to the atmosphere. When the pressure at the center of the producing element is higher than the specified outlet pressure, the production rate is calculated as Equation 5.13. When it is less than the specified outlet pressure, the production rate is zero. The condenser is simulated by assigning a high specific heat to maintain a constant temperature.

3.6 Henry’s law constant of 1,2-DCA

Henry’s law constant is important in determining the partitioning of a volatile organic compound from aqueous to gaseous phases. The values for chlorinated solvents are strongly dependent on temperature (Heron et al., 1998a). To better simulate the process of CVOC partitioning at elevated temperatures, it is necessary to include the temperature dependency of Henry’s law constant in the model.

As described in the chapter 4, the Henry’s law constant of 1,2-DCA at temperatures from 8 to 93°C (shown in Figure 5.5) were measured using modified equilibrium partitioning in closed systems (EPICS) procedure (Gossett, 1987; Heron et al., 1998a). In this method, six 160-mL serum bottles were used at each temperature: three containing 100 mL distilled deionized (DDI) water and three containing 25 mL DDI water. These bottles were placed at the desired temperature for 5 minutes to equilibrate the pressure before they were sealed with Teflon-lined rubber septa and crimp caps. A
mixture that contained methanol (0.963 g/g), carbon tetrachloride (0.0212 g/g) and 1,2-dichloroethane (0.0158 g/g) was prepared as a stock solution. Approximately 20 µL stock solution was then added to each sealed bottle and the exact amount added was determined gravimetrically. The equilibration at different temperatures was conducted as follows: for measurements at temperatures from 38°C to 93°C, the bottles were submerged in a water bath at the desired temperatures for 3 hours. They were taken out and shaken every 15 minutes. For the measurements at 21°C, the bottles were placed on a shaker table overnight. For the measurements at 8°C, the bottles were incubated for more than 24 hours in a water bath that was kept in a refrigerator.

Figure 5.5 Henry’s law constants of 1,2-DCA

Headspace concentration of 1,2-DCA at equilibrium was measured with a gas chromatograph (Hewlett Packard, 5890 Series II) equipped with a flame ionization detector. The temperature program used in this measurement was the same as described
by Gossett (1987). The dimensionless Henry’s law constant of 1,2-DCA was calculated with (Gossett, 1987):

\[
H = \frac{V_{w2} - \left[\left(\frac{C_{g1}/M_1}{C_{g2}/M_2}\right)V_{w1}\right]}{\left[\left(\frac{C_{g1}/M_1}{C_{g2}/M_2}\right)\right]V_{g1} - V_{g2}}
\]

(5.14)

where \(V_w\) and \(V_g\) denote the volumes of water and gas in serum bottles, \(M\) represent the mass of 1,2-DCA added to the bottles, \(C_g\) is the mass concentration of 1,2-DCA in the gas phase, and subscripts 1 and 2 stand for the serum bottles with different volumes of water. The \(H\) was calculated for every possible pair (9 pairs) of bottles with differing volumes of water, based on which the average and standard deviation were obtained. The results are shown in Figure 5.5.

![Figure 5.6 Solubility of 1,2-DCA](image)

The temperature dependence of Henry’s law constant of 1,2-DCA is simulated using

\[
H = \frac{P_v}{S}
\]

(5.15)
Figure 5.7 Simulated and experiment determined temperature profile where $P_v$ and $S$ denote vapor pressure and solubility, both of which are functions of temperature. The vapor pressures of 1,2-DCA at different temperatures are calculated from data fits given by Reid et al. (1987). The solubility of 1,2-DCA was measured from...
8 to 75°C. As shown in Figure 5.6, the temperature dependence of solubility is fit with a polynomial function:

\[ S = a + bT + cT^2 + dT^3 \]  \hspace{1cm} (5.16)

where parameters \( a, b, c, \) and \( d \) are curve fitting parameters, \( T \) is absolute temperature (K). The values of \( a, b, c, \) and \( d \) are \(-6.999 \times 10^{-4}\), \(9.711 \times 10^{-6}\) K\(^{-1}\), \(-6.769 \times 10^{-9}\) K\(^{-2}\), and 0, respectively.

3.7 Simulation Results

The simulated temperature profile is compared with the experimentally determined profile (Figure 5.7). Before boiling occurs, the simulated temperatures at all locations were in a good agreement with the experimentally determined temperatures. After the outlet valve was open to the atmosphere (2.73 h), the simulated core temperature at the outlet (\( T_{1\_Sim} \)) was similar to the experimentally determined one (\( T_{1\_Exp} \)), dropping the temperature to close to 100°C immediately. However, the simulated temperatures (\( T_{2\_Sim}-T_{7\_Sim} \)) at deeper locations were somewhat higher than the temperatures measured in the experiment (\( T_{2\_Exp}-T_{7\_Sim} \)). Therefore, compared to the experiment, a higher temperature gradient was observed in the simulated results.

Similar to the experiment, the simulated temperature gradient decreased as more pore water was boiled out due to the higher relative permeability. Further heating the core caused it to dry, resulting in a temperature increase. Due to the lack of phase change, the temperature increases with more heat is delivered under superheated vapor condition. The simulated temperature at the top (\( T_{1} \)) started to increase after heating for 4 hours,
followed by T2 (4.5 hours), T3 (5.2 hours), T4 (5.5 hours), T5 (5.8 hours), T6 (5.8 hours), and T7 (6.2 hours), respectively. This agrees with the experimental result quite well (Figure 5.7).

![Cumulative Condensate Produced](image)

Figure 5.8 Simulated and experimentally determined cumulative condensate produced

The simulated cumulative volume of condensate produced is in a good agreement with the experimental result (Figure 5.8). The only discrepancy occurred after 4 hours when the core started to dry. The simulated condensate production rate was a little higher than the experimental determined value. This might be because of the end effects in the experiment that has not been completely captured in the model.

Figure 5.9 shows the effluent concentrations of 1,2-DCA and NaBr from both the simulation and the experiment. The 1,2-DCA concentration removed from the core increased after the core was heated (Figure 5.9a). In the simulation, the effluent 1,2-DCA concentration reached around 1000 mg/L after 10 mL of condensate was produced. It decreased to 600 mg/L and reached another peak concentration of 1200 mg/L after 35 mL
of condensate was produced. However, a somewhat sharper effluent concentration of 1,2-DCA was observed in the experiment. A possible explanation for this discrepancy is that the steam relative permeability function used in the model is fit to the measurement data with air, which might cause an underestimation of the steam relative permeability.

The underestimation of the steam relative permeability is supported by the results of effluent tracer concentration (Figure 5.9b). In the experiment, bromide was used as a tracer to indicate the effluent steam quality, which is defined as the proportion of steam

![Graph](image)

Figure 5.9 Simulated and experimental effluent concentration of 1,2-DCA (a) and NaBr (b)
vapor in a saturated water/steam mixture. Since the bromide is nonvolatile, it can only be removed by dissolving in the liquid water, not by partitioning to the vapor phase (Chen et al., 2010). Therefore, the higher the bromide concentration in the effluent, the lower the percentage of water removed as water vapor. As shown in the Figure 5.9b, the simulated effluent bromide concentration remained at a high level until 30 mL pore water was boiled from the core. The effluent bromide concentration in the model was higher than in the experiment, suggesting a lower percentage of water removed from the core as vapor. Overall, the model and the experiment both show complete removal of the 1,2-DCA after about 45 mL of condensate has been produced from the core.

4 1-D SIMULATION WITHOUT END EFFECTS

The coupled contaminant mass and heat transfer during boiling is a very dynamic process. Small changes in boundary conditions such as heat loss at ends cause differences in temperature profile, thermodynamics, and contaminant removal. It is unavoidable to have some end effects in the experiment. To better understand the contaminant mass and heat transfer during boiling, it is helpful to conduct a simulation without experimental end effects.

The simulation without experimental end effects was conducted with a 1-D model. The Berea sandstone core was simulated with a mesh containing 48 elements and a fracture was simulated with a grid block above the subdomain of Berea sandstone. Properties such as porosity, intrinsic permeability, thermal conductivity, capillary pressure and relative permeability were identical to those used in the 2-D model as described before. Heat was generated in each grid block of Berea sandstone core at a
uniform rate. No flow boundary condition was applied to Berea sandstone subdomain. Deliverability model was applied to the fracture element (Equation 5.13). In the first 2.69 hours, the outlet pressure \( P_{wb} \) was specified as \( 2.047 \times 10^5 \) Pa to simulate the state of closing the outlet valve. No fluid extraction occurs until the pressure exceeds \( 2.04746 \times 10^5 \) Pa. After 2.69 hours, the outlet pressure was assigned with \( 1.103 \times 10^5 \) Pa in the fracture element to simulate the state of opening the outlet valve. Both subdomains have initial water saturation of 1.0, the concentrations of 1,2-DCA and tracer were 253 mg/L and 144 mg/L (as NaBr).

![Figure 5.10 Temperature in the 1-D model](image)

Similar to the simulation before, the core was heated for 2.69 hours with both inlet and outlet valves closed. When the outlet valve was open to the atmosphere, temperature at the top of the core dropped immediately, suggesting the boiling was initiated at the top (Figure 5.10). A temperature gradient was observed while pore water in the matrix was boiled. These are larger than what we observed in the experiment.
Since no heat loss was considered in this model, the duration of boiling is less than that in the experiment, and the rate of steam flow is higher. The temperature at different depths starts to increase gradually due to the drying-out of the core after heating for about 3.8 hours.

Before the valve was opened, contaminant was removed from the core by dissolving in the liquid water being pushed out due to the thermal expansion of fluid (Figure 5.11). After opening to the atmosphere, a high concentration of 1,2-DCA (up to 2250 mg/L) was removed, then maintained at about 700 mg/L (the concentration was 253 mg/L before heating). After boiling away approximately 50 mL condensate, the concentration of 1,2-DCA decreases to essentially 0.

![Figure 5.11 Simulated effluent 1,2-DCA concentration in the 1-D model](image)

The condensate produced increased at a higher rate after the core was boiled (Figure 5.12). After heating for 4 hours, all the pore water is boiled away.
Initially, 100% water was produced as liquid water before the temperature rise up to the water boiling temperature (Figure 5.13). This part of water was produced due to the thermal expansion as the temperature increases. As the outlet valve opened to the atmosphere, a large proportion of water was produced as steam vapor, corresponding to an immediate decrease of liquid water fraction to 20%. The percentage of liquid water produced then increased to 80% and decreased gradually as more and more water was boiled out. After approximately 50 mL water was removed, all the water was produced as steam vapor.

![Cumulative condensate produced](image)

**Figure 5.12 Simulated cumulative volume of condensate**

As a summary, a 1-D numerical model was used to simulate the removal of 1,2-DCA from the core without end effect. Similar to the experiment results, a temperature gradient was observed while pore water in the matrix was boiled. After opening to the atmosphere, a high proportion of steam vapor was produced, corresponding to high removal rate of 1,2-DCA. All of the 1,2-DCA mass was removed after boiling out around
50 mL pore water. Since no heat loss was considered in this model, the temperature gradients in this model are larger than what we observed in the experiment. The duration of boiling is less than that in the experiment, and the rate of steam flow is higher.

![Graph showing fraction of liquid water produced vs. volume of condensate produced](image)

**Figure 5.13** Fraction of water produced as liquid water

## 5 FIELD-SCALE SIMULATION

Flows and heat, water, and contaminants in fractured rock masses are simulated using four approaches. One approach is to use a uniform model with the equivalent permeability and average thermal properties. This approximation is capable of solving for total flux in a highly fractured system, but it cannot account for any fracture-matrix interactions. Another approach is the dual porosity/permeability method (Pruess and Battistelli, 2002; Warren and Root, 1963). This method involves a special discretization that subdivides each normal gridblock into two volume fractions, representing the fracture and matrix, respectively. Volume fractions, permeability, capillary and relative permeability functions, porosity, and thermal properties are assigned to their domains. In
the dual porosity method, the fracture volumes are globally connected in 3-D, and the matrix material is locally connected to the fracture elements. In the dual permeability method, both the fracture and matrix blocks are globally connected. The dual porosity/dual permeability methods can simulate transient multiphase fluid, heat and mass flows between the fractures and the matrix (Pruess et al., 1999), but they may poorly resolve heat and mass fluxes between the fracture and matrix in situations where temperature, saturation, pressure and concentration gradients in the matrix are variable with time and distance into the matrix. This occurs because the state variables in the matrix block (temperature, pressure, phase saturations, concentrations) are represented by single average values over the entire matrix, and the gradients are calculated using the single average nodal distance from the matrix centroid to the fracture.

Figure 5.14 Subgridding of the method of MINC (Pruess and Battistelli, 2002)

Another approach is the multiple interacting continua (MINC) method. This method can resolve local transient gradients of temperature, pressure, saturation, and
concentration in the matrix by extending the dual porosity method to include multiple nested matrix block elements (Pruess, 1983; Pruess and Narasimhan, 1985). It subdivides a normal 3-D gridblock into a fracture element, and multiple nested matrix elements. The fracture elements are connected globally in 3-D, while the matrix elements are only locally connected to each other, and ultimately to the fracture. The individual matrix element volumes and nodal distances are based on different conceptual models of the fracture orientation and spacing. With a 3-D set of orthogonal fractures, each nested matrix element has the shape of a hollow cube, the outer matrix element is connected to the fractures, and the inner matrix elements are connected to each other in 1-D (Figure 5.14). The nested matrix elements represent the average response of the matrix based on their distance from the nearest fracture. This method has been used to simulate energy production and mass transfer in fractured reservoirs in geothermal studies (Pruess 1983; Pruess and Narasimhan 1985; Pruess 2002). However, it appears that this method has not been applied to simulate contaminant transport in a non-isothermal process before.

![Figure 5.15 Six-phase electrical resistance heating pattern](image)

Figure 5.15 Six-phase electrical resistance heating pattern
Another approach is to simulate a fractured porous media with a discrete fracture-matrix model, where the fractures and matrix are fully discretized and connected in 3-D. This is the most accurate way to numerically represent a fractured porous media, however, the discretization must be limited to small domains for problems involving nonisothermal multiphase flow due to the high computational demands. Experience with these types of simulations shows that model meshes should be restricted to a few tens of thousands of gridblocks or less for reasonable run time.

Figure 5.16 Cross-sectional view of a single element in the electrical resistance heating array used in numerical simulation

In this study, the MINC method (Falta et al., 1995; Pruess et al., 1999; Pruess and Narasimhan, 1985) was used to demonstrate the possible behavior of a thermal remediation effort at a fractured site. A repeated 6-phase electrical resistance heating pattern (Figure 5.15) which has an electrode array diameter of 16 m was considered in this field-scale simulation. From a heating and contaminant transport perspective, the hexagonal symmetry elements can be approximated as axi-symmetric cylindrical volumes bounded by insulated and no-flow boundaries. In this model, a heating depth of
20 m and a volume of about 4,020 m$^3$ for each of these patterns were assumed (Figure 5.16).

Figure 5.17 Simulated average temperature (a) and steam extraction rate with time (b)

The system was assumed to be composed of fractured sandstone with a 3-D set of orthogonal fractures with fracture apertures ($b$) of 200 µm, and a fracture spacing ($D$) of 1 m. The properties of the sandstone matrix were identical to the core used in the experiment, which has an intrinsic permeability of $1.5 \times 10^{-13}$ m$^2$ and a porosity of 0.174. Capillary and relative permeability functions used for the matrix and fracture materials
were the same as those in the simulation of the laboratory experiment. The permeability of the individual fractures \((k_f)\) was estimated from the equation:

\[
k_f = \frac{b^2}{12} \tag{5.17}
\]

where \(b\) is the fracture aperture. Overall, the equivalent continuum permeability \((k_{equiv})\) of the rock mass would be calculated as:

\[
k_{equiv} = \frac{2k_fb}{D} = 1.33 \times 10^{-12} \text{m}^2 \tag{5.18}
\]

Here, \(D\) is the fracture spacing. The volume fraction that these fractures occupy (calculated from \(2b/D\)) was 0.0006 of the total volume. The initial conditions for the simulation were: the water table was 4.5 m below the ground surface, and the fractures and matrix above the water table were in gravity-capillary equilibrium with the gravity and capillary force. The initial average water saturation of the system, including the vadose zone, was 91.5%. All of the water in the matrix and fractures below the water table was initially contaminated with 253 mg/L of dissolved 1,2-DCA. An extraction well that penetrates the formation at the center of the pattern was simulated using the deliverability model as described in the equation 5.13. The productivity index \((PI = 6.68 \times 10^{-14} \text{ m}^3)\) was calculated with:

\[
PI = \frac{2\pi k_{equiv} \Delta z_l}{\ln\left(\frac{r_g}{r_w}\right)} \tag{5.19}
\]

where \(\Delta z_l\) is the layer thickness, \(r_g\) is the grid block radius, \(r_w\) is the well radius. The extraction well was placed at the top of the formation, applying a vacuum of about 0.5 atmosphere \((P_{wb}=5 \times 10^4 \text{ Pa})\). Similar to the standard practice at 6-phase field sites, the
ground surface was treated as a sealed and insulated boundary. To simplify the case, a no-flow boundary condition was applied to the bottom of the system, neglecting the possible heat loss from the bottom.

Figure 5.18 Simulated average water saturation (a) and average concentration of 1,2-DCA with time (b)

In the first stage of the simulation, the system was uniformly heated, with the extraction well on, at 200 W/m³ for 27 days. The average temperature increases almost linearly with time during this period, reaching 103 °C (Figure 5.17a). The vacuum extraction well initially produced a mixture of air and liquid water in the first 19.6 days, during which 1.4% of 1,2-DCA mass was removed (Figure 5.18b). The well started to extract steam after heating for 19.6 days. The steam volumetric flow rate (normalizing to
steam vapor density at 100°C) peaked at approximately $1.32 \times 10^4$ L/min at the end of the heating period (27 days). The peak water mass removal rate was approximately 8.94 kg/min. Overall, $1.5 \times 10^6$ kg water was removed during the heating period, accounting for 23% the initial water mass (Figure 5.18a). At the end of the heating period, 95.7% of 1,2-DCA mass was removed (Figure 5.18b).

In the second stage of the simulation, heating was turned off, and the system was depressurized with the vacuum extraction well. Because the temperature was still higher than the water boiling temperature, steam vapor continued to be produced from the system. The 1,2-DCA mass then decreased by orders of magnitude. After about 35 days of treatment, 27.8% of the pore water (including both steam vapor and liquid water) was extracted, and essentially all the 1,2-DCA mass (more than 99%) was removed from the site. Compared to the experiment and simulation results based on a 1-D cylindrical core, the field-scale simulation showed a higher contaminant removal rate, relative to the fraction of produced water. This is because the field scale model simulated a 3-D orthogonal fracture network. Compared to the 1-D geometry, it has a larger area of the matrix exposed to the fractures, which makes it more favorable for the thermal remediation.

This field-scale simulation suggests that thermal remediation using electrical or thermal conduction heating could be effective in treating fractured porous media at the field scale. With the low overall permeability, the fractured system seems to respond well to a heating period followed by a period of vacuum without heating. This conclusion is consistent with the field observations of contaminant recovery during the vacuum phase
of steam flooding operations in heterogeneous porous media system (Heron et al., 2005; Udell, 1996), and with previous numerical analysis of contaminant removal from low permeability sediments during heating and depressurization (Udell and Itamura 1998).

6 CONCLUSIONS

A laboratory experiment of CVOC removal from fractured rock by boiling (in Chapter 3) was simulated using a multiphase numerical model in TMVOC. The simulated results are similar to the experimental data, indicating the TMVOC code can predict the CVOC removal from fractured geologic media during boiling. One source of error in the simulation may be because air relative permeability data was used to represent steam relative permeability. Fitting the steam relative permeability curve to the air relative permeability data might underestimate the steam relative permeability, causing higher temperature gradient, less percentage of steam vapor production, and lower rate of CVOC removal during boiling.

Simulations of ideal 1-D system that ignores experimental end effects shows similar contaminant removal and water boiling patterns. When the temperature is above the water boiling temperature, a high percentage of steam vapor is produced as the outlet is opened to the atmosphere, corresponding to a high removal rate of CVOC. All of the 1,2-DCA is removed after boiling out half of the pore water.

After validation using the laboratory data, the TMVOC code was used to simulate the contaminant removal from fractured geologic media at the field scale with the MINC method. This method can resolve the local transient gradient of temperature, pressure, saturation, and concentration in the matrix. The field scale simulation shows boiling is an
effective mechanism for CVOC removal from fractured geologic media. After about 35
days of treatment, 28% of the pore water (including both steam vapor and liquid water)
was extracted, and essentially all the 1,2-DCA mass (more than 99%) was removed in the
simulation.
References


Pruess, K.; Battistelli, A. *TMVOC, A numerical simulator for three-phase non-isothermal flows of multicomponent hydrocarbon mixtures in saturated-unsaturated heterogeneous media; LBNL-49375; Lawrence Berkeley National Laboratory: Berkeley, CA, 2002.*


CHAPTER SIX
MULTIPHASE NUMERICAL ANALYSIS OF THERMAL REMEDIATION IN 3-D FIELD SCALE FRACTURED GEOLOGIC MEDIA

In this chapter, the model is scaled up to simulate contaminant mass transfer at the field scale. The numerical simulation presented here is to aid understanding of the factors that affect the performance of thermal remediation in the field.

Abstract

Thermal methods have recently received increasing attention for their promise in remediating contaminated fractured geologic media. However, the contaminant mass transfer phenomenon in boiling fractured porous media is complex due to the strong couplings among heat transfer, thermodynamics, and multiphase flow. In this chapter, a 2-D numerical model was constructed with the multiple interacting continua (MINC) method to demonstrate the behavior of contaminant removal and heat transfer in fractured geologic media at field scale. Sensitivity analysis was conducted over chemicals, fracture aperture, fracture spacing, diameter of heating pattern, matrix permeability, extent of vacuum, and various operational strategies. Under the same boiling conditions, the contaminant removal depends on the Henry’s law constant. The higher Henry’s law constant for a chemical, the higher the contaminant removal rate. Variations of fracture properties (aperture and spacing), size of heating pattern, and the extent of extraction vacuum have important effects on the subsurface temperature, but the contaminant removal is sensitive to the matrix permeability. Simulation in a 3-D model shows that the cooling effect caused by the influx of cold ground water is significant. When the fracture network is permeable, the extraction wells pull a large amount of cold water into the treatment zone, which holds the majority of the treatment zone below the water boiling temperature, minimizing the performance
of thermal remediation. Compared to the effect of water flow that flows into the treatment zone by extraction, the ground water flow caused by the natural hydraulic gradient is insignificant.

1 INTRODUCTION

Release of chlorinated volatile organic compounds to fractured geologic media is of concern due to ground water contamination. As CVOCs are released as DNAPL or in a dissolved form, they spread through the fracture network due to the high permeability and low entry pressure of the fractures. The contaminants in the fractures diffuse into the matrix driven by the concentration gradient (Parker et al., 1994; Parker et al., 1997; Reynolds and Kueper, 2001; Reynolds and Kueper, 2002; Ross and Lu, 1999). Over time, a significant amount of contaminant may be stored in the low-permeable matrix materials. After the fractures are cleaned by some natural or engineered processes, the contaminants in the matrix will diffuse back into the fractures, continue contaminating the ground water (Parker et al., 1994; Parker et al., 1997; Reynolds and Kueper, 2001; Reynolds and Kueper, 2002; Ross and Lu, 1999).

Remediation of fractured geologic media is challenging due to facts that the matrix material has low permeability and the fracture network geometry is complex. It is difficult to flush the system with fluids, such as water, air, alcohol, or surfactant, or reliably deliver remediation agents into the matrix. However, thermal methods are promising for cleaning up contaminated fractured geologic media (Chen et al., 2010; Heron et al., 1998b; Udell and Itamura, 1998). Methods including electrical resistance heating (Gauglitz et al., 1994), thermal conductive heating (Heron et al., 2009), and radio-frequency heating (Roland et al., 2008; Roland et al., 2010) can raise the temperature of fractured media to above the water boiling point. As the temperature approaches the water boiling temperature, depressurization in the fractures may result in water boiling in the matrix (Pruess, 2002; Udell and Itamura, 1998).
When boiling occurs, a volume of liquid water is converted to 1600 volumes of vapor at atmospheric pressure, potentially generating a large volumetric steam flow, which may strips the dissolved volatile contaminants from the matrix (Chen et al., 2010; Heron et al., 1998b; Udell and Itamura, 1998). This stripping effect is enhanced at high temperatures, because the Henry’s law constants of chlorinated volatile organic compounds (CVOCs) increase by a factor of 10 at steam temperatures (Heron et al., 1998a).

Limited studies have been conducted in removal of contaminants from fractured geologic media using heating. Recently, we demonstrated an effective removal of dissolved 1,2-dichloroethane (1,2-DCA) from a unfractured sandstone (representing the matrix) by boiling (Chen et al., 2010). After boiling away about 1/3 of the pore volume of water from a contaminated sandstone core, approximately 100% recovery of 1,2-DCA was achieved (Chen et al., 2010). The process of contaminant mass and heat transfer in the experiment was simulated with TMVOC, a numerical simulator widely used for multiphase flow with single and multiple volatile organic chemical(s) (Pruess and Battistelli, 2003; Tse et al., 2006). Good agreement was obtained between the experiment and simulation, which further established the reliability of the code in predicting the contaminant mass transfer between matrix blocks and fractures.

There are limited studies on simulation of contaminant mass transfer from fractured geologic media with boiling at the scale of typical field applications. Baston et al (2009; 2010) investigated conductive heating of fractured rock. They found that hydrogeological properties such as hydraulic gradient, fracture aperture and fracture spacing have larger impacts on subsurface temperature profile than material properties such as density, thermal conductivity and heat capacity (Baston and Kueper, 2009). The boiling temperature can be significantly elevated for low-permeability rock matrix due to raised high pore pressure at high temperature (Baston et
It is unknown how the geologic and flow parameters such as matrix permeability, extent of vacuum, fracture aperture, and fracture spacing affect the performance of thermal remediation. The effects of some operational and design parameters and strategies such as the diameter of heating pattern, and cycling of heating and extraction are not well understood. In typical field settings, cold water is present outside of the heating pattern in the field. The water table can be either flat or have a gradient. While applying thermal remediation in fractured site, it is unknown how the presence of ambient ground water affects the treatment. In this chapter, sensitivity analysis was conducted over a series of matrix and fracture properties (matrix permeability, fracture aperture, and fracture spacing), and design and operational parameters and strategies (diameter of heating pattern and cycling heating and extraction). Also, field application of thermal remediation fractured geologic media was simulated by considering the presence of cold water intrusion.

2 TMVOC SIMULATOR

The TMVOC code was developed for simulating multiphase and non-isothermal flow of multicomponent mixture of volatile organic compounds (VOCs) in the Lawrence Berkeley National Laboratory. It formulates a multiphase system with several mass balance equations and an energy balance equation that sum over the fluid and rock phases. The multiphase flow of NAPL, liquid water, and gas is simulated with multiphase extension of Darcy’s law. The relative permeability effects are calculated using standard 2-phase functions of the phase saturations (van Genuchten. 1980, Verma. 1986). The flow of fluid is driven by the phase pressure gradient with capillary pressure, and a gravity term depending on the phase density. Mass transport by advection, and diffusion including temperature and pressure dependent diffusion coefficients, and phase saturation dependent tortuosities are considered. Heat transfer including multiphase
convection (both latent and sensible heat), and thermal conduction is considered. The thermodynamic properties of water are built into the code and those of CVOCs are calculated with the corresponding states method (Falta et al. 1995, Falta et al. 1992a, Pruess and Battistelli. 2002). The nonlinear coupled mass and energy balance equations are linearized by exploiting an implicit residual-based Newton-Raphson iterative technique, and solved with a selection of direct and iterative matrix solvers (Pruess and Battistelli. 2002).

Table 6.1 Parameters used in the field-scale model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume fraction</td>
<td>0.01, 0.1, 0.2, 0.3, 0.49</td>
</tr>
<tr>
<td>Fracture spacing</td>
<td>1 m</td>
</tr>
<tr>
<td>Fracture aperture</td>
<td>$2 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>Fracture porosity</td>
<td>0.5</td>
</tr>
<tr>
<td>Effective fracture continua permeability</td>
<td>$1.33 \times 10^{-12}$ m$^2$</td>
</tr>
<tr>
<td>Matrix permeability</td>
<td>$1.0 \times 10^{-15}$ m$^2$</td>
</tr>
<tr>
<td>Matrix porosity</td>
<td>0.1</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>3.0 W/m°C</td>
</tr>
<tr>
<td>Specific heat</td>
<td>1000 J/kg°C</td>
</tr>
</tbody>
</table>

3 MULTIPLE INTERACTING CONTINUA

The multiple interacting continua (MINC) method, as an extension of the dual porosity concept, is used for modeling flow in fractured porous media (Pruess and Battistelli, 2002; Pruess and Narasimhan, 1985). Similar to the dual porosity method, the MINC method embeds the low-permeable matrix blocks in a network of interconnected fractures. Global flow occurs
only through the fracture system, while the matrix is locally connected to the fracture, exchanges fluid (or heat) locally with the fracture system. The fluid (heat) flow between the fracture and matrix is driven by the difference in pressures (or temperatures) between them. The MINC method is capable of resolving the gradients with a special discretization, appropriately sub-discretizing a normal matrix block into multiple subgrids (Figure 5.14). The fluid and heat flow between the fractures and the matrix blocks can then be modeled as a one-dimensional process.

4 SENSITIVITY ANALYSIS

It is assumed that a repeated 6-phase electrical resistance heating pattern (Figure 5.15) is used to treat a fractured rock site. From a heating and contaminant transport perspective, the hexagonal symmetry elements can be approximated as axi-symmetric cylindrical volumes bounded by insulated and no-flow boundaries, and the heat is assumed to be uniformly generated within the model (Figure 6.4). For the base model, a diameter of the heating pattern of 16 meters, a heating depth of 20 m and a volume of about 4,020 m³ for each pattern are assumed (Figure 5.16). The model is composed of a radially symmetrical 5×10 mesh (Figure 6.4). The system is assumed to be composed of a 3-D set of orthogonal fractures with the fracture apertures (b) of 200 µm, and a fracture spacing (D) of 1 m (Table 6.1). The matrix permeability is 1.0×10⁻¹⁵ m² and the porosity is 0.1.

Capillary pressure and relative permeability functions used for the matrix and fracture materials are shown in Table 6.2. The capillary pressure uses the van Genuchten equation (Parker et al., 1987; van Genuchten, 1980). The matrix material has a residual water saturation of 0.35 and the fracture has a residual water saturation of 0.1. A relatively weak capillary pressure is assigned to the fractures (Figure 6.1). The relative permeability uses scaled power functions.
for both the gas and water relative permeabilities. The relative permeability functions for the matrix material are shown in Figure 6.2, and the functions for the fracture shown in Figure 6.3.

Table 6.2 Capillary pressure and relative permeability

<table>
<thead>
<tr>
<th>Fracture</th>
<th>Capillary pressure</th>
<th>Relative permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture</td>
<td>$P_{cgw} = -\rho_w g \left( \frac{1}{\alpha_{gn}} + \frac{1}{\alpha_{nw}} \right) \left[ \left( \frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{-1/m} - 1 \right]^{1/n}$</td>
<td>$k_{rg} = \left[ \frac{S_g - S_{gr}}{1 - S_{wr}} \right]^n$; $k_{rw} = \left[ \frac{S_w - S_{wr}}{1 - S_{wr}} \right]^n$</td>
</tr>
<tr>
<td></td>
<td>$S_{wr}=0.1, n=3.00, m=1-1/n, \alpha_{gn}=\alpha_{nw}=28$</td>
<td>$S_{wr}=0.1, S_{gr}=0, n=2$</td>
</tr>
<tr>
<td>Matrix</td>
<td>$P_{cgw} = -\rho_w g \left( \frac{1}{\alpha_{gn}} + \frac{1}{\alpha_{nw}} \right) \left[ \left( \frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{-1/m} - 1 \right]^{1/n}$</td>
<td>$k_{rg} = \left[ \frac{S_g - S_{gr}}{1 - S_{wr}} \right]^n$; $k_{rw} = \left[ \frac{S_w - S_{wr}}{1 - S_{wr}} \right]^n$</td>
</tr>
<tr>
<td></td>
<td>$S_{wr}=0.35, n=2.00, m=1-1/n, \alpha_{gn}=\alpha_{nw}=0.5$</td>
<td>$S_{wr}=0.35, S_{gr}=0, n=3$</td>
</tr>
</tbody>
</table>

The permeability of the individual fractures is estimated with:

$$k_f = \frac{b^2}{12} \quad (6.1)$$

where $b$ is the fracture aperture. Assuming a 3D orthogonal network of fractures, the equivalent continuum permeability of the rock mass is calculated as:

$$k_{equiv} = \frac{2k_f b}{D} = 1.33 \times 10^{-12} \text{ m}^2 \quad (6.2)$$

where $D$ is the fracture spacing. The volume fraction that the fractures occupy is assigned with 0.01 of the total volume. Although it is a little higher than the true value calculated from $3b/D$,
its effect to the simulated results is negligible, and it allows the model to run more smoothly (Pruess and Narasimhan, 1985).

Figure 6.1 Capillary pressure curves

Figure 6.2 Matrix relative permeability curves
Figure 6.3 Fracture relative permeability curves

Figure 6.4 Approximation of a heating pattern
The initial conditions for the base simulation consist of a water table 4.5 m below the ground surface, and the fractures and matrix above the water table are in gravity-capillary equilibrium. The initial average water saturation of the system, including the vadose zone, is 97.9%. All of the water in the matrix and fractures below the water table is initially contaminated with 7.53 mg/L of dissolved 1,2-DCA. An extraction well that penetrates the formation at the center of the pattern is simulated using the deliverability model:

\[ q_β = \frac{k_{r_β}}{μ_β} \rho_β PI (P_β - P_{wb}) \]  \hspace{1cm} (6.3)

The productivity index is calculated with

\[ PI = \frac{2π k_{equiv} \Delta z_l}{\ln\left(\frac{r_e}{r_w}\right)} \]  \hspace{1cm} (6.4)

where \( k_{equiv} \) is effective continua permeability, \( \Delta z_l \) is the layer thickness, \( r_e \) is the grid block radius, \( r_w \) is the well radius. The extraction well was placed at the top of the formation, applying a vacuum of about a half atmosphere \((P_{wb}=5\times10^4 \text{ Pa})\). The ground surface was treated as a sealed and insulated boundary. To simplify the case, a no-flow boundary condition was applied to the bottom of the system, neglecting the possible heat loss from the bottom.

4.1 Results of Sensitivity Analysis

For the base model, the saturated zone is heated at a uniform rate of 200 W/m² with the extraction well on for 18 days. After that, the heater is turned off and the extraction well is left on with a vacuum of 0.5 atm.

4.1.1 Effect of Chemical Properties

Different chlorinated solvents might have different response for thermal remediation. Chlorinated solvents such as 1,2-dichloroethane (1,2-DCA), chloroform (CF), carbon tetrachloride (CT), tetrachloroethylene (PCE), trichloroethylene (TCE) are among the most
Figure 6.5 Average temperatures for the cases contaminated with different chemicals frequently detected at contaminated sites. In chapter 4, the Henry’s law constants and aqueous solubility of these chemicals were measured as functions of temperature. Here, removal of these chemicals from the fractured site is simulated as described in the base model. The temperature dependency of the Henry’s law constant has been considered in the model by fitting to measured data. For different chemicals, it is unsurprising that the patterns of temperature (Figure 6.5) and the average water saturation (Figure 6.6) changes with time are similar because the properties of chemicals have little effects on the water boiling. However, under the same boiling conditions, the contaminant removal rates vary for different chemicals (Figure 6.7). Among these chemicals, carbon tetrachloride has the best removal rate, followed by tetrachloroethylene, trichloroethylene, chloroform, and 1,2-dichloroethane, respectively. The order is the same as the Henry’s law constants for these chemicals. The higher the Henry’s law constant, the higher the contaminant removal rate.
4.1.2 Effect of Diameter of Heating Pattern

The size of heating pattern is important for thermal remediation. Diameters of 4, 8, 16, and 32 meters have been simulated to demonstrate the average temperature (Figure 6.8), the
average water saturation (Figure 6.9), contaminant removal efficiencies (Figure 6.10), and vapor extraction rate (Figure 6.11).

![Figure 6.8 Average temperatures for the cases with different diameters of heating pattern](image)

For a heating diameter of 4 meters, the average temperature increases to 85.8 °C after heating for 13 days (Figure 6.8). Boiling occurs earlier, and at a lower temperature compared to the cases with larger diameters, because the system is more effectively depressurized by the close proximity to the extraction well. As boiling occurs and steam is extracted, the temperature decreases to 82.9 °C by day 18, when the heater is turned off. After 18 days, the heaters are turned off but the extraction wells remains on. Temperature decreases quickly to 75 °C by day 23, and then stabilizes at this value.

The initial average water saturation is 0.978. After heating for 13.32 days, the water saturation (0.982) is slightly increased due to thermal expansion. Further heating and extracting causes the water to boil. The average water saturation decreases to 0.632 in day 18, and 0.546 in day 23 (Figure 6.9). In the first 13.6 days, 14.2% of 1,2-DCA mass removed is due to the extraction of liquid water. From days 13.6 to 23, 73.8% of 1,2-DCA mass is removed. The steam
vapor extraction rate reaches $4.65 \times 10^3$ L/min at day 13.3, and gradually decreases to zero in day 28.

For a heating diameter of 8 meters, the average temperature increases to 85.7 °C after heating for 13.3 days. It continues to increase to 93.2 °C at day 18 at which point the heater is turned off. It then decreases to 79.6 °C by day 48, and then stabilizes.

![Graph showing water saturation over time for different heating diameters.](image)

Figure 6.9 Average saturations for cases with different diameters of heating pattern

The initial average water saturation was 0.978. During the first 13.3 days, the average water saturation increases to 0.98 due to thermal expansion. Then it decreases to 0.75 by day 18, and 0.59 in day 48. The 2% 1,2-DCA mass is removed due to extraction of liquid water during the first 10 days. From day 10 to 18, 69.2% 1,2-DCA mass is removed, primarily in the vapor phase. Further extraction corresponding to another 8.8% removal of 1,2-DCA mass occurs after the heater is turned off. After 48 days, there is not much further contaminant removal. The vapor extraction rate increases to $6.72 \times 10^3$ L/min after heating for 18 days, followed by decreasing to zero in day 78.
For the heating pattern with a diameter of 16 meters, the average temperature increases to 103.2°C after heating 18 days. This increased average temperature is due to the lower influence of the vacuum well on the average pressure in the heating pattern. After 18 days, the heater is turned off with only extraction wells on. The temperature gradually decreases to 81.4 °C by day 383.

Figure 6.10 Fraction of initial 1,2-DCA mass for cases with different diameters of heating pattern

Due to thermal expansion, the average water saturation increases from 0.978 to 0.983 after heating for 13.32 days. After boiling occurs, water saturation decreases rapidly to 0.827 in day 18, and further to 0.581 in day 48. Then the water saturation decreases slowly to 0.518 in day 383. About 1.8% 1,2-DCA mass is removed in the first 10 days due to extraction of water. The heating and extracting from days 10 to 18 corresponds to a removal of 41.6% 1,2-DCA mass. Further extraction from day 19 to 28 removes another 42.7% 1,2-DCA mass. At the end (day 383), only 9.35% of the 1,2-DCA mass remains in the treatment zone. The vapor extraction rate increases to the maximum of 1.12×10^4 L/min in day 18, and decreases gradually to 0.207 L/min in day 383.
For the heating pattern with a diameter of 32 meters, the average temperature increases to 107.56 °C after heating for 18 days. After the heater is turned off, further extraction causes the temperature decrease to 82.15 °C in day 383. The average water saturation decreases to 0.892 in day 18 after a slight increase due to thermal expansion. Further extraction decreases the water saturation to 0.528 in day 383. The contaminant removal is as follows: 1.6% due to extraction of liquid water at early times (before boiling), 22.4% from days 5 to 18, 65.3% in the vapor phase from days 18 to 218, and 3.62% in the vapor phase from days 218 to 383. There is approximately 7.08% 1,2-DCA mass remaining after treating for 383 days. Due to its larger volume and heat content, steam vapor production from the well is maintained for a longer period of time in this larger pattern and the peak steam production rate is larger than that seen in the other patterns (Figure 6.11).

![Figure 6.11 Vapor extraction rates for different heating diameters](image)

The sensitivity analysis on the diameter of heating pattern shows that as long as the fracture network is well connected, effective contaminant removal can occur at a variety of heating pattern sizes. For a smaller diameter, the extraction well has stronger influence on the
treatment zone. Water boils at lower temperatures due to the decreased pressure by extraction. The disadvantage is that a higher percentage of heat is extracted out of the treatment zone at early times, causing the boiling to cease earlier after the heater is turned off. The contaminant mass from farther regions re-contaminates the zones that are close to the extraction well.

For the larger diameter pattern, a smaller percentage of the thermal energy is removed by the extraction well at early times, leading to higher temperatures, and a longer steam drive. However, for the regions that is far away from the extraction well, there is little pressure drop in the fractures, and it takes a longer time to remove the contaminant from these regions. It is good to have a diameter that could allow the extraction well to effectively drop the pressure at the far end of the treatment zone. In this series of simulations, the contaminant removal efficiencies were similar at early times, but the larger patterns showed slightly higher removal efficiencies at later times due to the prolonged steam drive.

4.1.3 Effect of Fracture Aperture

Figure 6.12 Average temperatures for the cases with different fracture apertures
The simulation results are sensitive to the fracture aperture, because the effective continuum permeability of the rock mass varies as the cube of the fracture aperture. The simulation results show that sites with smaller fracture aperture can reach higher temperature than those with larger apertures (Figure 6.12). For the fracture aperture of 100 micrometer case, the average temperature increases to 107.6 °C after heating for 18 days, and decreases gradually to 83.97 °C after 383 days. The average water saturation was initially 0.98 (Figure 6.13). It increases to 0.99 after heating and extracting for 13.36 days, due to thermal expansion, and only a small amount of liquid water production. The average water saturation decreases to 0.94 after 18 days when the heaters are turned off, and steadily to 0.527 after 383 days. In the first 10 days, 1.6% 1,2-DCA mass is removed by pumping the water (Figure 6.14). From day 10 to 18, 12.9% 1,2-DCA is removed. From day 19 to 78, 79.92% 1,2-DCA is removed. After 383 days, there is 2.51% of the 1,2-DCA mass remaining in the treatment zone. The vapor extraction rate reaches its maximum of $4.75 \times 10^3$ L/min in the day 18 (Figure 6.15). Then it decreases gradually to 69.3 L/min after 383 days.

![Figure 6.13 Average water saturations for the cases with different fracture apertures](image)
For the fracture aperture of 200 micrometer case, the average temperature increases to 103.39 °C after 18 days, and decreases to 81.36 °C after 383 days. The average water saturation decreases to 0.83 after heating and extracting for 18 days. Further extraction decreases the average water saturation to 0.518 after 383 days. About 43.4% of the 1,2-DCA mass is removed during the first 18 days of heating and extracting. Further extraction causes the removal of another 47.25% contaminant mass. The vapor extraction increases to $1.12 \times 10^4$ L/min after 18 days and decreases to 0.207 after 383 days.

![Graph showing fraction of initial 1,2-DCA mass in cases with different fracture apertures](image)

Figure 6.14 Fraction of the initial 1,2-DCA mass in the cases with different fracture apertures

For the case of fracture aperture of 300 micrometers, the average temperature increases to 98.52 after 18 days. It decreases to 81.35 after 383 days. The average water saturation decreases to 0.817 after heating and extracting for 18 days, indicating a more rapid removal of water and energy from the system at early times compared to the previous cases. It further decreases to 0.604 after 383 days. The first 18 days of heating and extracting corresponds to a removal of 56.8% 1,2-DCA. The following extraction for another 365 days corresponds to another 22.5%
1,2-DCA removal. The maximum vapor extraction rate occurs at $1.89 \times 10^4$ L/min in day 18. After 383 days, it decreases to $6.23 \times 10^{-2}$ L/min.

![Vapor Extraction Rate vs Time](image)

**Figure 6.15** Vapor extraction rates for the cases with different fracture apertures

This sensitivity analysis shows that when heating and extracting at a fractured site, lower average temperature will be achieved for the case with higher fracture aperture if the vacuum well is operated during the heating period. Due to the increased average permeability, more heat and water are removed from the treatment zone. At the same time, better contaminant removal is achieved for the case with higher fracture aperture. When the heater is turned off with only the extraction wells on, the performance for the extraction is in a reversed order. There is better removal rate for the case with smaller fracture aperture than the larger fracture apertures. Because less heat is removed by extraction in the case of small aperture, the treatment zone remains at a relatively high temperature. In this case, the later time extraction results in a higher contaminant removal rate. After 383 days, the masses remaining in the treatment zone are 2.51% (100 micrometers), 9.35% (200 micrometers), and 20.7% (300 micrometers). It is effective to extract for a long time for the case with small fracture, but less effective for the case with large
fracture apertures. In all cases, the removal efficiency would be improved by adding more heat to the system to increase the amount of in situ steam generation.

4.1.4 Effect of Fracture Spacing

![Average temperatures in the cases with different fracture spacing](image)

Figure 6.16 Average temperatures in the cases with different fracture spacing

![Average water saturations in the cases with different fracture spacing](image)

Figure 6.17 Average water saturations in the cases with different fracture spacing

The base model considered a 3D orthogonal network of fractures with a uniform 1m spacing. Here, cases with one-half, and twice this fracture spacing are evaluated. These different
cases are constructed by generating new MINC grids to reflect the different fracture-matrix relationships. Changing the fracture spacing changes the effective permeability of the fracture network, and it alters the fracture-matrix geometry by affecting the average proximity of the matrix volumes to the fractures.

Figure 6.18 Fraction of initial 1,2-DCA mass in the cases with different fracture spacing

Figure 6.19 Vapor extraction rate in the case with different fracture spacings
In the simulations, after heating and extracting for 18 days, the average temperatures increase to 99.5, 103.2, and 105.1 °C for the cases with fracture spacing of 0.5, 1, and 2 meters, respectively (Figure 6.16). With the same fracture aperture, larger fracture spacing corresponds to a lower average permeability. Thus, less water and heat are removed for the case of larger fracture spacing during this time. After 18 days, the water saturations are 0.804 (0.5 m), 0.827 (1 m), and 0.849 (2 m) (Figure 6.17). In terms of contaminant removal, the performance of heating and extracting for 18 days are: 0.5 m (63.3% removal) > 1 m (43.4% removal) > 2 m (26.6% removal) (Figure 6.18). The vapor extraction rates after 18 days for the cases with fracture spacing of 0.5, 1, and 2 meters are $1.57 \times 10^4$ L/min, $1.12 \times 10^4$ L/min, and $8.38 \times 10^3$ L/min, respectively (Figure 6.19). After 18 days, the heaters are turned off, but the extraction wells remain on. At the end of the simulation, the highest overall removal efficiency occurs the case with the larger fracture spacing (94.4% for 2 m spacing), and the efficiency decreases with fracture spacing (90.6% for 1 m spacing and 80.9% for 0.5 m spacing). The removal efficiencies during the extracting period are in reverse order compared to the initial heating period: 2 m (67.82% removal)>1 m (47.25% removal) > 0.5 m (17.6% removal). More contaminant is removed from the closely spaced fractures early, so less is removed during the extraction-only period. As before, the removal efficiencies of all cases would be improved by the addition of more heat to the system.

4.1.5 Effect of Matrix Permeability

Cases with matrix permeability ($k$) of $10^{-14}$ m$^2$, $10^{-15}$ m$^2$, $10^{-16}$ m$^2$, $10^{-17}$ m$^2$ were simulated to cover the range from moderate to very low intrinsic permeability. Air entry pressure is scaled to permeability as (Leverett, 1941):
\[ P_{clg} \propto \frac{1}{\sqrt{k}} \]

In this case, the van Genuchten formulation was used for capillary pressure. Values of \( \alpha_{gn} \) and \( \alpha_{nw} \) are scaled as a function of permeability (Leverett, 1941), according to values in the base model (Table 6.3).

Table 6.3 \( \alpha_{gn} \) and \( \alpha_{nw} \) values as a function of intrinsic permeability

<table>
<thead>
<tr>
<th>Intrinsic Permeability (m²)</th>
<th>( \alpha_{gn} = \alpha_{nw} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \times 10^{-14} )</td>
<td>1.58</td>
</tr>
<tr>
<td>( 1 \times 10^{-15} )</td>
<td>0.5</td>
</tr>
<tr>
<td>( 1 \times 10^{-16} )</td>
<td>0.158</td>
</tr>
<tr>
<td>( 1 \times 10^{-17} )</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The average temperature histories for the four cases during heating are similar with peak temperatures reaching 102 °C to 104 °C by the end of the heating period (Figure 6.20). The cases with lower matrix permeability show slightly higher temperatures than the cases with higher matrix permeability. The temperatures decline to 81 to 83 °C by the end of the extraction period. It decreases at a slower rate for the matrix that has lower permeability. For the matrix permeability of \( 10^{-17} \) m², the temperature remains above 100 °C for approximately 160 days. The maximum system temperature is mainly influenced by the heating rate, and by the vapor extraction rate, which is sensitive to the fracture network permeability, but less sensitive to the matrix permeability.

The average water saturation histories for the four cases are also fairly similar (Figure 6.21). For matrix permeability from \( 10^{-14} \) m² to \( 10^{-17} \) m², little water is removed until boiling begins during the initial heating period. Despite the four order of magnitude variation in matrix
permeability, the peak vapor extraction rates during boiling only vary by about a factor of two (Figure 6.23), with vapor extraction rate increasing with permeability. As would be expected from the peak vapor extraction rates, the average saturation during the simulation is highest for the case with low matrix permeability (0.59 at the end of the simulation) and lowest for the case with the high matrix permeability (0.52 at the end of the simulation).

![Figure 6.20 Average temperatures in the cases with different matrix permeability](image1)

![Figure 6.21 Average water saturations in the cases with different matrix permeability](image2)
In contrast to the system temperature, vapor production rates, and average water saturation histories, the contaminant removal appears to be highly sensitive to the matrix intrinsic permeability (Figure 6.22). Here, the case with the highest permeability has a removal efficiency of 96.7%, whereas the cases with lower permeability show substantially lower removal efficiencies (90.7% for $1 \times 10^{-15} \text{ m}^2$; 80.4% for $1 \times 10^{-16} \text{ m}^2$; and 58.1% for $1 \times 10^{-17} \text{ m}^2$). The
primary reason for the striking difference in removal efficiency is the location of boiling in the fractured rock mass. At higher permeabilities, boiling occurs both in the fractures and throughout the matrix. The phase change in the matrix leads to a strong stripping effect, which removes the contaminant from the matrix. At lower permeabilities, however, most of the boiling takes place in the fractures, and in the matrix near the fractures. This has the effect of limiting the contaminant mass transfer out of the low-permeability matrix blocks. The lower vapor extraction rate, and higher average water saturation for the low permeability matrix case also reduce the contaminant removal efficiency.

Despite the lower removal efficiency for the low permeability matrix case, there is still substantial mass removal (40%) of the contaminant from the matrix. This removal would be increased if additional heat was added to the system. In particular, as the average water saturation in the system drops, the contaminant removal efficiency would be expected to increase as boiling moves deeper into the matrix.

4.1.6 Effect of Vacuum Extraction Magnitude

![Temperature results with different vacuum extent](image-url)

Figure 6.24 Temperature results with different vacuum extent
Figure 6.25 Water saturation at different vacuum extent

The extent of vacuum determines the extent of pressure drop, as well as the lowering of the water boiling temperature, in a fractured system. We simulated the cases at which extraction wells maintain their pressures at 50 kPa, 70 kPa, and 90 kPa (Figure 6.24-Figure 6.27). With higher extent of extraction, a lower average temperature is reached (Figure 6.24). The maximum average temperature reaches 110°C while the extraction well maintains at 90 kPa. After the heaters are turned off, the average temperature decreases to about 97 °C. When the extraction well operates at 50 kPa, the average temperature reaches 103 °C after heating for 18 days, and then decreases to 81°C when the heater is turned off. More water is removed from the fractured system when the extraction well operates more aggressively (Figure 6.25). After heating for 18 days and extracting for 365 days, the water saturation decreases from 0.98 to 0.51 at 50 kPa. It decreases to 0.82 at 90 kPa. The contaminant removal efficiency is ranked as follows: 50 kPa>70 kPa>90 kPa. After treatment, there are 90.7%, 82.4%, and 76.5% of 1,2-DCA mass removed at 50 kPa, 70 kPa, and 90 kPa, respectively (Figure 6.26). This comparison shows that aggressive
extraction stimulates more throughout boiling in the conditions simulated here, higher rate of vapor flow is generated (Figure 6.27), which in turns results in better contaminant removal.

Figure 6.26 Fraction of initial contaminant mass at different vacuum extent

Figure 6.27 Vapor extraction rate at different extraction vacuum

4.1.7 Effect of Operational Strategies

Different operational strategies (Table 6.4) have been simulated to demonstrate the contaminant removal from fractured rock (Figure 6.28).
The base case (case 1) considers heating and extracting for 18 days, followed by extracting for 365 days. There is 43.4% of 1,2-DCA mass removed after 18 days of heating and extraction. Further extraction for 365 days removes another 47.3% contaminant mass. At the end, there is 9.4% mass that remains in the zone (90.7% mass removal).

Case 2 simulates heating the fractured site for a longer time (23 days, with extraction during heating), followed by extracting for 360 days. Contaminant removal improves compared to case 1. Removal of 88.8% of 1,2-DCA mass occurs during heating and extracting, and the extraction-only stage removes another 10.6% of mass. After treatment, only 0.6% of 1,2-DCA mass remains, for a removal efficiency of 99.4%.

Table 6.4 Operational strategies

<table>
<thead>
<tr>
<th>Case #</th>
<th>Heating</th>
<th>Extraction</th>
<th>Heating</th>
<th>Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18 d, well on</td>
<td>365 d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>23 d, well on</td>
<td>360 d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>18 d, well on</td>
<td>50 d</td>
<td>5 d, well on</td>
<td>310 d</td>
</tr>
<tr>
<td>4</td>
<td>18 d, well off</td>
<td>365 d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>16 d, well off</td>
<td>50 d</td>
<td>2 d, well off</td>
<td>315 d</td>
</tr>
<tr>
<td>6</td>
<td>23 d, well off</td>
<td>365 d</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>18 d, well off</td>
<td>50 d</td>
<td>5 d, well off</td>
<td>310 d</td>
</tr>
<tr>
<td>8</td>
<td>18 d, well off</td>
<td>50 d</td>
<td>5 d, well on</td>
<td>310 d</td>
</tr>
</tbody>
</table>

Cycling is simulated in the third case (case 3). In this case, the site is heated with extraction wells on for 18 days; then the heater is off leaving the extraction on for another 50 days; then heating is assumed for another 5 days (with extraction), followed by extracting for
310 days. The same amount of energy is used in case 3 and case 2. 43.4% of 1,2-DCA is removed during the first heating period. Removal of another 44.7% 1,2-DCA mass occurs during the first extraction. Further heating and extracting for 5 days (2nd heating & extracting) removes an additional 2.33% 1,2-DCA removal. The last part of extracting removes another 9.39% 1,2-DCA mass. By the end of the simulation, this process removes 99.82% of the 1,2-DCA mass.

All the above strategies considered the cases of heating the contaminated site with the extraction well on. However, the fourth case (case 4) considers heating the site without extracting for 18 days, followed by extracting for 365 days. The same amount of energy for heating is consumed as in the case 1. Because there is no extraction during the heating period, no contaminant is removed in the first 18 days. After the heater is turned off and the extraction wells on, the 1,2-DCA mass is quickly removed. After extracting for 30 days (in the day 48), 94.3% 1,2-DCA mass is removed. After 383 days, there is only 3.07% contaminant mass remained, which is better than the case 1.

![Figure 6.28 Contaminant removals by different operational strategies](image)
Cycling without extraction during heating is tested in the case 5. The model simulates heating the assumed site for 16 days without extraction, followed by extracting for 50 days, then heating for another 2 days without extraction, followed by extracting for 315 days. There is no contaminant removal in the first 16 days because the extraction is off, but 83.1% 1,2-DCA mass is removed during the next 50 days. The second round of heating followed by extracting removes 8.18% 1,2-DCA mass. At the end of 383 days, 8.72% contaminant mass remains. Compared to the cases 1 and 4, the same amount of total energy for heating is consumed. In terms of contaminant removal, it is less effective than the strategy used in the case4, but more effective than in the case1.

The previous simulations in the cases1 to 5 suggest that it is important to heat the zone to a high temperature before it is extracted. Case 6 simulates a heated case, where the heated site is heating for 23 days without extraction, followed by extraction for 365 days. The simulated results in the case 6 show a much improved contaminant removal is obtained when the treatment zone is heated to a higher temperature before it is extracted. In this case, due to no extraction during the heating, all the energy is used to increase the temperature. When the extraction wells are turned on, a quick removal of 1,2-DCA is observed. Extraction for 30 days decreases the residual 1,2-DCA mass by more than 4 orders of magnitude. After 383 days, only $9.43 \times 10^{-6}$ of the initial 1,2-DCA mass remains. This is the most effective strategy that has been simulated here. However, heating without extraction increases the pressure of the treatment zone (volumetric average pressure increases to 166 kPa after heating for 23 days), which might cause the migration of contaminant to other regions.

The purpose of case 7 is to investigate the performance of cycling heating and extraction when increased amount of thermal energy is delivered. It simulates heating for 18 days without
extraction, followed by extraction for 50 days, and heating for 5 days without extraction, and extracting for 310 days. The total energy for heating is the same as in the cases 2, 3 and 6. The simulation results (Figure 6.28) show that, although the same amount of thermal energy is consumed, this strategy is less effective than the case 6 in terms of contaminant removal. After treatment for 383 days, it removes about 99.7% of 1,2-DCA mass, remaining 0.33% of 1,2-DCA mass untreated. It is less effective than the case 3 where cycling is used and extraction wells are on while heating, but more effective than the case 2 where no cycling is used. From the comparison of the cases 2, 3, and 7, with 6, we can conclude that for the same amount of thermal energy budget, the best way is to use them all to increase the formation temperature, try to avoid boiling during heating. If the temperature cannot increase too high, it is better to heat the formation in several cycles (e.g. the cases 3 and 7 are better than the case 2). However, the comparison between the cases 3 and 7, shows that the case 7 has a better removal rate than the case 3 in the first round (e.g. After treatment of 68 days, 95.2% removed in the case 7 while only 88.1% removed in the case 3), but has a lower removal rate than the case 3 in the second round (e.g. from days 69 to 383 days, 11.72% 1,2-DCA is removed in the case 3 while only 4.4% is removed in the case 7).

The case 8 simulates heating for 18 days without extraction, followed by extraction for 50 days, then heating and extracting for 5 days, followed by extraction for 310 days. Different from the case 7, the extraction well is turned on in the second round of heating (from days 69 to 73). It seems that turning on the extraction well during the second round of heating improves the contaminant removal: 4.61% 1,2-DCA mass is removed from the days 69 to 383. At the end of treatment, only 0.15% 1,2-DCA remains, which is a little less than the remaining mass in the case 3 (0.18% 1,2-DCA).
As a summary, simulations of the contaminant removal with the different treatment strategies show that increased thermal energy input will increase the performance of thermal remediation. If the energy consumption is a concern, it is recommended to use as much of the energy as possible to increase the subsurface temperature, following by extraction. If for some reasons, the temperature cannot be too high, it is better to deliver the energy in several rounds. Extraction might be beneficial in the second round of heating.

5 SIMULATION OF THERMAL TREATMENT IN THE FIELD WITH THE PRESENCE OF COLD GROUND WATER

Figure 6.29 Field with flat water table

Application of thermal remediation in the field is complicated by the presence of ground water at ambient temperatures. The water could be static, surrounding the treatment zone, e.g. flat water table, or it could be driven by horizontal hydraulic gradients. The presence of cold water might affect the performance of thermal remediation in many ways. It cools the periphery of the treatment zone by thermal conduction (Baston and Kueper, 2009). Also, the ground water influx into treatment zone might delay the attainment of target temperature (Baston and Kueper, 2009) and change the water distribution in the treatment zone. In some cases, cold ground water
could flow through the treatment zone due to hydraulic gradients, carrying heated water out of the treatment zone.

To demonstrate the possible contaminant removal behavior with cold water passing the treatment zone, we simulate a fractured site with a dimension of 158 m×156 m×85 m (Figure 6.29). The fractures are assumed to be well connected. Both flat and a sloping water tables are considered. For the flat water table case, the water table is 4.5 m below the ground surface. The sloping water table case considers a hydraulic gradient of 0.005 in the x direction, the water table at the center is 4.5 m below the ground surface (Figure 6.37). The contaminated region is located at the center of the site, 16 m long, 16 m wide and 14 m below ground surface. Here, it is assumed that only the saturated zone in this region is contaminated with 7.53 mg/L of dissolved 1,2-DCA, and the unsaturated zone and other regions are uncontaminated.

![Meshes before sub-discretization by MINC](image)

Due to the symmetry, only half of the site is simulated. The model blocks domain is 158 m×78 m×85 m. It is discretized into 16×11×11 (1036) active elements (Figure 6.30), among which 392 elements that have grid spacings (Δx=Δy=Δz) of 2m are used for the treatment zone. The treatment zone includes both the contaminated zone and 4 surrounding and a underlying
Table 6.5 Capillary pressure and relative permeability in the field scale model

<table>
<thead>
<tr>
<th>Fracture</th>
<th>Capillary pressure</th>
<th>Relative permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( P_{cgw} = -\rho w g \left( \frac{1}{\alpha_{gn}} + \frac{1}{\alpha_{nw}} \right) \left[ \left( \frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{-1/m} - 1 \right]^{1/n} )</td>
<td>( k_{rg} = \frac{S_g - S_{gr}}{1 - S_{wr}}^n ); ( k_{rw} = \left[ \frac{S_w - S_{wr}}{1 - S_{wr}} \right]^n )</td>
</tr>
<tr>
<td></td>
<td>( S_{wr} = 0.1, n = 2.00, m = 1 - 1/n, \alpha_{gn} = \alpha_{nw} = 18.3 )</td>
<td>( S_{wr} = 0.1, S_{gr} = 0, n = 2 )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Capillary pressure</th>
<th>Relative permeability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( P_{cgw} = -\rho w g \left( \frac{1}{\alpha_{gn}} + \frac{1}{\alpha_{nw}} \right) \left[ \left( \frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{-1/m} - 1 \right]^{1/n} )</td>
<td>( k_{rg} = \frac{S_g - S_{gr}}{1 - S_{wr}}^n ); ( k_{rw} = \left[ \frac{S_w - S_{wr}}{1 - S_{wr}} \right]^n )</td>
</tr>
<tr>
<td></td>
<td>( S_{wr} = 0.35, n = 2.00, m = 1 - 1/n, \alpha_{gn} = \alpha_{nw} = 0.5 )</td>
<td>( S_{wr} = 0.35, S_{gr} = 0, n = 3 )</td>
</tr>
</tbody>
</table>

layers (2m thick), which is consistent with typical operations of thermal remediation to prevent the contaminants from migrating into the uncontaminated zones during the treatment. To resolve the transient gradient of temperature, pressure, and contaminant concentration from the matrix to fracture and within the matrix, MINC is used in the model, where each active grid is further discretized into 5 subgrids, 1 is for the fracture and the other 4 for the matrix. Different properties as well as different capillary pressure and relative steam-water permeability functions are assigned for the fracture and the matrix materials (Table 6.1). The permeability of a single fracture is calculated from the cubic law (Witherspoon et al., 1980). The overall effective continua permeability the 3-D fracture is calculated based on the permeability of a single fracture, fracture aperture, and fracture spacing. The capillary pressure and relative permeability
curves are shown in Table 6.5. The MINC method assumes the fractures are well connected. All the fracture grids are globally connected, and the matrix grids are locally connected, and ultimately to the fracture network.

Remediation of the contaminated site is assumed to be conducted with typical 6-phase electrical resistive heating. This method is able to heat the subsurface in a relatively uniform manner (Carrigan and Nitao, 2000). In the model, we simulate the treatment zone are heated at a uniform rate of 200 W/m³. Extraction wells, 6 meters apart, are uniformly distributed in the treatment zone (Figure 6.31). The penetrating depths of the wells are 14 m, and a vacuum of $5 \times 10^4$ Pa (absolute pressure) is applied at the top. Similar to the sensitivity analysis, the extraction wells are simulated with the deliverability model (Equation 5.13), and the productivity index is calculated based on the effective continua permeability, layer thickness, and effective well block radius (Equation 5.19). The effective radius for a regular Cartesian well block is calculated with (Anderson and Woessner, 1992):

$$r_e = 0.208a$$

(6.5)

![Figure 6.31 The top view of the treatment zone](image)
Figure 6.32 Simulation results at location 1 for flat water table

The initial conditions for the flat water table trial consist of a water table 4.5 m below the ground surface, and the fractures and matrix above the water table are in gravity-capillary equilibrium. For the sloping water table case, there is a 0.005 hydraulic gradient in the x direction. The cells in the contaminated region are assigned with a dissolved 1,2-DCA concentration of 7.53 mg/L. It is assumed that the physical states at the locations far away from the treatment zone remain constant. So, we apply fixed conditions at the three boundaries (x=0 m, x=158 m, and y=0 m) of the model, where the hydraulic head (water table of 4.5 m deep), contaminant concentration (C_{1,2-DCA}=0 mg/L), and water temperature (T=20°C) are held constant. A no flow boundary is applied at the plane of y=78m because of the symmetry of the system.
Heat transfer and fluid flow between the treatment zone and its surroundings are considered in this model. The ground surface was treated as a sealed and insulated boundary.

5.1 Flat Water Table

To demonstrate the flow and heat behavior of the model, we plot the simulation results (temperature, pressure, water saturation, and 1,2-DCA concentration data) at locations 1, 2, 3, and 4, as shown in Figure 6.31. Figure 6.32 shows the simulation results at spot 1, located at southwestern corner of the contaminated zone. From the temperature profiles, we can see that the
Figure 6.34 Simulation results at location 3 for flat water table

temperature increases to about 90 °C at depths of 3 and 5 m, and about 75°C at depth 7 m due to the uniform heat delivered in the saturated zone (Figure 6.32 a). Thermal energy is not delivered to the vadose zone. It is heated by thermal conduction and extraction of hot fluid from the heated zone. For regions under the water table, the temperature increases are followed by a drop of temperature in 13 days. The temperature drop is not caused by the boiling because the water saturation at these regions remains 1.0 (Figure 6.32 b). When boiling occurs, water saturation is expected to decrease because a portion of the liquid pore water is converted to steam vapor. The
temperature at deeper location drops quicker than the shallow location: 7m>5m>3m. This suggests that it cools by the flow of cold water, and this cooling effect is greater at deeper locations. The temperature above the water table keeps increasing until the system reaches steady state after 110 days. The effect of the extraction wells on at location 1 is shown in Figure 6.32 c. Initially there is a drop of pressure as the extraction wells are turned on. It is followed by a slight increase of pressure at all locations under the water surface, possibly due to thermal expansion. The subsequent decrease of pressure could be explained as further extraction causes the water in the fractures to flow upward, and eventually fill the channel with water. This increase of water
saturation makes the channel more permeable for the flow of liquid water, and in turn for the extraction wells to more effectively drop the pressures under the water table. Without boiling in the matrix, there is essentially no contaminant removed from this location (Figure 6.32 d).

![Graph showing contaminant removal over time](image)

**Figure 6.36 Overall contaminant removal**

Similar results are observed for locations 2 (Figure 6.33) and 3 (Figure 6.34), where no boiling occurs due to the cooling effect caused by the flow of cold water. However, boiling occurs at the shallow layers of location 4 (Figure 6.35), which is centered in the treatment zone. In this location, temperature at 3 m increases to and remains around 97 °C. The water saturation decreases to about 0.82. Correspondingly, the 1,2-DCA mass is removed. There is slight boiling in the matrix at the depth of 5 m, causing a slight drop of water saturation at day 13. However, it ceases soon. The possible explanation is that the thermal expansion, extraction, and possibly boiling at deep locations and condensing at shallow locations fill the fractures above the water table with liquid water, which forms a well-connected and fully saturated channel from the
Figure 6.37 Field with sloping water table

Figure 6.38 Simulation results at location 1 for sloping water table
Figure 6.39 Simulation results at location2 for sloping water table bottom to the extraction well (located at the top). So, this well-connected channel has a higher permeability for liquid water due to the increased water saturation. As a result, a larger amount of cold water was pulled from the bottom and surroundings under the same vacuum (or head difference). This in turn causes larger cooling effect on the treatment zone. Only a small fraction of contaminant is removed at 5-m depth. Boiling does not occur in the deeper locations (7 m). Simulation shows that the effect of the presence of cold water in the surrounding is significant for applying thermal remediation in field. In this case, we simulated the case with effective continua permeability of $1.33 \times 10^{12}$ m$^2$. Due to the high permeability, cold water flows from the surroundings while the extraction wells are on, which cools the treatment zone. Also the results
show that even though heat is delivered at the same rate (200 W/m$^3$), the treatment zone is heated non-uniformly due to the cooling effect of the cold water. The top layer is heated faster than the bottom, the center faster than the edges. The majority of the treatment is below the water boiling temperature, even after heating for 383 days. In this case, minimal contaminant mass is removed, and 86% of the 1,2-DCA mass remains after treatment (Figure 6.36).

Figure 6.40 Simulation results at location 3 for dipped water table
5.2 **Sloping Water Table**

To demonstrate the effect of ground water influx under ambient condition, we conduct the simulation considering a hydraulic gradient of $5 \times 10^{-3}$ in the x direction in the model. The simulation results plotted at the locations 1-4 (Figure 6.38-Figure 6.41) are similar to the one observed in flat water table. The cooling effect is significant in the periphery of the treatment zone, preventing boiling from occurring in these regions. Compared to the heat loss caused by the extraction, the amount of heat that was brought away by the groundwater flow is insignificant. Boiling occurs in the shallow regions in the center of the treatment zone. The overall contaminant removal rate is very close to the one with flat water table (Figure 6.36).
The simulation results show that heat loss due to the cold water flux caused by the extraction is significant. Due to the high permeability of the fracture network, a large amount of cold water is extracted from the surroundings, cooling the treatment zone as it passes by. The limited boiling minimizes the performance of thermal remediation. In this suite of simulations, ground water flow caused by the field hydraulic gradient has little effect on the performance of thermal remediation. Strategies such as installation of impermeable barriers at the periphery of the treatment zone, decreased extraction rate, and increased heating rate might help to improve the performance.
References


CHAPTER SEVEN
SUMMARY AND CONCLUSIONS

Thermal methods are promising for remediating contaminated fractured geologic media. The procedure involves heating the low-permeable matrix material to above the water boiling temperature. Relatively low pressure in the fracture then induces boiling in the adjoining matrix. The generated steam flow strips volatile contaminants out of the matrix. However, contaminant mass transfer during boiling is a complex phenomenon, where the convective and conductive transfer, multiphase flow of liquid water and steam vapor, and thermodynamics are coupled.

To understand this phenomenon, we demonstrated the thermal removal of dissolved chlorinated solvents from a sandstone rock matrix. The core was initially contaminated with 1,2-DCA. After heating the core above 100 °C and subsequently opening one end of the core to the atmosphere, boiling occurs in the core. A temperature gradient towards the outlet was observed, indicating that steam was generated and a pressure gradient developed towards the outlet, pushing the generated steam flux out of the matrix. When the boiling occurred, the effluent concentration of 1,2-DCA peaked at 6.1 times higher than before being heated, and the 1,2-DCA was quickly removed from the matrix. When 38% of the pore volume of condensate was produced as condensate, nearly 100% of the 1,2-DCA was recovered. Non-volatile bromide concentration in the condensate was used as an indicator of the percentage of water coming out as liquid water. Combined with the 1,2-DCA concentration curve, it shows that a higher percentage of condensate coming out as vapor corresponds to increased 1,2-DCA removal from the core, and demonstrates that the chlorinated volatile compound is primarily removed by partitioning to vapor phase flow. This study provides a platform for further understanding the key factors that control contaminant mass transfer from heated fractured rock by boiling.
Henry’s law constant is important in determining the partitioning of a chemical between the aqueous and gaseous phases at equilibrium. To accurately predict contaminant removal at boiling temperature, we measured the Henry’s law constants for 12 chlorinated solvents (tetrachloroethylene, trichloroethylene, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1-dichloroethane, dichloromethane, carbon tetrachloride, cis-1,2-dichloroethylene, chloromethane, chloroethane, and vinyl chloride) over temperatures from 8 to 93 °C. The measurements show that Henry’s law constant is strongly dependent on temperature, increasing by factors of 3 (chloromethane) to 30 (1,2-DCA) as temperature increases from 8 to 93 °C. The measured results show that Henry’s law constant is strongly dependent on temperature, increasing by factors from 3 (chloromethane) to 30 (1,2-DCA) as temperature increases from 8 to 93 °C. The temperature dependency of Henry’s law constants was modeled with the Van’t Hoff equation. Better fitting is obtained by assuming that the enthalpy of dissolution is a function of temperature, suggesting the inappropriateness of extrapolating the Henry’s law constant from measurements at low temperature using a linear function. Using measured data for solubility, the vapor pressure-solubility model gives a reasonable prediction of the Henry’s law constants. With improved data on Henry’s law constants at high temperatures for the 12 common CVOCs measured in this study, it will be possible to more accurately model subsurface remediation processes that operate near the boiling point of water.

The laboratory experiment was simulated with a 2-D multiphase numerical model using the TMVOC codes. The simulated results are in reasonable agreement with the experiment, which provides confidence for the TMVOC codes in predicting the CVOC removal from fractured geologic media by boiling. Steam relative permeability might be different from the air relative permeability. Fitting the steam relative permeability curve to the air relative permeability
data might underestimate the steam relative permeability, causing a higher temperature gradient, a lower percentage of steam vapor production, and a lower rate of CVOC removal during boiling.

To exclude the unavoidable end effects (e.g. heat loss from ends) of the experiment, a 1-D numerical model was further used to demonstrate the contaminant mass transfer from the core without end effects. Similar to the experiment results, a temperature gradient was observed while pore water in the matrix was boiled. After opening to the atmosphere, a high proportion of steam vapor was produced, corresponding to a high removal rate of 1,2-DCA. All of the 1,2-DCA mass was removed after boiling out around 50 mL of pore water. Since no heat loss was considered in this model, the temperature gradients are larger than what we observed in the experiment. The duration of boiling is less than that in the experiment, and the rate of steam flow is higher.

Contaminant removal from fractured geologic media at the field scale was simulated using the MINC method. As an extension of the dual porosity method, this method is capable of resolving the local transient gradient of temperature, pressure, saturation, and concentration in the matrix by applying a special discretization, subdiscretizing the matrix block into multiple subgrids. The field scale simulation shows boiling is an effective mechanism for CVOC removal from fractured geologic media. After about 35 days of treatment, 27.8% of the pore water (including both steam vapor and liquid water) was extracted, and essentially all the 1,2-DCA mass (more than 99%) was removed from the fractured site.

Effects of chemicals, fracture spacing, fracture aperture, diameter of heating pattern, matrix permeability, extent of vacuum, and different operational strategies on the performance of thermal treatment of a fractured site are investigated. The base model assumes the site is heated with the extraction well on for 18 days. Then the heater is turned off, but extraction is continued
for another 365 days. The simulation results show that, under the same boiling conditions, the contaminant removal rates vary for different chemicals, depending on their Henry’s law constants. The higher Henry’s law constant for a chemical, the higher the contaminant removal rate. Variations of fracture properties (aperture and spacing), size of heating pattern, and the extent of extraction vacuum have larger effects on the system temperature than the matrix permeability due to the differentiated percentage of heat extracted from the system. The contaminant removal is more sensitive to the matrix permeability. Further simulation in a 3-D model by considering the effects of unheated native water shows that the cooling effect caused by the influx of unheated ground water is significant. When the fracture network is permeable, the extraction wells pull a large amount of cold water into the treatment zone, which holds the majority of the treatment zone below the water boiling temperature, minimizing the performance of thermal remediation. Compared to the effect of water flow pulled by extraction, the ground water flow caused by the regional hydraulic gradient is insignificant.
APPENDICES
Appendix A: Simulation with increased gas relative permeability

Increased gas relative permeability was used to simulate the experiment as described in the chapter 3 (Figure A.1). Other conditions such as boundary conditions, properties of materials, capillary pressure functions are similar to the simulation described in the chapter 4. The simulation results show improved fits on temperature (Figure A.2), effluent contaminant concentration (Figure A.3), and effluent tracer concentration (Figure A.4). The simulated condensate production is still in a good agreement with the experimental data (Figure A.5).

Figure A.1 Increased gas relative permeability; dash line: gas relative permeability curve fitted to air relative permeability data, red line: increased gas relative permeability, green line: liquid water relative permeability
Figure A.2 Comparison of the simulated and experimental temperature results in the model using the increased the gas relative permeability
Figure A.3 Comparison of the simulated effluent contaminant concentration in the model using the increased the gas relative permeability to the experimental data
Figure A.4 Comparison of the simulated effluent bromide concentration in the model using the increased the gas relative permeability to the experimental data
Figure A.5 Comparison of the simulated cumulative volume of condensate in the model using the increased gas relative permeability to the experimental data
APPENDIX B: Circuit of transistor board

Figure B.1 Scheme of the circuit board of transistor