THE INFLUENCE OF PHYSICAL HETEROGENEITY ON IMMISCIBLE-LIQUID DISSOLUTION AND PERMEABILITY-BASED IN SITU REMEDIATION

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DEDICATION

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ABSTRACT

Minimal research has been conducted to examine dissolution and remediation of NAPL located in lower-permeability (K) media. The purpose of this research was to investigate dissolution of non-uniformly distributed residual NAPL located in lower-K media and how mass transfer was affected. Additionally, in situ chemical oxidation (ISCO) effectiveness using KMnO₄ in the laboratory and field was examined.

A series of column and flow cell experiments were conducted with trichloroethene (TCE). For uniformly distributed residual NAPL control experiments, reduced interfacial pool area and resonance time were likely the most important mass transfer limitation. For non-uniformly distributed residual NAPL, by-pass flow attributed to reduced effective permeability was initially the most important factor affecting non-ideal mass transfer. Dissolution times increased with physical heterogeneity due to by-pass flow. Mass transfer was more non-ideal for non-uniformly distributed NAPL. Non-ideal mass transfer was most pronounced for non-uniformly distributed NAPL in lower-K zones. NAPL location influences dissolution behavior and ultimately remediation. Mass flux reduction versus mass reduction comparisons for the experiments exhibited how mass transfer trends vary between systems.

The effectiveness of KMnO₄ ISCO of residual TCE located in lower-K media was examined. KMnO₄ solution was flushed through a flow cell followed by water flushing to evaluate long-term mass flux behavior, which was then compared to a water-flush control. For water flushing following KMnO₄ flushing, mass flux was similar to the control experiment. However, since contaminant mass was reduced, the number of pore
volumes required for complete TCE removal via water flushing was estimated to be reduced by half.

1,1-Dichloroethene (DCE) is thought to be located in lower permeability strata adjacent to the water table at the Samsonite Building Area. Eight injection wells were emplaced in the source zone area, with well screens spanning the vadose and saturated zones, and injected with ~250 kg of 1.7% KMnO₄ solution. Bench-scale studies using core material determined that DCE was readily degraded by KMnO₄, even at lower reagent concentrations (< 1 mM). The natural oxidant demand was determined to be 1.0 x 10⁻⁵ g of KMnO₄/g of sediment. Aqueous DCE levels dropped below detection after KMnO₄ solution was present.
CHAPTER 1. INTRODUCTION

Research Statement

The contamination of groundwater by hazardous organic chemicals and the associated risks to human health and the environment are issues of great importance. One of the most critical issues associated with hazardous waste sites is the potential presence of immiscible-liquid contamination in the subsurface. Unfortunately, immiscible-liquid contamination, such as chlorinated solvents, creosote, coal tars, and fuels, is present at many contaminated sites. Immiscible liquids introduced into the subsurface become entrapped due to capillary forces. Once entrapped, the immiscible liquid is very difficult to remove. Hence, immiscible liquids serve as long-term sources of subsurface contamination. The behavior of chlorinated solvents is further complicated by the fact that they are more dense than water; a property that influences their transport, retention, and distribution.

The presence of immiscible-liquid contamination at a site can greatly impact the costs and time required for site remediation. For example, at sites contaminated by dense nonaqueous-phase liquids (DNAPLs), it is estimated that upwards of hundreds of years may be necessary to achieve health-based groundwater cleanup objectives using standard pump-and-treat systems (ITRC, 2002). This clearly illustrates the critical importance of addressing DNAPL contamination when it is present at a site. Unfortunately, as is widely acknowledged, cleaning up sites contaminated by DNAPLs is one of the greatest challenges in the field of environmental remediation. In fact, according to several
reviews conducted by expert panels convened by the National Research Council, the presence of DNAPL is usually the single most important factor limiting the cleanup of organic-contaminated sites (NRC 1994, 1997, 1999, 2000). Thus, there is great interest in understanding the dissolution processes involved when DNAPL is present.

Immiscible liquids like trichloroethene (TCE) prove to be difficult to remediate in the saturated zone for several reasons including: pore-scale limited mass transfer, limited solubilities, and/or limited contact between advecting water and NAPL. Limited contact can be caused by nonuniform distribution and “by-pass flow” due to large residual NAPL saturation and decreased permeability. Limited contact between the NAPL and aqueous phase can also be attributed to the NAPL being located in lower-permeability (K) media leading to preferential flow around the contaminated zone. Finally, limited contact can be caused by NAPL pools (e.g., Brusseau et al., 2000). Knowledge of NAPL dissolution behavior under field conditions is important for conducting risk assessment and implementing appropriate remediation strategies for NAPL contaminated sites (Brusseau et al., 2000). Of particular interest for this research was investigating trapped NAPL like TCE within lower-K zones.

There is also significant interest in innovative remediation methods that can degrade significant amounts of mass from DNAPL source zones and in turn eliminate long term dissolution from contaminated sources. In-situ chemical oxidation (ISCO) using permanganate is one such method (Vella and Veronda, 1992; McKay et al., 1998; Siegrist et al., 1999; Moes et al., 2000; Mott-Smith et al., 2000). ISCO has been a
promising innovative remediation technology for source zones which necessitates further research at the intermediate scale and at the field scale.

**Objectives**

The specific, primary objectives of this work are:

1. Investigate NAPL dissolution for non-uniformly distributed NAPL in homogeneous media and heterogeneous lower-K media.

2. Examine performance of KMnO$_4$-based ISCO when NAPL is entrapped in lower-K zones and determine the influence on mass flux after KMnO$_4$ flushing.

3. Assess the feasibility and performance for in situ chemical oxidation (ISCO) application in a heterogeneous perched aquifer containing 1, 1-dichloroethene contamination at the Samsonite Building area, which is part of the Tucson International Airport Authority Superfund Site.
**Literature Review: NAPL Dissolution**

Non-aqueous phase liquids (NAPLs) are one of the greatest environmental remediation challenges since NAPL contamination is extremely complex and their behavior in heterogeneous systems is unpredictable (ITRC, 2003). NAPL can be a long-term contamination source and create significant dissolved phase contamination in the subsurface. Although most NAPLs are not highly water soluble, they are soluble enough to be a potential risk to the environment and potable use. When a NAPL has a density greater than water, it is referred to as denser-than-water non-aqueous-phase liquid (DNAPL). NAPL migration in the subsurface is affected by the following: volume of NAPL release, area of infiltration, time duration of release, properties of the NAPL release, properties of the media, an subsurface flow conditions (Feenstra and Cherry, 1988). NAPLs migrate as a separate phase through the subsurface due to gravity and capillary effects. As the contaminant migrates, some of the NAPL is trapped leaving behind zones of residual NAPL or ganglia, which can be a source of long-term contamination due to capillary forces (Illangasekare et al., 1995). As NAPL migrates downward to the water table and the saturated zone, sufficient fluid must build up to overcome entry pressure. At this point lateral spreading can occur; however, if enough NAPL is present it will penetrate the water table and continue to move downward until contacting a lower-K zone or other impermeable layer (Mercer and Cohen, 1990). The vertically migrating NAPL will displace the aquifer pore water (Schwille, 1988). As
NAPL encounters water in the saturated zone, it will dissolve and create a downgradient solute plume. Some of the NAPL can become trapped and will essentially be immobile for typical hydraulic gradients (Hunt et al., 1988). For saturated systems, it is usually assumed that NAPL will be found in the higher-K formations since the capillary pressure is too great for entry into the lower-K formations (Kueper et al., 1989). A schematic of a DNAPL spill is illustrated in Figure 1.

![Figure 1. DNAPL distribution in the subsurface from ITRC (1999).](image)

Depending on whether the NAPL is the wetting or non-wetting fluid determines if the invading fluid will displace the resident fluid (Huling and Weaver, 1991). If the NAPL is the wetting fluid, it will preferentially flow and reside in lower-K regions. On the other hand, if it is the non-wetting fluid the immiscible liquid will be located in higher-K regions. If the water table fluctuates, it is possible to have an immiscible liquid trapped within a lower-K zone in the saturated zone (Oostrom et al., 2003). Ultimately, NAPL distribution will not be uniform or readily predictable in the subsurface due to
minute variations in pore size distributions, soil texture, soil structure, and mineralogy (ITRC, 2003).

Once the NAPL has become trapped in the subsurface, it is a long-term contamination source. If the NAPL is trapped in the vadose zone, it can volatilize or dissolve in infiltrating water. NAPL trapped in the saturated zone can partition directly into the aqueous phase. Many papers have been published describing physical and chemical phenomenon that influence NAPL dissolution in the subsurface and several will be discussed that relate to the current research.

Miller et al. (1990) investigated the mass transfer between a NAPL phase and an aqueous phase. Seventy different column experiments were packed with various sized glass beads and then toluene was injected into the column followed by water flushing. Mass transfer rate coefficients were determined over a range of aqueous phase velocities, NAPL saturations, and solid media particle sizes. Results supported increasing mass transfer rate coefficient with NAPL saturation which supports increasing interfacial area with increasing NAPL saturation. NAPL saturation also seemed to have a greater influence on mass transfer rate coefficients at higher aqueous phase velocities. Mass transfer rates were found to be directly related to aqueous velocity and NAPL saturation.

Powers et al. (1991) examined potential factors governing the importance of non-equilibrium effects between NAPL and groundwater. Only interphase mass exchange rate was considered in this paper. A model was developed to explain NAPL dissolution. Several factors can limit mass transfer from the NAPL to the aqueous phase including: rate limited mass transport between phases, physical by-passing of the aqueous phase
around the contaminated region which has a low aqueous phase relative permeability, nonuniform flow of aqueous or organic phases due to aquifer heterogeneities, or misinterpretations of field data concentrations for organic phases consisting of a mixture of compounds. Based on the sensitivity analysis, solute concentrations depends on NAPL blob shape and size, Darcy velocity, lateral dimensions of exposure, and the mass transfer coefficient correlation used. None of the existing mass transfer coefficient correlations adequately describe the specific flow and geometric shape of dissolving NAPL blobs. The steady state approximation is valid only for short periods of time since over time NAPL blobs dissolve and the size of blobs decreases (residual saturation decreases) because of this, interstitial velocity, mass transfer coefficients, and dispersion tensor change. Based on these results, previously using equilibrium conditions to predict groundwater remediations times will underestimated the actual time required and pulse pumping might not necessarily be more efficient. The final two primary conclusions were that interfacial mass transfer may be a limiting factor in the dissolution of NAPLs in groundwater and that the design of cost effective pump-and-treat remedial schemes must allow for longer pumping periods than predicted with thermodynamic equilibrium partitioning relationships.

Powers et al. (1992) carried out column experiments to investigate conditions limiting the interphase exchange of organic species and derive a phenomenological model describing the “steady state” dissolution process in terms of measurable properties of the porous media and NAPL. For these experiments, effluent concentrations decreased with increasing velocity and different grained sands experienced different effluent
concentrations as well. Based on effluent concentrations, it was determined that graded or mixed sands have a lower mass transfer coefficient or specific interfacial area or both when compared to uniform sand. Also, greater volumes of NAPL are entrapped in the graded media based on the frequency of large styrene blobs and higher saturation rates did not necessarily correspond to higher mass transfer in the graded media. Finally, for the mixed media, residual saturation did not correlate to surface area due to the varying blob sizes. A modified Sherwood number incorporating a mass transfer coefficient and the specific surface area of the NAPL was used to describe rates of NAPL dissolution.

Powers et al. (1994) conducted a series of column experiments with homogeneous sand and uniformly distributed styrene. Problems when using local equilibrium assumptions for modeling NAPL dissolution needed to be addressed. The specific objectives of the paper were to generate data from a serious of column experiments which could be used to develop a correlation for transient NAPL dissolution processes. Based on elution curves for the column experiments, a mass transfer model was developed that incorporates the influence of pore structure on transient dissolution of NAPL blobs:

\[ Sh' = \alpha \text{Re}^{\beta_1} \text{Ca}^{\beta_2} U_i^{\beta_3} \left( \frac{\theta_n}{\theta_{n0}} \right)^{\beta_4} \]  

(1)

where \( Sh \) is the modified Sherwood number \( \left( k_L a d_{50}^2 / D_m \right) \), \( \text{Re} \) is the Reynolds number, \( \theta_{n0} \) is the initial volumetric fraction of NAPL in the system, \( \text{Ca} \) is the normalized grain size, \( \theta \) is the normalized grain size, and \( U_i \) is the uniformity index for the porous medium. The coefficients, \( \alpha, \beta_1, \beta_2, \beta_3, \beta_4 \) were
determined by regression of the elution data. $\beta_4$ was dependent upon blob shape and thus porous medium characteristics. Blob distributions were incorporated into the model to describe NAPL dissolution rates. The theta model is applicable to other systems in the literature to explain NAPL dissolution. The primary limitation of the model is that it cannot be applied to NAPL entrapment and dissolution in heterogeneous porous media.

In the paper by Imhoff and Miller (1996), the authors described model predictions and examined dissolution fingering at residual NAPL and how it might affect the rate of NAPL removal. The accompanying paper Imhoff et al. (1996) used column experiments and a flow cell to study the effects of porous medium structure, Darcy flux, initial residual NAPL saturation, median particle diameter, gravity and NAPL composition on dissolution fingering and relate back to the modeling predictions. The NAPL in the experiments was uniformly distributed throughout the entire apparatus and water was the flushing agent. Fingering was important when looking at realistic groundwater velocities and large-scale experiments. Also, fingers grew at a faster rate for smaller NAPL saturations and for larger Darcy fluxes. The experiment with largest particle diameter did not exhibit fingering like the smaller diameter experiments. Three criteria were necessary for dissolution fingering: the length of the dissolution front must be less than the length of the region of NAPL residual, at least $11\,e$-fold times ($e$-fold represents the growth rate multiplied by dimensionless time) must have occurred, and the width of the NAPL region perpendicular to aqueous phase flow must be larger than the cutoff wavelength. Dissolution fingers was shown in the experiments to dramatically affect the distribution and NAPL saturation and aqueous phase concentrations. However, further investigating
would be needed to expand these results to different scales and especially to heterogeneous systems.

A handful of studies have investigated NAPL dissolution in systems that were physically homogeneous but heterogeneous with respect to effective permeability due to the presence of non-uniformly distributed NAPL. Anderson et al. (1992) emplaced a column of sand with residual concentrations of PCE within a larger chamber of the same media and flushed water through it. Reduction of mass removal due to reduced permeability was determined to be minimal. Effluent concentrations were less than solubility, but PCE concentrations in the middle of the source zone were at or near solubility. The possible causes of low effluent concentrations were attributed to preferential formation of thin pools rather than fingers of PCE, dispersion during transport, or dilution by uncontaminated water.

Geller and Hunt (1993) investigated the dissolution of residual organic liquids in saturated, homogeneous porous media under non-equilibrium conditions. Column experiments were packed with homogeneous glass beads. NAPL was slowly injected into the center of the water-saturated column with either toluene, benzene, or both. Columns were flushed with water at a constant velocity, and mass was calculated from integrating under the elution curve. The elution curve was successfully fit to a quantitative model when the NAPL was modeled as discrete spheres. Experimental observations were the following: increasing aqueous concentration during initial water flooding, quasi-steady effluent concentrations as the mass transfer zone propagates downstream, and the decline in effluent concentration as the NAPL region shrank.
For a series of flow cell experiments, Saba and Illangasekare (2000) created an organic contaminant zone within the same media. Aqueous samples were taken downstream of the zone at different flow rates. It appeared that dissolution fingers occurred; the flushing water infiltrated the contaminated zone as multiple fingers instead of a uniform front. As flushing velocity increased, aqueous concentrations increased which was attributed to increased pressure head able to penetrate the organic zone. Increased flow through the contaminated zone led to increased dissolution. Based on their flow cell results, a natural dissolution phenomenological model was proposed. It was noted that their study results demonstrate possible errors that might occur when model parameters are obtained from column experiments to predict dissolution in field systems.

A series of the experiments by Powers et al. (1998), Nambi and Powers (2000), and Nambi and Powers (2003) varied initial NAPL saturation in column and flow cell experiments and were physically heterogeneous. Powers et al. (1998) examined NAPL dissolution rates from a coarse media surrounded by a finer grained sand in column and flow cells experiments. The basis for the experiment was to provide a better understanding of the important mechanisms controlling NAPL dissolution in well defined and characterized heterogeneous media. The zones had an initially high NAPL saturation (0.72 and 0.92). Increased NAPL saturation caused a longer period of constant concentration at the beginning of the experiment and increased the period of time required to dissolve the greater mass of NAPL. Water flowing through the coarse NAPL zone was responsible for dissolution. Dissolution rates increased with time as effective
permeability increased due to NAPL removal; however, the flushing time required to remove the NAPL greatly increased compared to the homogeneous system. In homogeneous column systems, mass transfer rates were dependent upon: aqueous phase velocity, NAPL saturation, and mean particle size (Powers et al., 1998).

Nambi and Powers (2000) conducted similar experiments with NAPL injected into a coarse lense surrounded by finer sand. To prevent pore drainage from the coarse source zone, O-toluene was used since its density is almost the same as water. Effluent concentrations were mostly affected by intrinsic permeabilities and NAPL saturations. Mass transfer could be limited by a decrease in the NAPL interfacial area and increases in the aqueous phase velocity. Also, mass transfer processes could be effected by the exterior surface area of the contaminated zone. Mass transfer was important at the beginning of the experiment when the majority of water was flowing around the course source zone due to the reduced effective permeability associated with the large NAPL saturation.

Brusseau et al. (2000) conducted experiments in a flow cell with zones of residual NAPL to examine the effects of nonuniform distributions of NAPL saturation, porous-media heterogeneity, and sampling method on the magnitude of aqueous concentrations measured under dynamic conditions of flow and transport. The flow cell contained two zones with residual NAPL. For zone 1, the medium had a lower-K than the surrounding media and for zone 2 the medium was the same as the media. Dissolution from zone 2 occurred uniformly across the upgradient edge and moved downgradient along the longitudinal axis as well as from the upper and lower boundaries. Zone 1 which had a
much smaller effective permeability showed limited dissolution at the perimeter of the TCE saturation zone. Aqueous concentrations immediately downgradient of zone 2 were at or near solubility while concentrations for zone 1 were four times lower than solubility. Effluent samples from vertically integrated ports were much less than the point samplers immediately behind the contaminated zones indicating significant dilution effects; thus, the presence of a NAPL phase can not be ruled out even when aqueous concentrations are only a fraction of the expected equilibrium concentrations.

Brusseau et al. (2002) examined the effect of nonuniform distributions of immiscible organic liquid on dissolution behavior. Their focus was on the condition dependency of dissolution rate coefficients associated with applying mathematical models of differing complexity to measured data. The experimental setup was the same as Brusseau et al. (2000). A three-dimensional mathematical model analyzed the effects of immiscible-liquid distribution, permeability variability, and sampling effects. The complexity of the model determined the magnitude of the dissolution rate. When the three-dimensional model was used that accounted for immiscible-liquid distribution, permeability variability, and sampling effects reasonable aqueous concentrations, saturation distributions, and mass removals were well predicted. Using simpler models that did not incorporate are the variables required much larger rate coefficients. From this, it was shown that local-scale dissolution rate coefficients which represent local-scale dissolution processes can be used in models to successfully predict dissolution and transport of immiscible-liquid constituents at larger scales. Also, it was shown that
nonuniform distribution, permeability variability, and sampling dilution control dissolution behavior.

Considerable research has been conducted examining NAPL dissolution; however, there still exist NAPL dissolution research issues that require further investigation. The role that physical heterogeneity plays in NAPL dissolution is one such topic. Few laboratory experiments have been conducted that investigate the role heterogeneity plays in NAPL dissolution. Thus, further research is required that examines how heterogeneity affects NAPL dissolution especially when NAPL is located in a lower-K matrix. Specifically, how is rate-limited dissolution behavior affected when low residual saturations of NAPL are located in lower-K material. This research examines this issue via column and flow cell experiments.
**Literature Review: In-situ Chemical Oxidation**

In-situ chemical oxidation (ISCO) is an emerging technology that has been developed to augment traditional methods of remediation like pump and treat. Pump and treat technology consists of pumping water from the plume and treating the contaminated water at the surface before discharging it. The ISCO process involves injecting an oxidant solution into the groundwater and/or vadose zone that enables direct contact between the oxidant and the contaminant source zone/plume. By-products are innocuous substances including water, carbon dioxide, chloride, and precipitates (manganese oxide). Since it is an emerging innovative technology, ISCO experimentation by laboratory experiments and pilot-scale studies has been on-going and will be required before full scale deployment of ISCO will be permitted. ISCO has the potential for remediating a wide range of contaminants including but not limited to the following: BTEX (benzene, toluene, ethylbenzene, and xylenes), tetrachlorothene (PCE), trichloroethene (TCE), dichloroethenes (DCE’s), vinyl chloride (VC), MTBE (methyl- tert-butyl-ether), and PAH (polyaromatic hydrocarbons) compounds (ITRC, 2002).

ISCO has a number of advantages over traditional remediation technologies like pump and treat. Instead of withdrawing contaminated water that would need to be treated at the surface, ISCO eliminates this step by treating the contaminant at the point of contact with the contamination; thus, large quantities of waste do not need to be treated or disposed of on the surface. ISCO is a rapid treatment process that is designed to degrade the contaminant source zone instead of contaminant plume. Some ISCO reagents i.e. \( \text{KMnO}_4 \) are persistent in the groundwater and can transport with the natural flow treating
a large area. Unlike pump and treat, little equipment is required except during the injection process. It is worth noting that diffusive properties could enable ISCO oxidants to come into contact with contaminants in lower-K zones and thus remediate problematic long-term sources.

There are several different types of ISCO reagents including hydrogen peroxide and iron (Fenton’s reagent), ozone, and sodium/potassium permanganate. Hydrogen peroxide alone is an effective oxidizing agent. However, in order to degrade organics in a reasonable time frame hydrogen peroxide can be amended with a metal catalyst like iron know as Fenton’s reagent. The process involves the production of a hydroxyl radical which serves as a powerful oxidizing agent. This process is fast acting and non-specific. A side benefit is the production of oxygen during hydrogen peroxide decomposition that would then be available for bioremediation.

Another oxidant available for ISCO is ozone (O₃). Ozone is a strong oxidant that oxidizes organic contaminants by two different methods: direct oxidation or by generation of free radical intermediates. Ozone must be generated on-site and upon decomposing also produces oxygen that can be beneficial for microbial communities. However, ozone is a sterilizing agent over extended periods of time or in large doses, so caution is needed to prevent destruction of indigenous microbial populations.

The final group of ISCO agents currently in use are permanganates. Two typical forms of permanganates are available—potassium and sodium. Potassium permanganate (KMnO₄) has a long history as a non-selective oxidizing agent in drinking and waste water. Potassium permanganate is one of the most common oxidants used to precipitate
soluble iron and manganese. (Hamann et al., 1990). Furthermore, chemical oxidants like KMnO₄ are also used in water treatment for color removal, taste and odor control, biological growth control in pipelines, flocculation aids, disinfection, and reduction of specific organic compounds (Hamann et al., 1990). Taste and odor issues are the major two complaints of potable water by water consumers (Bruchet and Duguet, 2004), and KMnO₄ has often been used for taste and odor problems and color removal. Relatively high doses are often required though. Due to the sorptive properties of manganese dioxide for certain organic substances, it is thought that its formation may play an important part in the removal of organics during the KMnO₄ treatment process (Lalezary et al., 1986). Careful control of KMnO₄ dosage is required, however, to prevent pink water from entering the distribution system.

Using KMnO₄ as a remediation agent has gained momentum recently, but has been investigated for over a decade. Vella and Veronda (1992) evaluated Fenton’s reagent and KMnO₄ for TCE remediation in controlled laboratory experiments with distilled and well water. It was determined that both effectively mineralized TCE and could be used in soil and groundwater treatment. Also that KMnO₄ is slower than Fenton’s reagent but applicable over a wider pH range.

Gates and Siegrist (1995) investigated TCE degradation of H₂O₂ in slurry reactors to assess the potential for in-situ oxidation of VOC contaminated soil. They found that with a 1.5% solution of H₂O₂ as much as 98% of the TCE could be degraded and stated that chemical oxidation destruction efficiency would probably be limited by the ability to deliver oxidant to the contaminant source. Later, Gates-Anderson et al. (2001) compared
KMnO₄ and H₂O₂ effectiveness in laboratory slurry experiments for a range of VOCs (PCE, TCE, and TCA) and SVOCs (naphthalene, phenanthrene, and pyrene). KMnO₄ constantly degraded 90% or more of the alkene VOCs (TCE and PCE) and 99% of the polyaromatic SVOCs for the soil slurries. H₂O₂ was more sensitive to the soil slurries and even when augmented with iron only degraded 90% of the SVOCs. Neither was effective in removing TCA, and multiple oxidant additions did not increase VOC treatment efficiency.

Schnarr et al. (1998) conducted laboratory experiments and a field scale experiment to investigate the degradation of PCE and TCE. KMnO₄ was flushed through columns with residual TCE and PCE and both were rapidly degraded to CO₂ and chloride. Chloride was determined to be an effective means of monitoring the oxidation process. Two field experiments were conducted within a section of the CFB Borden aquifer. In the first experiment complete source zone removal was achieved, but in the second field experiment, a heterogeneous source, only 60% of DNAPL mass was removed. Dissolution processes were determined to be the principle determinant of DNAPL mass removal rates and that the rate of dissolution during an oxidant flush was more rapid than during the water flush. In conclusion, it was stated that ISCO has the potential to be an effective means of removing mass at rates greater than conventional pump and treat strategies; however, 100% removal of DNAPL would be unlikely.

McKay et al. (1998) evaluated the feasibility of using KMnO₄ to treat residual TCE in a low-permeability strata embedded within silt and clay zones. ISCO was considered because of the depth of the TCE in the unsaturated zone, 15 to 35 feet below
ground surface. Two sites were selected for the pilot test and evaluated for extent of TCE destruction, changes to soil chemistry and permeability, and permanganate distribution. Core samples were collected to visually determine strata and identify layers with high moisture content. A 1.5% solution was prepared from tap water and injected via direct-push wells. Over a 53 day period 200 gallons were injected into site 1 and over a 21 day period 358 gallons were injected into site 2. Results were mixed, and it was thought that a larger volume of KMnO₄ solution needed to be injected for complete cleanup.

Siegrist et al. (1999) examined the effectiveness of ISCO at an old land treatment site with low permeability but naturally fractured media. It is noted that there needs to be effective in situ methods for contaminants of concern in low permeability media. Two test cells were constructed. In the first cell, KMnO₄ particles were suspended in a mineral-based gel which was used to create three permanganate-filled fractures. In the second cell the KMnO₄-filled fractures yielded a broad zone of reactivity and the degradation potential for high TCE levels was sustained after 10 months. The MnO₄⁻ ions were transported via diffusion throughout a broad region of the test cell. This could prevent the further release of TCE into the atmosphere and aquifer as well as degrade the TCE in the lower permeability media. It is noted that further work is needed to completely understand all processes involved and implementation techniques.

Nelson et al. (2001) injected KMnO₄ solution into an unconfined aquifer contaminated with PCE at Canadian Forces Base Borden, Ontario. The geology consists of an unconfined, carbonate mineral-containing sand aquifer. Soon after injection two distinct KMnO₄ geochemical zones formed dependant on the amount of PCE present in
the aquifer. In the first zone, KMnO$_4$ solution was completely utilized and noticeable increases of chloride and hydrogen occurred. The increase in hydrogen ions was neutralized by dissolution of carbonate minerals which in turn increased calcium concentrations. In the second zone where there was less PCE, KMnO$_4$ solution persisted for more than 14 months and the pH of the porewater increased between 9 to 10. Manganese oxides were collected from the grains and analyzed with energy-dispersive X-ray spectroscopy which showed that the coatings contained many impurities including Al, Ca, Cl, Cu, Pb, P, K, Si, S, Ti, U, and Zn. Coating thickness was on the order of 1 µm thick and the calculated decrease in porosity and permeability was not considered significant especially when dissolution of carbonate minerals were occurring. Carbonate presence was beneficial because Mn(VII) was reduced to Mn(IV) instead of Mn(II), and the Mn(IV) form will be immobilized in the aquifer as Mn oxide as long as the system does not become more reducing. Manganese oxides are well known to have the ability to absorb a variety of cations on their surfaces (e.g. Goldberg, 1954; Tebo et al., 1997; Marble, 1998).

Crimi and Siegrist (2003) also investigated the effects of KMnO$_4$ on metal distribution in the subsurface and the potential effects on hydraulic and geochemical transport of post-oxidation groundwater through an uncontaminated aquifer via column experiments and field observations. From their study, they showed that ISCO can affect subsurface geochemical conditions and cause elevated concentrations of Mn, Cr, and Ni, but this was related to the natural aquifer materials, mass of permanganate added, and DNAPL mass. Contaminated sites with high levels of NAPL can expect extensive
amounts of Mn oxides which can be beneficial when acting as sorption sites for heavy metals or be detrimental by increasing long-term Mn concentrations. They, however, point out that the deposition of Mn oxides can occur without having a harmful effect on the hydraulic conductivity. In the same paper, they investigated possible affects of mobilizing metals after KMnO₄ flushing at a field site (Cape Canaveral Air Station, Florida). High concentrations of KMnO₄ (1 to 2%) were injected into the subsurface as part of a pilot-scale project. There was the potential for long-term immobilization of a portion of the introduced manganese and no treatment-induced loss of permeability due to manganese oxide formation. Elevated levels of manganese, chromium, and nickel concentrations were detected at the treated region, which can be attenuated by uncontaminated aquifer sediments.

Crimi and Siegrist (2004) examined chromium sorption by manganese oxides formed from the degradation of TCE by KMnO₄. They found that Cadmium, Cd, sorption onto manganese oxides is a function of several factors including particle concentration, pH, presence of Ca and maybe the rate of particle generation and agglomeration. After 6 months, desorption of Cd occurred in studies with low initial KMnO₄ condition but not with higher initial KMnO₄ conditions. It is important to consider the subsurface geochemical conditions like pH, cation and anion content, reactant concentration and even reactions rates when determining sorption of Cd onto newly formed Mn oxides since they could act as a long term metal contaminant source.

Yan and Schwartz (1999) examined the degradation of chlorinated ethylenes (PCE, TCE, the three isomers of DCE) via permanganate in batch kinetic tests. The
degradation process was rapid with pseudo-first-order rate constants. At \( \text{MnO}_4^- = 1 \text{ mM} \), kinetic rates ranged from \( 4.5 \times 10^5 \) to 0.03 s\(^{-1}\) with rate increasing as the number of chlorine molecules decreased on the molecule and half-lives ranging from 0.4 minutes to 4 hours. TCE degradation was determined to be a second-order reaction over a wide pH range (4 to 8). In order to compensate for total organic carbon competition with TCE, a large quantity of \( \text{MnO}_2 \) would promote the reaction between TCE and permanganate.

Hood et al. (2000) also measured oxidation rates of PCE with \( \text{KMnO}_4 \) over a range of excess oxidant. PCE and \( \text{KMnO}_4 \) reaction was determined to be first-order with respect to both and an overall reaction rate coefficient of \( 2.45 \pm 0.65 \text{ M}^{-1} \text{ min}^{-1} \). Results also confirmed that \( \text{KMnO}_4 \) was able to degrade PCE to the maximum groundwater concentration and can be used in a transport model to determine the effectiveness of \( \text{KMnO}_4 \) flushing.

Reitsma and Dai (2000) investigated the enhancement of interphase mass transfer of dissolved NAPLs from the NAPL phase to the aqueous phase and the enhancement of dispersive mass transport from a NAPL zone due to destruction of dissolved NAPL compounds. Since PCE and TCE reaction rates are slow, permanganate was not expected to increase local mass transfer coefficients. However, permanganate may significantly increase ‘local scale’ reaction and increase mass transfer from dead-end pores. Mass transport enhancement factors were 45 for PCE and 5 for TCE with a permanganate concentration of 63.3 mM. Therefore, active flushing with permanganate of a NAPL zone would be expected to increase mass removal from pools.
Schroth et al. (2001) conducted a series of nearly meter long column experiments. The column was packed with a homogeneous sand and TCE NAPL was imbibed into the column. After a series of water flushes, residual TCE remained, which was then flushed with either a 5 mM KMnO$_4$ solution or a mixture of 5 mM KMnO$_4$ and an oxidant buffer solution. The purpose was to determine if TCE oxidation and the subsequent CO$_2$ and MnO$_2$ by-product formation would affect hydraulic properties. They concluded that KMnO$_4$ initially increased aqueous TCE concentrations by being consumed in a fast oxidation reaction with TCE. However, aqueous head increases and reduction in relative permeability locally due to by-product formation and outweighed the early benefit of elevated aqueous concentrations. Also interesting to note was that even at low KMnO$_4$ concentrations, 5 mM, detrimental effects to permeability were noticed. When a buffer was added to control acidity, aqueous head and relatively permeability increases were much less which would mean that ISCO would probably be more effective in buffered natural systems. Finally, transferring their results to flow cell apparatus or to the field would mean that the local increases in permeability would create areas that the flushing solution would by-pass and NAPL would remain as long term source zones instead of being oxidized.

Conrad et al. (2002) constructed a flow cell with varying layers of media to mimic a natural system. DNAPL was injected at the surface and allowed to migrate downward, which resulted in a series of DNAPL pools. When KMnO$_4$ was flushed through the flow cell, a manganese oxide rind formed on the outside of the pool and hindered contact
between the DNAPL and flushing solution. During flushing it was noticed that flow in the region where the rinds formed around the DNAPL decreased as well.

Struse et al. (2002) looked at the transport of permanganate into low permeability media contaminated with TCE with intact cores. KMnO$_4$ was added to a cell and transport was observed for one month. It was determined that permanganate can migrate due to diffusion and have little effect on the pore structure. Also, soil organic matter remained after 40 to 60 days of exposure. The formation of MnO$_2$ did not affect the apparent matrix tortuosity even with TCE present. KMnO$_4$ was able to degrade 97% of the TCE mass added to the silty clay low permeability media.

Since it has been observed that by product formation of manganese oxides can affect permeability and ultimately the success of ISCO in laboratory experiments, Li and Schwartz (2004) examined the mineralogy of the manganese oxide formed and investigated methods that could be used to dissolve it. It was determined that the manganese oxides that formed from KMnO$_4$ by oxidation with TCE were a semi-amorphous potassium-rich birnessite. This form of birnessite is relatively active and can react with organic and inorganic matter. Citric acid, oxalic acid, and ethylenediaminetetraacetic acid (EDTA) were added to batch experiments to determine if the organic acids could dissolve the Mn oxides. All the organic acids did dissolve the Mn oxides, which could prove to be important if reduced permeability occurs.

Hrapovic et al. (2005) examined if ISCO and biodegradation would be effective in sequence. Specifically they were interested if permanganate flushing affected the indigenous microbial activity, if biostimulation after permanganate flushing would be
sufficient for bioremediation, and finally to determine the impact of bioaugmentation with halorespiring microorganisms. Experiments were done in columns with natural soils from Launch Complex 34 (Kennedy Space Center, FL). TCE was imbibed into the columns and flushed to obtain residual TCE saturation. KMnO₄ was flushed at 2,500 mg/L for 22 days. Bioaugmentation consisted of mixed bacterial cultures. Columns with KMnO₄ flushing experienced enhanced TCE DNAPL dissolution based on chloride effluent concentrations. After KMnO₄ flushing, water was flushed through the columns and TCE concentrations rebounded indicating to the authors that a polishing technology needs to be implemented after KMnO₄ flushing. Bioaugmentation was not substantially successful in promoting biodegradation of TCE until groundwater was used in conjunction with ethanol and acetate; however, it was noted that bacteria could have been introduced by using the groundwater. Nonetheless, DNA levels were similar for control and permanganate flushed experiments. Sequential treatment of ISCO followed by biostimulation and bioaugmentation can be a feasible TCE treatment. KMnO₄ would be expected to adversely affect the indigenous microbial population and either migration from untreated areas or groundwater flushing would be required for significant microbial activity to be observed.

To summarize, ISCO with KMnO₄ has gained notice as an innovative technology for source zone remediation of NAPLs. Laboratory experiments have investigated the ability of KMnO₄ to degrade NAPLs, the reaction rates, by-products affects, and how indigenous populations could be affected. Laboratory research has also investigated column and flow cell dynamics especially involving by-product. It has been observed
that Mn oxide formation is an important issue that might need to be addressed in field situations since permeability can be decreased. Pilot scale studies have investigated the effectiveness of KMnO₄ flushing, possible reductions in K, and mobilization of metals. Further information on ISCO can be found in Seol et al. (2003) which is a review paper examining the impact of physical and chemical heterogeneity.

A substantial number of laboratory and field experiments have been conducted examining ISCO as a possible innovative remediation technology for chlorinated hydrocarbons. ISCO has shown promise as a source zone in both field and some laboratory experiments; however, questions still remain regarding the effectiveness of ISCO using KMnO₄. For instance, it still needs to be determined if ISCO by-products have substantial detrimental effects that might inhibited remediation. Additional research is needed to establish optimal applications conditions for both laboratory and field use. Of particular interest is examining the effectiveness of ISCO for heterogeneous, deep contamination sources. Specifically, is KMnO₄ solution able to penetrate into a lower-K zone with residual NAPL or will by-products inhibit penetration. This research examines these issue via flow cell experiments and a pilot-scale field project at the Tucson International Airport Superfund Site.
Overview of Format

Chapter 2 is a summary of the results and most important findings from this research. The research is divided into the three appendixes A, B, and C. A brief overview of each as well as contributions of different authors follows.

Appendix A examines TCE NAPL dissolution for physically homogeneous and heterogeneous zones in column and flow cell experiments using water as the flushing agent. Effluent curves and mass flux were analyzed for the varying systems. All dissolution experiments from non-uniform lower-K zones were conducted by the author. G. R. Tick provided control data for comparison from two uniform column experiments. Z. Zhang conducted the modeling simulations. M. L. Brusseau oversaw and guided the project as research advisor.

Appendix B examines ISCO using KMnO₄ in a physically heterogeneous flow cell. Zones consisting of lower-K material containing TCE NAPL were flushed first with KMnO₄ solution and then followed by a water flush. Mass flux was examined and compared to identical experiments with water as the sole flushing agent. The author conducted all experiments and analysis. M. L. Brusseau supervised the project as research advisor.

Appendix C discusses the pilot-scale project using ISCO with KMnO₄ at the Samsonite Building Area, which is part of the Tucson International Airport Authority Superfund Site. Three separate topics were investigated: core analysis, bench-scale experiments, and pre- and post-injection monitoring. The author wrote the proposal for the field project; oversaw and collected core samples and pre-injection groundwater
samples; conducted all laboratory batch experiments; advised during KMnO4 injection; and oversaw and collected post-injection monitoring. L. Fuhrig assisted during field sampling. M. Plaschke supervised injection well drilling and injection equipment. M. L. Brusseau oversaw and guided the project as research advisor.
CHAPTER 2. PRESENT STUDY

The methods, results, and conclusions of this study are presented in the papers appended to this dissertation. The following is a summary of the most important findings in this document from laboratory and field experiments. Implications and possible future research are also discussed.

The research conducted in the following three papers was diverse. Experimental scale ranged from column experiments to flow cell experiments to a pilot-scale remediation project. Also, experiments varied from physically homogeneous to physically heterogeneous model systems to an actual field site. Additionally, the location of residual NAPL in the experiments varied. The source zone was uniformly distributed in the control experiments, non-uniformly distributed as localized cubes or zones in lower-permeability (K) media, and distributed within heterogeneous natural media at the field site. However, the overriding purpose of the research deals with investigating NAPL dissolution and how NAPL location can affect the observed elution behavior, especially when it is located in a lower-K media. The term lower-K media does not necessarily represent an extreme case like a clay aquitard. Rather, it could be a silty-sand or a clayey-silt lens located in a sandy aquifer. The point is that the subsurface is heterogeneous by nature, be it subtle or distinct, and the location of the NAPL within the source zone is hypothesized to be an important factor influencing contaminant mass transfer and the efficacy of remediation efforts. This research provides insights into the role that NAPL distribution and location plays in mass flux and remediation. Of
particular interest in the first paper was the dissolution of residual NAPL trapped in lower-K media. Then, the effectiveness of in situ chemical oxidation (ISCO) for residual NAPL trapped within lower-K media was examined. Finally, ISCO using KMnO₄ was implemented for a perched aquifer system with 1,1-dichloroethene contamination located in lower-K media.

The objective of the first paper (Appendix A) was to examine NAPL dissolution for a variety of conditions to gain a better insight into physical processes that could affect dissolution. First, NAPL dissolution was compared between uniformly and non-uniformly distributed NAPL in column and flow cell experiments. Then NAPL dissolution was compared between NAPL located in physically homogeneous and heterogeneous zones in column and flow cell experiments.

It was observed that NAPL dissolution for uniformly distributed NAPL experiments exhibited more ideal mass transfer behavior than NAPL dissolution for non-uniformly distributed experiments. Ideal mass transfer behavior is based on local equilibrium assumptions that predict that effluent concentrations will remain at solubility until all the NAPL is dissolved, at which point effluent concentrations will rapidly decrease to zero. While in controlled experiments this assumption might work, in general this is not the case due to several factors that create non-ideal mass transfer behavior including: rate-limited dissolution, limited contact with advecting water, non-uniform distribution, location of NAPL, NAPL pools, and sampling-associated dilution. For the uniformly distributed NAPL control experiment, effluent concentrations were initially at solubility during the steady-state stage as predicted by local equilibrium assumptions.
When elution shifted to the transient stage, instead of immediately decreasing to zero, effluent concentrations gradually decreased. This non-ideal behavior was likely caused by the reduced interfacial area of the DNAPL pools versus residence time of the water flow.

Experiments involving non-uniformly distributed NAPL exhibited non-ideal mass transfer behavior throughout the experiment from sample dilution. All of the flushing water was not coming into contact with the residual NAPL zone, so effluent concentrations were not at solubility during the “steady-state” stage. Also, residual NAPL could have decreased effective permeability for water flowing through the contamination zone leading to advecting water by-passing the source zone. To determine if residual NAPL reduced effective permeability enough to affect water flow, the initial aqueous relative permeability ($k_{i0}$) was calculated for each experiment. For the homogenous column, $k_{i0}$ was 0.59, so water flow in the residual zone could have been decreased. However, in the homogeneous flow cell experiment, $k_{i0}$ was 0.80; therefore, reduced effective permeability was probably not an issue. As NAPL dissolution progressed, effective permeability would increase for the water, and would decrease in significance. However, like in the uniformly distributed experiments, reduced interfacial area of the NAPL pools versus residence time was important during the transient stage.

Experiments employing a physically heterogeneous system contained NAPL in lower-K zones. In addition to the above mentioned factors contributing to non-ideal mass transfer, NAPL dissolution was limited by by-pass flow associated with advecting water flowing around the lower-K source zone. The $k_{i0}$ values for the heterogeneous
experiments ranged from 0.59 to 0.66; therefore, reduced effective permeability probably also decreased the advecting water through the residual zones. Unlike other non-ideal variables that can change as NAPL dissolves, the reduced water flux caused by the lower-K medium is independent and constant throughout flushing. As source zone heterogeneity increases, so does non-ideal mass transfer behavior. Dissolution from lower-K zones is a much slower process and traditional methods for remediating aquifers to drinking water standards are not realistic.

Mass flux reduction versus percent mass removal was analyzed in the dissolution experiments. Mass flux is a measure of spatially integrated total mass discharge and a tool that has be used to determine source zone removal. Systems with homogeneously distributed NAPL and physically homogeneous exhibited the most ideal mass transfer. The mass flux did not change until a majority of the NAPL mass had been removed. Systems with either non-uniformly distributed NAPL or physically heterogeneous conditions exhibited greater non-ideal mass transfer behavior. Mass flux decreased quickly with little change in mass reduction, or mass flux constantly decreased as mass was reduced. Mass flux reduction was unique for each experiment, but principally non-ideal mass transfer conditions increased with the complexity of the system i.e. heterogeneity and non-uniform NAPL distribution.

One, two, and three-dimensional models were employed to gain greater insight into NAPL dissolution phenomenon. For the 3-D experiments when NAPL location and mass were known, local-scale parameters for the NAPL zones could be used to accurately describe the dissolution behavior. The mass transfer coefficient was obtained from
uniformly distributed NAPL column experiments for the same medium. However for the
1-D and 2-D models, which were simplified representations of the systems, a lumped
mass transfer term was required to adequately describe dissolution.

These experiments and consequent modeling have increased understanding of
source zone dissolution behavior when NAPL is located in lower-K zones and
subsequently demonstrated effects on non-ideal mass transfer behavior. For uniformly
distributed NAPL, mass flux shows little change until almost all of the mass has
dissolved following ideal mass transfer behavior. Non-uniformly distributed NAPL in
physically homogeneous systems initially exhibits non-ideal mass transfer behavior due
to reduced effective permeability and dilution. Non-uniformly and physically
heterogeneous systems exhibited the greatest variations in mass flux and varying degrees
of non-ideal mass transfer due to by-pass flow. Non-ideal mass transfer was affected the
most by NAPL in lower-K zones. Based on the experimental results and analysis, relying
solely on mass flux to determine NAPL mass existing in a system or effectiveness of
remediation could be a deceptive indicator depending on NAPL location. As the results
exhibit, NAPL located in lower-K media had a reduction in mass flux with small changes
in mass reduction, which indicates mass flux could conceivably be misconstrued. In
natural porous media, knowing the location of NAPL would enable a better understanding
of appropriate methods for remediation and possible prevent underestimation of NAPL
massed based solely on mass flux. NAPL location would be an important factor to
consider when examining remediation technologies and determining specific
effectiveness.
The objective of the second paper (Appendix B) was to investigate the effectiveness of in situ chemical oxidation (ISCO) using KMnO₄ for remediating NAPL trapped within a lower-K media. In the first paper, non-ideal mass transfer properties were discussed that demonstrated difficulties associated with remediating NAPL located in lower-K media. ISCO using KMnO₄ as the oxidant has been considered a source zone remediation technology that has been gaining acceptance, and the effectiveness of ISCO for treating NAPL located in lower-K zones needs to be further investigated. Also, determining the ability of KMnO₄ to distribute and persist within a heterogeneous system could aide in determining its effectiveness in natural porous media. When KMnO₄ oxidizes compounds such as TCE, the by-products, manganese oxides and carbon dioxide, could conceivably inhibit further oxidation due to limiting contact. Examining any detrimental effects by these by-products in heterogeneous systems would provide better insight into methods for controlling reduced effective permeability especially for residual systems. Finally, the effectiveness of source zone remediation needs to be examined in terms of mass flux. As exhibited in appendix A, mass flux can be misleading as a true indicator of short term remediation effectiveness. Further elucidation of mass flux after ISCO would also provide better understanding of mass flux data from field demonstrations projects.

A flow cell experiment was conducted with non-uniformly distributed NAPL located in lower-K zones. KMnO₄ solution was flushed through the system. Effluent concentrations were monitored and visual observations were made of the interaction between the contaminated zone and the flushed KMnO₄ solution. It was observed that
although manganese oxides formed around the lower-K zones with residual TCE, KMnO₄ solution was still able to penetrate the lower-K zones by the continued formation of manganese oxides inside the zones. Precipitate and carbon dioxide formation did not appear to hinder KMnO₄ solution penetration inside the lower-K zones where the residual TCE was located. Given enough time, it has been suggested that KMnO₄ solution would be able to penetrate the entire lower-K zones and degrade the NAPL.

After the KMnO₄ solution penetrated into the lower-K zones, water was flushed through the flow cell to determine if NAPL mass reduction affected the mass flux of the system compared to the mass flux of a similar experiment that only had water flushing. Even though NAPL mass was reduced in the flow cell, mass flux in the short term was similar to the solely water flushing experiment. This observation is important and necessitates further examination. Visibly, NAPL mass was degraded indicated by the formation of manganese oxides at the peripheral of the zones and which also penetrated into the lower-K zone with time. However, manganese oxides formation did not appear to inhibit NAPL dissolution since mass flux was similar to the water flushing experiment. It is important to recognize that the manganese oxide formation did not appear to have any detrimental affect on KMnO₄ penetration into the lower-K zone. Other research has shown that manganese oxides can adversely affect the ability of KMnO₄ solution to contact the contaminant.

In the laboratory experiments, though, creating the opportunity for KMnO₄ to contact the contaminant was not only by advective forces. Diffusive forces also contributed between KMnO₄ pulses. It was observed between pulses that precipitates
continued to form inside the lower-K zones as well as form outside the lower-K zones. This was indicative of TCE dissolving from the lower-K zones to the surrounding media. These results are important when considering field applications. KMnO₄ would be initially injected into the source zone, but then allowed to distribute due to the natural gradient and not by induced gradients such as created in a pump and treat remediation system. Even if manganese oxide precipitates formed around areas where organic oxidation takes place, KMnO₄ solution would still be able to penetrate further into the media. Eventually the KMnO₄ in the flow cell was completely utilized and another pulse was injected into the flow cell exhibited the same results.

Mass reduction in the non-uniformly distributed and physically heterogeneous system did not appear to affect mass flux to any appreciable degree even though TCE mass was visible degraded in the short term. However, looking at the long term, the amount of water flushing that would be required for complete removal would be reduced because of the reduced mass. Therefore, relying on mass flux as an indicator of remediation effectiveness in the short term can be misleading as observed in these experiments. ISCO appears to be an effective remediation technology for heterogeneous sources since KMnO₄ would be able to contact the contaminant even if it was located in a lower-K zone.

The objective of the third paper (Appendix C) was to determine optimal conditions and the effectiveness of ISCO for 1,1-dichloroethene (DCE) in a perched aquifer system at the Samsonite Building Area part of the Tucson International Airport Authority Superfund Site in Tucson, Arizona. The field site has DCE contamination and
the approximate source zone area has previously been determined by soil gas sampling. The source zone has been thought to be in a heterogeneous perched aquifer system. This field site provides an excellent opportunity to transfer lessons learned from previous laboratory experiments to the field scale and examine the effectiveness of ISCO with KMnO$_4$ when the organic contaminant is located in lower-K sediments.

In previous laboratory research, it was determined that non-ideal mass transfer increases with non-uniform NAPL distribution and with heterogeneity. At the field site, the exact location of the organic contaminant was unknown, but it was believed that the source zone consists of a lower-K region in a perched aquifer adjacent to the water table of a local groundwater zone. Since aqueous concentrations from the monitoring well were below solubility it would be assumed that the field site is a non-uniformly distributed system with contaminant located in various media including both large and lower-K aquifer materials. Therefore, one of the main concerns using ISCO remediation on the site would be creating the opportunity for DCE and KMnO$_4$ to come into contact especially for the lower-K media.

Bench-scale experiments using core sediments determined that the reaction between DCE and KMnO$_4$ even at low concentrations was on the order of minutes. Furthermore, the natural oxidant demand of the aquifer was quite small since total organic carbon was low. Injection of KMnO$_4$ lasted for several weeks, and eight injection wells had over 250 kg of a ~1.7% solution of KMnO$_4$ injected into each injection well. The injection wells were screened in the vadose zone and the saturated zone. The hypothesis was that KMnO$_4$ solution entering the vadose zone would be able to have
increased distribution and percolate downward into the saturated zone creating the greatest possible distribution of KMnO$_4$ solution. Regular monitoring began before injection and continues. KMnO$_4$ solution currently exists in the monitoring and injection wells even though injection ceased on August 15, 2005. Persistent KMnO$_4$ is advantageous for source zone remediation in lower-K zones. Besides relying on strictly advective forces to transport the KMnO$_4$ solution to the contaminant source, diffusive forces would contribute to KMnO$_4$ transport and enable penetration into lower-K zones.

When KMnO$_4$ solution is no longer present in the injection and monitoring wells, an additional core will be collected from the source zone to examine distribution of KMnO$_4$ solution and manganese oxide formation in the aquifer. DCE sampling from the wells will resume when all the KMnO$_4$ solution has been removed due to transformation or transported due to natural groundwater flow from the injection area. The source zone remediation project will be deemed successful if DCE concentrations do not rebound or only rebound slightly after KMnO$_4$ has been flushed from the system.

To summarize, this research examines mass transfer limitations when NAPL is located in lower-K zones and discusses an innovative technology that can be used to remediate NAPL located in lower-K contaminant source zones. It was determined that NAPL dissolution was affected by non-uniform distribution when located in lower-K zones. Also, ISCO using KMnO$_4$ is a promising technology that appears to be able to penetrate lower-K source zones and sufficiently distribute in an aquifer given enough time. Developing better predictive models and understanding the underlying properties that control NAPL dissolution is an important step in optimizing remediation techniques.
Future work examining NAPL dissolution would build on flow cell experiments. Flow cell systems would be created to represent realistic heterogeneous systems with natural sediments. Residual NAPL would be emplaced in lower-K media and flushed with water. Incorporating in-situ monitoring of NAPL saturation via gamma ray attenuation or another technique would enable additional understanding of the NAPL dissolution processes for individual contaminated zones (e.g. Brusseau et al., 2000). Additionally, expanding to multi-component NAPLs like diesel or gasoline in lower-K zones would be studied. KMnO₄ flushing experiments would be incorporated with the dissolution experiments. Water flushing and KMnO₄ flushing would be alternated. Mass flux after a KMnO₄ flush would be compared with water flushing. The affects of KMnO₄ by-products on NAPL dissolution would be analyzed for variations between flushes. Also, long term affects on mass removal would be examined. Finally, additional field scale demonstration projects using ISCO would be located to further examine and understand the effectiveness of ISCO. This would include monitoring indigenous microbial populations before and after KMnO₄ flushing to determine if monitored natural attenuation (MNA) would effectively control any remaining organic contaminants.
REFERENCES


APPENDIX A: RESIDUAL IMMISCIBLE LIQUID DISSOLUTION FROM LOW PERMEABILITY ZONES: MASS FLUX COMPARISONS
RESIDUAL IMmiscIBLE LIQUID DISSOLUTION FROM LOW PERMEABILITY ZONES: MASS FLUX COMPARISONS

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ABSTRACT

Dissolution of nonaqueous phase liquid (NAPL) into the aqueous phase can be influenced by NAPL-water mass transfer, local-scale NAPL morphology and distribution, bypass flow, and dilution effects. The purpose of this research was to investigate residual non-aqueous phase liquid dissolution from non-uniformly distributed residual NAPL in physically heterogeneous systems. A series of experiments were conducted with a column and a flow cell with trichloroethene (TCE). Immiscible liquid zones were emplaced inside the apparatus and were then flushed with water. Mass transfer limitations increased as system complexity increased and changed during the lifetime of each experiment. For experiments conducted with uniformly distributed NAPL, limited contact between NAPL and advecting water was the most important mass transfer limitation. Additionally, effluent aqueous concentrations were not at solubility due to dilution from flushing water not coming into contact with the contaminated zone. For non-uniformly distributed NAPL, by-pass flow attributed to reduced intrinsic permeability was initially the most important factor affecting non-ideal mass transfer. Dissolution from non-uniformly distributed NAPL in lower-K zones was principally controlled by mass transfer limitations associated with flushing water by-passing the residual zone. Similar mass transfer limitations associated with previous experiments were present but not as paramount. Dissolution occurred at the peripheral and upgradient edge. Elution times greatly increased with heterogeneous complexity. Mass flux reduction was more non-ideal for non-uniform NAPL distribution versus uniformly distributed NAPL. Non-ideal mass transfer was greatest for non-uniformly distributed
NAPL which was located in lower-K zones. Heterogeneity was determined to be a major contributor to non-ideal mass transfer than cannot be overlooked when designing and implementing source zone remediation.
INTRODUCTION

Subsurface nonaqueous-phase liquids (NAPL’s) are immiscible organic chemicals that can cause long-term contamination of groundwater. NAPL’s include chlorinated solvents, fuels, coal tar and polychlorinated biphenyls (PCB’s). Free-phase NAPL can become entrapped in the subsurface and be a source for groundwater contamination. Immiscible liquids like trichloroethene (TCE) prove to be difficult to remediate for several reasons in the saturated zone including: limited solubilities, low immiscible liquid-water contact area, pore-scale rate limited mass transfer by-pass flow occurring when large immiscible liquid saturation, and preferential flow around low-hydraulic conductivity (K) zones (Brusseau et al., 2000). Knowledge of NAPL dissolution behavior under field conditions is important for conducting risk assessment and implementing appropriate remediation strategies for NAPL contaminated sites (Brusseau et al, 2000).

Few intermediate scale studies exist for NAPL dissolution with physically heterogeneous conditions. Experiments examining NAPL dissolution in physically homogeneous intermediate scale systems were conducted by Anderson et al. (1992); Geller and Hunt (1993); Imhoff et al. (1996); and Saba and Illangasekare (2000). Physically heterogeneous intermediate scale experiments have usually dealt with flushing with surfactants or in-situ chemical oxidation (i.e. Taylor et al., 2001; Conrad et al., 2002; Rathfelder et al., 2003). Other physically heterogeneous intermediate scale experiments injected NAPL into the system and allowed it to distribute throughout the system with pools forming on top of lower-K medium (Oostrom et al., 1999). In some cases
surfactant was added to the system allowing penetration of the NAPL into the finer
grained medium (Van Valkenburg and Annable, 2002). Previous research has examined
physically heterogeneous systems with finer media surrounding a NAPL entrapped coarse
NAPL into a coarse zone surrounded by finer grained sand. Water was flushed through
the system and effluent samples were collected and analyzed. Increased $S_n$ caused a
longer period of relatively constant effluent concentration at the beginning of the
experiment and increased the period of time required to dissolve the greater mass of
NAPL. TCE and o-toluidine were both injected into the zone and the only difference
between the two immiscible liquids was the total number of pore volumes required to
reach detection limits based on their solubilities. It was determined that water flowing
through the coarse NAPL zone was responsible for NAPL dissolution behavior. The
effect of entrapped NAPL on tracer experiments in heterogeneous systems was examined
by Barth et al. (2003). Physically heterogeneous intermediate-scale systems with NAPL
in lower-K zones surrounded by a coarser media was examined in Brusseau et al. (2002).
Intermediate scale system with NAPL in lower-K zones might have been largely been
overlooked since NAPL head might not large enough to overcome entry pressures in
saturated systems. However, immiscible liquids can be found in lower hydraulic
conductivity zones in saturated zones (Oostrom et al., 2003) especially in aquifers with
changing water table levels and can act as a long term source zone.

Examining the mass flux from a source zone and the changes with source zone
remediation efforts have recently gained attention (Soga et al, 2004; Falta et al, 2005).
Mass flux is defined as the spatial integrated rate of total mass discharge. Since it is difficult to assess the effectiveness of source zone remediation, the mass flux from the source zone has often been used. Depending on the heterogeneity of the system and the location of the NAPL in the source zone, simply relying on mass flux to determine the effectiveness of source zone remediation could be misleading. For instance, in an idealized homogenous system if NAPL mass removal decreases there is little effect on the mass flux until most of the NAPL is removed. If the system is non-ideal due to heterogeneity or non-uniformly distributed NAPL, a small amount of mass removal may quickly decrease mass flux reduction (Figure 1).

Immiscible liquid contamination continues to be a source of remediation problems; thus, the purpose of this paper was to examine the effects of nonuniform distributions of immiscible liquid and porous-medium heterogeneity on complete immiscible-liquid dissolution. Experiments were conducted to characterize TCE dissolution and mass flux with column and flow cell systems. TCE contaminated media were emplaced within the system and flushed with water. Effluent samples are collected during the course of the experiment. Variations in effluent break through curves are compared between the different systems as well as mass flux versus mass removal.
MATERIALS AND METHODS

All porous media used in the experiments are commercially available, natural sands obtained from Unimin Corporation (Le Sueur, MN). Three media with different mean particle diameters were used, 724 µm (20-30 mesh), 360 µm (40-50 mesh), and 172 µm (70-100 mesh). Relevant properties of the silica sands are reported in Table 1. The 724 µm sand was used as the flow-cell matrix, with the two finer media serving to create the lower-K zones. The porous ceramic cube was obtained from Fairey Industrial Ceramics (Newcastle-under-Lyme, United Kingdom) and physical properties are reported also in Table 2 (Whalley et al., 2001). TCE was ACS grade (Aldrich Chemical Col, Inc., Milwaukee, WI), and was dyed with certified Sudan IV (Aldrich Chemical Col, Inc., Milwaukee, WI) at a concentration of 100 mg/L. Dichloromethane (DCM) used in extractions was ACS/HPLC certified solvent (Burdick and Jackson, Muskegon, MI).

All column experiments were conducted in a flanged stainless steel MODcol (St. Lois, MO) model FMB-3010 column 7.6 cm in diameter and 9.8 cm in length. Media was supported at the inlet and outlet ends by stainless steel dispersion frits and bed support frits. Stainless steel tubing (Alltech) was used throughout and was either 0.318 cm or 0.159 cm outer diameter. Two types of packed systems were used. First, the column was packed homogeneously and the zone with NAPL consisted of the same material. Second, the column was packed with the same sand as in the previous experiment, but the NAPL zone was either a finer grained sand or a ceramic cube. The column was wet-packed with the coarse sand having a initial 20% moisture content. A cube zone 2.54 cm x 2.54 cm x 2.54 cm was placed in the middle of the column 3.65 cm
from the inlet and outlet end plates. The cube zone was formed by a styrofoam cube molding with edge length of 2.54 cm wrapped in aluminum foil and placed in the middle of the column. Coarse sand was then packed around the molding. When the sand was level with the cube molding, the molding was removed by inserting an exactoknife into the styrofoam cube and slowly removing it without disturbing the surround sand. When adding the ceramic cube or sand that contained TCE, an aluminum foil circle the same diameter as the column and with a 2.54 cm square cut out of the middle was laid on the top of the sand to act as a protective shield for already packed sand. A schematic of the column is shown in Figure 2.

The zone material consisted of either the same coarse grain sand, a finer grain sand, or a porous ceramic cube. Sand used in the zone initially had TCE saturated aqueous solution added to obtain a 10% moisture content. Then neat TCE was added to the sand, quickly mixed, and packed into the cube space. Extraction samples were taken before and after packing. When the ceramic cube was used, it was place into the cube location and then TCE was added to the ceramic cube. It was shown in preliminary trials that the TCE distributed evenly throughout the ceramic cube. The circular aluminum foil sheet was removed and additional sand was added to the column until completely packed at which point the column was sealed. The column was initially flushed with a saturated aqueous TCE solution for 3 pore volumes with a SSI model 300 piston pump. Finally, the column was flushed with water with an Accuflow Series II piston pump. The effluent was monitored throughout.
The first set of experiments consisted of physically homogeneous conditions but non-uniformly distributed NAPL. A NAPL zone was added to the column that consisted of the same media as its surrounds ($d_{50} = 724 \mu m$). The column was flushed with water for 79 pore volumes. The next set of column experiments consisted of physically heterogeneous conditions. TCE was added to sand with a $d_{50} = 360 \mu m$ while the surround media had a $d_{50} = 724 \mu m$. Water was flushed through the column for 146 pore volumes. The following experiment was the same except that a ceramic cube was used as the lower-K zone. Water was flushed for 454 pore volumes.

A control experiment for the column experiments consisted of a 5 cm column packed homogeneously with $d_{50} = 724 \mu m$ sand. TCE NAPL was uniformly distributed throughout the column and was flushed with water for 131 pore volumes. The initial $S_N$ was 6.7%, and the volume of the column was 24.5 cm$^3$, which was greater than the volume of the zones used in the column experiments (15.6 cm$^3$).

Flow cell experiments were conducted using a system constructed of 1.78-cm thick Type 304 stainless steel at the University of Arizona University Research Instrumentation Center. The inner flow cell dimensions were 39.5 cm long by 20.2 cm high by 5.6 cm thick. Series 1100 0.1-cm thick stainless steel porous plates (Mott Corporation) with 0.22 micron pore diameter were welded into both ends of the flow cell. Four evenly spaced connectors (Swagelock, SS-200-7-2) were welded at both ends to serve as inlet and outlet ports. A tempered glass plate (Romanoski Glass, Tucson, AZ) was attached to the flow cell with 7.62-cm C-clamps (Wilton 540A-3). A 0.635-cm wide by 0.238-cm thick expanded-PTFE joint sealant (John Crane, Morton Grove, IL) was
placed between the glass plate and the flow cell flange to prevent leaks. All tubing was stainless steel (Alltech), either 0.318-cm or 0.159-cm outer diameter. A schematic of the flow cell is shown in Figure 3.

Prior to each experiment, the flow cell was thoroughly cleaned and then wet packed with sand, added in approximately 600 g lifts. The sides of the flow cell were tapped with a rubber mallet to ensure uniform packing and to remove air bubbles. This process continued until the media was flush with the edge of the flow cell, at which time the flow cell was sealed and the back side was tapped with a rubber mallet. If gaps appeared along the edge of the flow cell, the flow cell was opened and additional sand was added. This process was repeated until the desired porosity was attained and no gaps appeared along the edges of the flow cell.

After the flow cell was packed, it was connected to a single-piston HPLC pump (Gilson model 305) and water was flushed vertically through the flow cell for several pore volumes to saturate the system and remove entrapped air. The mass of the flow cell was periodically measured to check for complete saturation, which was assumed when a constant mass was achieved. The flow cell was saturated with distilled, deionized water. The flowrate was gradually increased during the saturation process until the flowrate that was planned for the experiment was achieved. After the flow cell was saturated with water, a saturated aqueous TCE solution was flushed through the flow cell for three pore volumes to reduce

Following media saturation, the glass plate was removed and stainless-steel forms (2.5 cm wide and 16 cm long) were inserted into the flow cell at designated locations.
After the form had been fully emplaced into the flow cell, the media inside the form was removed and placed in a beaker for mass determination. In a separate beaker, the selected finer media was combined with aqueous TCE solution to create a moisture content of 10%. Sudan IV dyed TCE was then added to the beaker, mixed thoroughly, and immediately packed into the forms. Subsamples were collected to during the procedure to determine initial TCE saturation. After the zones were emplaced, the stainless-steel forms were removed and the glass plate reattached. The water flush was then initiated.

Effluent samples were collected with a 5 mL glass syringe and injected into a 20-mL Kimble autosampler glass vial. The samples were stored at 4°C until analyzed. All effluent samples were analyzed using gas chromatography (Shimadzu -17A) with an electron capture detector (ECD) and a Tekmar 7000 headspace sampler. The quantifiable detection limit for TCE was 0.0001 mg/L. Effluent flow rate was monitored during sample collection. Upon completion of the experiment, the flow cell was opened and sub-samples of the porous media were collected for solvent-extraction analysis. The sub-samples were added to a vial containing excess DCM. The samples were then sealed and shaken. Aliquots of the extractant were removed and analyzed for TCE using a gas chromatography (Shimadzu GC-14) with a flame ionization detector (FID). Digital photographs (Nikon Coolpix 885) were taken throughout each experiment for visual documentation.

The homogeneous flow cell experiment was packed with d_{50} = 724 µm sand. Two zones made of the same media that contained TCE NAPL were emplaced in the flow cell. Water was then flushed for 94 pore volumes. The next flow cell experiment was exactly
the same except that the zones were made of two different lower-K sands $d_{50} = 172 \, \mu m$ and $360 \, \mu m$ for zone 1 and zone 2, respectively. Water was then flushed through the flow cell for 362 pore volumes which equates to 157 days. The corresponding heterogeneous flow cell experiment consisted of two lower-K zones with TCE NAPL in $d_{50} = 172 \, \mu m$ (zone 1) and $d_{50} = 360 \, \mu m$ (zone 2) sands surrounded by $d_{50} = 724 \, \mu m$ sand. Water was then flushed through the flow cell for 362 pore volumes, which equates to 157 days.

A control experiment for the flow cell experiments consisted of a 15 cm column packed homogeneously with $d_{50} = 724 \, \mu m$ sand. TCE NAPL was uniformly distributed throughout the column and was flushed with water for 33 pore volumes. The initial $S_N$ was 11.3%, and the volume of the column was 73.6 cm$^3$, which was less than the volume of the zones used in the flow cell experiments (224 cm$^3$ per zone).

**Modeling**

Measured elution data was compared to simulated elution curves generated by a three dimensional mathematical numerical model based on that presented by Zhang and Brusseau (1999). The immiscible liquid dissolution was described by the following first-order mass transfer equation:

$$\frac{\partial \theta N}{\partial t} - k_{la}(C - C_t)$$

(1)

where $C$ is the aqueous concentration of the immiscible-liquid solute; $C_s$ is the aqueous solubility of the immiscible liquid; $\theta_N$ is the fractional volumetric content of immiscible liquid; $\rho_N$ is density of the immiscible liquid; $k_{la}$ is the mass transfer rate coefficient for
dissolution; and $t$ is time. The mass transfer coefficient depends on several factors
including pore-water velocity, specific immiscible-liquid/water interfacial area, and
properties of the porous medium and immiscible liquid (e.g., Miller et al., 1990; Powers
et al., 1992, 1994; Imhoff et al., 1994). A three-dimensional governing equation for
solute transport in the flow cell with dissolution of immiscible liquid was described by:

$$\theta_a \frac{\partial C}{\partial t} + \rho^N \frac{\partial \theta N}{\partial t} = \frac{\partial}{\partial x_i} \left( \theta_a D_{ij} \frac{\partial C}{\partial x_j} \right) - q_i \frac{\partial C}{\partial x_i}$$

(2)

where $\theta_a$ is fractional volumetric water content; $D_{ij}$ is the dispersion coefficient tensor; $q_i$ is the Darcy velocity; and $x$ is the spatial coordinate (Zhang and Brusseau, 2004).

RESULTS AND DISCUSSION

Uniform and Non-Uniform TCE Distribution for Physically Homogeneous Media

A series of physically homogeneous column and flow cell experiments with non-
uniform residual immiscible liquid were flushed with water to examine elution and mass
flux behavior and were compared to uniformly distributed control experiments (Table 3).

Control experiment 1 (Control 1 in Table 3) consisted of a 5 cm column experiment
(Tick, 2003). TCE concentrations were at “steady-state” for the first 47 pore volumes.
Since NAPL was uniformly present in the column, effluent concentrations were at
solubility during the initial “steady-state” period. The initial NAPL saturation, $S_N$, was
6.7%. After 47 pore volumes, effluent concentrations started to decrease below solubility
indicating that not all of the water flowing through the column was contacting NAPL; thus, residual NAPL was decreasing. When effluent concentration started to decrease, the elution curve shifted from “steady-state” to the transient state. Effective permeability for the water in the column would be increasing as NAPL saturation decreased during the transient state. Since the sand was homogeneous, mass transfer limitations are limited to by-pass flow due to differences in local scale permeability, decreased interfacial area, and rate-limited dissolution due to possible local scale velocity. NAPL continued to dissolve in the transient stage but dissolution efficiency decreased; it took more pore volumes to remove less NAPL mass. Most of the NAPL was removed in the initial “steady-state” flushing period, but in order to reach effluent concentrations below the maximum concentration level (MCL), further water flushing would be required (Figure 4).

Control experiment 2 (Control 2 in Table 3) was a uniformly distributed 15 cm column with an initial $S_N$ of 11% which was flushed with water (Tick, 2003). “Steady-state” lasted for the first 105 pore volumes. Then elution concentrations decreased and entered the transient state until flushing ceased at 147 pore volumes. As in control experiment 1, effective permeability would increase for water as $S_N$ decreased. When $S_N$ decreased to the point were NAPL was no longer uniformly distributed throughout the entire column, effluent concentrations would start to decrease and the elution curve would enter the transient stage. Dissolution would be limited by interfacial area contact and rate-limited dissolution.

Experiment 1 was a 10 cm column experiment with one localized NAPL zone which was emplaced in the column surrounded by the same media (non-uniform
conditions) and was flushed with water. Unlike the previous experiments, NAPL was non-uniformly distributed in the column. The initial zone’s $S_N$ was 16%, and residual NAPL was assumed to be uniformly distributed within the zone. Based on the area of the cube zone (6.3 cm$^2$) compared to the column area (45.1 cm$^2$), only a portion, 14%, of the water flushing through the column would be able to directly flow through the residual NAPL zone. Effluent concentration would be less than solubility because the majority of water was not contacting the residual TCE zone. During the initial flushing period, a “steady-state” region existed with approximate $C/C_0$ values of 0.15 to 0.12, which corresponds to approximately 180 to 140 mg/L and lasted for the first 40 pore volumes. By-pass flow due to decreased permeability would be minimal since $S_N$ was relatively small and the contaminated zone consisted of the same medium. After the initial “steady-state” stage, effluent concentrations steadily decreased during the transient state stage until 94 pore volumes when the experiment was stopped (Figure 4). During the transient state elution stage, $S_N$ would be decreasing and effective permeability would be increasing for water. Mass transfer would be limited by low interfacial area of NAPL blobs trapped in the media and by rate-limited dissolution due to advection.

TCE concentrations for the flow cell experiment, experiment 2, with two residual zones of physically homogeneous media closely resembled the 10 cm column experiment during the initial 30 pore volumes (Figure 4). Like in the 10 cm column experiment, effluent concentrations were less than solubility since 75% of the flushing water bypassed the residual NAPL zones; zones area were 28 cm$^2$ and total flow cell area was 113 cm$^2$. The average initial $S_N$ for both zones was 7%. Effluent concentrations were
relatively constant ("steady-state") during this initial stage. Effective permeability within
the emplaced residual zones would be slightly less than the surrounding media, as a result
by-pass flow would be minimal. Conceptually, NAPL would be expected to dissolve
uniformly along the longitudinal axis as flushing water penetrated the residual NAPL
zones. After 50 pore volumes, effluent concentrations started to decrease (transient stage)
until flushing stopped at 69 pore volumes. Since elution concentrations did not
immediately drop after the initial "steady-state" period as predicted by local equilibrium
assumptions, mass transfer limitation occurred. Some regions of NAPL could have
dissolved slower due to limited interfacial area contact and rate-limited dissolution with
the advecting water. Additionally, preferential flow paths could have been existed within
the contaminated zones due to unconformities in packing and/or due to non-uniform
NAPL distribution creating local by-pass zones.

Non-Uniform TCE Dissolution from Physically Heterogeneous Media

The next set of experiments examined elution behavior from non-uniform,
physically heterogeneous NAPL zones. Residual TCE in lower-K media was emplaced in
column and flow cell experiments, which were flushed with water (Table 3). Experiment
3 was a 10 cm column experiment that contained NAPL in one lower-K zone, and initial
$S_n$ for the zone was 13%. As in the non-uniform homogeneous experiments, the
contaminated zone was only 14% of the flushing area, so most of the water would by-pass
the zone. For the first 100 pore volumes, effluent concentrations were at "steady-state",
and $C/C_0$ were approximately 0.036 to 0.014 or 43 to 17 mg/L, respectively. During the
“steady-state” period, mass transfer between NAPL and the flushing water would be limited by several factors. First, by-pass flow would be occurring due to the lower-K medium and due to reduced effective permeability. Contributions due to the lower-K medium would be greater than reduced effective permeability, however, since $S_N$ was relatively small. Second, increased velocities at the peripherals of the zone where the majority of dissolution would be occurring would increase rate-limited dissolution. However as NAPL dissolved at the peripherals, concentration gradients would be created between the outer peripheral and middle of the zone and dissolved NAPL inside the zone would then diffusive to the peripheral. Not all of the water would by-pass the zone, some would penetrate the upgradient edge and slowly move along the longitudinal axis through the zone. Water velocities inside the zone would be less than the surrounding media; therefore, rate-limited dissolution would be less crucial. Eventually, water would flow the length of the contaminated zone and effluent concentrations would start to decrease indicating the start of the transient stage of the elution curve. The elution curve entered the transient phase after 100 pore volume and lasted until 146 pore volumes (Figure 5).

The transient portion of the elution curve was mainly due to limited interfacial area contact with advecting water and reduced flow due to lower-K.

The following 10 cm column experiment, 4, was the same as experiment 3 except that the heterogeneous zone was a ceramic cube instead of the lower-K sand medium. The initial $S_N$ for the cube was 13%. The ceramic cube initially exhibited a similar “steady-state” stage as the lower-K sand cube, but the length increased from 100 pore volumes to 150 pore volumes. Normalized concentration, $C/C_0$, was approximately
0.085, 102 mg/L, at the start of the “steady-state” stage and approximately 0.02, 24 mg/L, at the end. After 150 pore volumes, the elution curve appeared to enter the transient stage with effluent concentrations decreasing. However, at 175 pore volumes another “steady-state” stage began and lasted until 400 pore volumes (Figure 5). The ceramic cube unlike the porous sand media could have contained dead-end pores. The dead-end pores could have contained small amounts of NAPL that became entrapped and were slowly dissolving due to limited interfacial area relying solely on diffusion as the dissolution mechanism.

Experiment 5 was a heterogeneous flow cell experiment that consisted of two lower-K zones. The average $S_N$ for both zones was 16%. Unlike the column experiments which had pronounced “steady-state” stages, the flow cell experiment had a more subtle “steady-state” stage for the first 50 pore volumes (Figure 5). Following the “steady-state” stage was two subtle but distinct transient state stages. The first transient stage lasted from ~50 pore volumes to ~100 pore volumes, and the next lasted from ~100 pore volumes until water flushing ceased at 362 pore volumes. The initial “steady-state” stage was likely caused from the most readily accessible NAPL dissolving, which was NAPL located at the peripherals of the two lower-K zones. The majority of flushing water would by-pass the lower-K zones due to heterogeneity differences and water velocities at the interphase between the two zones would be greater. Rate-limited dissolution would be occurring at the peripherals but would still be the main dissolution process. As in the column experiments, dissolved NAPL within the lower-K zones could diffusive to the peripherals due to concentrations gradients and contribute to NAPL dissolution. A
portion of the water would enter the upgradient edge of each zone and travel along the longitudinal axis. Since zone 1 consisted of $d_{50} = 172 \, \mu m$ sand and zone 2 consisted of $d_{50} = 360 \, \mu m$ sand, water velocities within zone 2 would be greater but less than the surrounding media. Consequently, NAPL dissolution from zone 2 would be expected to be completed sooner than in zone 1. The velocity differences between the zones can explain two transient stages. The first transient stage represents dissolution contributions from both lower-K zones. The second transient stage represents dissolution only occurring from zone 1 after all the NAPL dissolved from zone 2. In a complex system like natural soil, the elution curve would consist of multitudes of zones that could cause shifts in the transient stage since NAPL trapped in different medium would be dissolving at different rates due to uniform distribution, by-pass flow, and rate-limited dissolution.

**Homogeneous verus Heterogeneous TCE Distribution**

The observed dissolution behavior between the homogeneous and heterogeneous experiments varied in several aspects. Uniform and non-uniform distributed experiments had different initial normalized concentrations. For the 5 and 15 cm control experiments, NAPL was uniformly distributed and normalized effluent concentrations were at solubility during the “steady-state” stage. The initial $S_N$ for the experiments was 6.7% and 11% for the 5 and 15 cm columns, respectively. The 5 cm control experiment was at “steady-state” for 47 pore volumes while the 15 cm control experiment was at “steady-state” for 105 pore volumes about twice the 5 cm column (Figures 4). For homogeneous, uniformly distributed NAPL, initial $S_N$ appears to determine the length of the “steady-
All the experiments had non-uniform distributed NAPL and effluent concentrations were less than solubility ($C/C_0 < 1$). The initial “steady-state” pore volume lengths varied between experiments. The column experiment with one local NAPL zone and an initial $S_N$ of 16%, experiment 1, had a “steady-state” length of 40 pore volumes. The column experiment with the lower-K NAPL zone and an initial $S_N$ of 13%, experiment 3, was more than double at 100 pore volumes (Figure 6). When NAPL was present in a lower-K zone, “steady-state” pore volume length was greater; thus, the length of the “steady-state” for heterogeneously non-uniformly distributed NAPL was more dependant on the location of the NAPL instead of the initial $S_N$.

For the flow cell experiments, it was more difficult to observe a trend in the “steady-state” portions of the elution curve. The initial “steady-state” stage for the homogeneous two zone flow cell, experiment 2, was 40 pore volumes in length while the heterogeneous two zone flow cell, experiment 5, was 50 pore volumes in length. The initial “steady-state” was slightly longer for the homogeneous flow cell, but the telling portion of the elution curve for the flow cells was the transient stage. For the homogeneous flow cell, it was 29 pore volumes and for the heterogeneous flow cell it was over 300 pore volumes. The transient stage was greater for the flow cells than column experiments due to three factors. First, there was larger difference in initial $S_N$ for the flow cell experiments. Next, the length of the flow cell contaminant zones were longer. Finally, the heterogeneous flow cell had two zones once of which had a lower-K ($d_{50} = 172 \mu m$) than the heterogeneous column experiment ($d_{50} = 360 \mu m$). Thus for the
flow cell experiments non-uniform, heterogeneous distribution of TCE NAPL slightly increases the “steady-state” stage but greatly increases the transient stage.

Concentrations during the “steady-state” stage also varied. Normalized effluent concentrations during “steady-state” one local NAPL zone, experiment 1, ranged from 0.15 to 0.12 while for the one local heterogeneous NAPL zone, experiment 3, ranged from 0.20 to 0.014. It was hypothesized that effluent concentrations were similar since most of the dissolution was initially occurring at the peripheral of each zone. After the peripheral NAPL was dissolved, dissolution would initiate inside each zone. For the homogeneous zone, advecting water traveling through the zone was only impeded by reduced effective permeability; thus, effluent concentrations remained relatively constant since $S_N$ were relatively small. However, for heterogeneous experiments, advecting water through the zones was less, so effluent concentrations decreased. It was important to note, that the “steady-state” stage for the homogeneous experiments was more stable than the heterogeneous experiments, but the “steady-state” stage was still discernable from the subsequent transient state stage for the heterogeneous experiments. To conclude, effluent concentrations for non-uniform distribution of NAPL were less than solubility, the “steady-state” stage lasted longer for the heterogeneous experiments, and “steady-state” concentrations fluctuated a fortiori for the heterogeneous experiments.

**Mass Flux**

Mass flux reduction was compared to percent mass removal for column and flow cell experiments to determine and compare the ideality of mass transfer for the different
experiments. The physically homogeneous 5 and 15 cm control experiments with TCE NAPL evenly distributed throughout the column exhibited the most ideal mass transfer behavior (Figure 7). The 15 cm column exhibited more ideal behavior than the 5 cm column, which might be attributed to length affect. For the 5 cm control experiment, mass flux reduction changed little until 50% of the mass was removed from the column. Then mass flux increased as mass removal increased. The physically homogeneous 15 cm control experiment did not have exhibit mass flux reduction until >90% of the mass was removed and then rapidly increased (Figure 7).

The physically homogeneous column experiment with one local NAPL zone was similar to the 5 cm control experiment. Mass flux did not change until mass removal was 30 percent, then mass flux reduction increased as mass removal increased. Non-ideal mass transfer behavior was exhibited to a greater extent than the control experiments. Mass flux for the physically homogeneous flow cell experiment, experiment 2, with two local NAPL zones rapidly increased after 5% mass removal. Mass flux reduction was approximately 0.3 after 10% mass removal at which point mass flux gradually increased as mass reduction did for the remainder of the experiment. The initial, rapid increase would be expected since the most non-ideal mass transfer would occur when \( S_N \) was the largest at the beginning of the experiment and would decrease as the experiment \( S_N \) decreased and effective permeability increased for water.

The mass transfer behavior of the heterogeneously packed experiments exhibited varying degrees of non-ideal behavior (Figure 8). The column experiment with the ceramic cube, experiment 4, exhibited the most ideal mass transfer behavior of the
heterogeneous systems; however, it was more non-ideal than the control experiments. Mass flux reduction fluctuated from 0 to 0.25 until 40% of the mass was removed. Then mass flux reduction steadily increased until 100% removal. The lower-K zone column experiment, 3, exhibited the most non-ideal mass transfer behavior. For the first 10% of mass removal, mass flux showed little change, then at 20% mass removal mass flux increased to 0.35, which at that mass removal was the largest of the experiments. Mass flux reduction values remained the largest until 80% of the mass was removed at which point the flow cell, experiment 5, had slightly greater mass flux until the end. The heterogeneous flow cell experiment, 5, exhibited mass transfer results between ideal and non-ideal. Percent mass removal and mass flux reduction both steadily increased throughout the entire experiment.

To summarize the mass flux results, all non-uniformly distributed experiments exhibited greater non-ideal mass transfer than the uniformly distributed control experiments. Also, for the physically homogeneous experiments, the greater non-uniformity experiments (two zone flow cells) exhibited greater non-ideal mass transfer than non-uniform column experiments. Finally, heterogeneous non-uniform experiments exhibited the most non-ideal mass transfer conditions. Uniformly distributed experiments were dependent on limited contact between the advecting water/NAPL and pore-scale rate limited mass transfer. Non-uniformly distributed experiments were additionally dependent upon reduced effective permeability due to $S_N$ that created local by-pass flow around the residual zones at the beginning of the experiments. Heterogeneous experiments besides being influenced by non-uniform distribution and reduced intrinsic
permeability were also affected by the residual zones residing in lower-K media that had by-pass flow occurring. Thus, the heterogeneous experiments exhibited the most non-ideal mass transfer conditions throughout the entire flushing process.

**Modeling results**

One-dimensional and two-dimensional models were used to fit the elution curves for the flow cell and column experiments. In addition, a three-dimensional multiprocess mathematical model based on that presented in Zhang and Brusseau (1999) was used to simulate immiscible-liquid dissolution for the flow cell experiment. $K_L$, $\beta$, and effective $S_N$ values from the models at different dimensions were determined for the column (Table 4) and flow cell (Table 5) experiments. The 1-D model used a weight-averaged porosity and $d_{50}$ for the entire length of the column. $S_N$ was assumed to be uniformly distributed along the entire length of the column and was determined by dividing the NAPL volume by the pore volume. In contrast, the 2-D model separated the NAPL zone from the rest of the column, so NAPL was not present up and downgradient of the residual NAPL zone. In addition, porosity and $d_{50}$ changed along the length of the column based on the media the water was flowing through. The 3-D model simulated the known system. Therefore, porosity, $d_{50}$, and $S_N$ did not have to be adjusted. A local-scale mass transfer coefficient could also be used for the residual zones unlike in the 1-D and 2-D models where a lumped mass transfer coefficient had to be used.

A 1-D model was used to determine the $K_L$, $\beta$, and $S_N$ values for the control experiments that consisted of uniformly distributed NAPL in columns. The 1-D model
assumed a The reported $K_{\text{la}}$ value was 6 hr$^{-1}$ and $\beta_{\text{a}}$ was 0.8 (Brusseau et al., 2002). The elution curves for the column experiments with one local NAPL zone in homogeneous media (experiment 1) and one lower-K NAPL zone (experiment 3) were also fitted with a 1-D mathematical model that assumed uniform NAPL and did not include lateral diffusive processes or non-uniform flow. Elution curves were then fitted with a 2-D model that considered non-uniform NAPL distribution but not lateral diffusive processes.

Two distinct regions were apparent for each column experiment that corresponds to the “steady-state” stage and the transient stage (Figure 9). $K_{\text{la}}$, the lumped mass transfer coefficient for dissolution, and $\beta_{\text{a}}$, related to the particle size distribution, were optimized for each column experiment. From the 1-D model, the $K_{\text{la}}$ term for the homogeneous local NAPL zone was larger, 0.095 hr$^{-1}$, than the heterogeneous lower-K NAPL zone column experiment, 0.07 hr$^{-1}$, which was expected since the homogeneous local NAPL zone experiment should exhibit more ideal mass transfer. Also, $\beta_{\text{a}}$ was slightly larger for the homogeneous than heterogeneous experiment, 0.9 and 0.8 hr$^{-1}$ respectively, indicating $K_{\text{la}}$ would decrease scarcely faster in the homogeneous experiment. For the 2-D model, the results were more difficult to compare since two domains were used for the heterogeneous column experiment to best simulate the elution (Table 4). For the homogeneous local NAPL zone experiment, $K_{\text{la}}$ was 0.80 hr$^{-1}$ and $\beta_{\text{a}}$ was 0.72. Compared to the 1-D model, $K_{\text{la}}$ was almost an order of magnitude larger indicating more ideal mass transfer.

The elution curve for the flow cell was also fitted with the same 1-D and 2-D mathematical model (Table 5). The $K_{\text{la}}$ for the 1-D and 2-D models were 0.015 and
0.033 hr\(^{-1}\), respectively, and \(\beta\) was 2.5 and 1.3, respectively. \(K_{La}\) for the 2-D model was large indicating more ideal mass transfer than the 1-D model. \(\beta\) was larger for the 1-D model indicating that \(K_{La}\) was decreases faster than for the 2-D model. Since the 1-D model assumes uniform NAPL distribution, contact with the NAPL zone would be less of a factor; thus, \(K_{La}\) would be expected to decrease faster.

The elution curve for the physically heterogeneous flow cell, experiment 5, was also modeled with a 3-D model wherein the system configuration was explicitly accounted for in the model (Figure 10). As exhibited in Figure 10, if an uniform-\(K\) was assumed then the model was unable to accurately simulate NAPL dissolution. However, the model was configured to account for the non-uniform \(K\) zones, then the elution curve could be simulated. \(K_{La}\) for the simulations was 5.6 hr\(^{-1}\), which was based independently on the uniform NAPL column system. If an uniform-\(K\) was assumed, the tailing part of the elution curve starting at 500 hours, which was associated with non-ideal mass transfer, could not be described, but when a non-uniform \(K\) was used, the tailing portion of the elution curve could be predicted. This highlights the importance of the source zone location in homogeneous and heterogeneous systems. Also, if the contaminant source occurs in lower-\(K\) media, then using an uniform \(K\) to predict site remediation will vastly under predict cleanup time. It is interesting to note that the \(K_{La}\) used for the 3-D model was two orders of magnitude larger than the fitted \(K_{La}\) obtained from the 1-D model, 5.6 hr\(^{-1}\) versus 0.033 hr\(^{-1}\), respectively. This indicates that \(K_{La}\) was no longer a lumped parameter as in the 1-D and 2-D models. Finally, the sensitivity of \(K_{La}\) was analyzed (Figure 11). \(K_{La}\) was varied by an order of magnitude larger and smaller than the
determined value. When $K_{La}$ was an order of magnitude too large, the initial concentration was over predicted to compensate for little predicted tailing. Likewise, when $K_{La}$ was an order of magnitude smaller, the transition from the “steady-state” to the transient state was lost and basically one “steady-state” was predicted that was lower than the measured concentration.

**CONCLUSION**

A series of column and flow cell experiments were conducted to examine mass transfer dissolution differences between uniformly distributed and non-uniformly distributed residual NAPL in physically homogeneous and heterogeneous constructed systems. A set of control, column experiments contained uniformly distributed residual NAPL and were flushed with water. The second set of column and flow cell experiments were comprised of non-uniformly distributed residual NAPL and wereflushed with water. The final set of experiments consisted of physically heterogeneous media with non-uniformly distributed NAPL zone(s) that were water flushed.

The first set of experiments deviated from equilibrium conditions due to pore-scale rate limited mass transfer associated with limited contact between the advecting water and NAPL blobs. The second set of experiments initially were mass transfer limited by localized reduced effective permeability zones, which created by-pass advective flow. As $S_N$ decreased due to dissolution, effective permeability increased as did the flow of advecting water through the zone. Then, mass transfer limitations reverted to the same set of limitations as in the first set of experiments, contact between
the advecting water and NAPL blobs. Non-ideal mass transfer would be greater at the beginning of the experiment when $S_n$ was the largest.

In the third set of experiments, initial mass transfer limitations were due to residual NAPL residing in lower-K zones that created by-pass flow. Unlike the previous experiments, heterogeneous mass transfer limitation was inherent with the experimental conditions. Additional mass transfer limitations included rate-limited dissolution around the peripherals of the lower-K zones and decreased pore water velocities within the lower-K zones. Diffusive transport to the peripherals of the zone could have played a role in dissolution. As $S_n$ decreased within the zone effective permeability would increase but mass transfer limitations would still be controlled by lower-K differences. In fact, since the lower-K zones consisted of smaller diameter sand material, interfacial area mass transfer limitations could conceivably be less than with larger diameter sand. Finally, as the level of heterogeneity increased, the overall non-ideal mass transfer increases. As shown through these laboratory experiments, mass transfer from NAPL located in lower-K media was a major source of non-ideal mass transfer and needs to be weighed when characterizing a system.
ACKNOWLEDGMENTS

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Asami Murao at the University of Arizona in the Contaminant Transport Group

Larry Acedo at the University of Arizona in the University Research Instrumentation Center
REFERENCES


Table 1. Physical properties of silica sand*

<table>
<thead>
<tr>
<th>$d_{50}$ (µm)</th>
<th>724</th>
<th>360</th>
<th>172</th>
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<tr>
<td>Particle density (kg/m³)</td>
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<td>2663</td>
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<td>Hydraulic conductivity (cm/hr)</td>
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<td>Porosity</td>
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<td>0.38</td>
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*Brusseau et al. (2000)

Table 2. Physical properties of ceramic substrate*

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<td>Air entry pressure (kPa)</td>
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*adapted from Whalley et al. (2001)

Table 3. Column and flow cell experimental conditions.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Apparatus</th>
<th>System Length (cm)</th>
<th>NAPL zone length (cm)</th>
<th>Initial $S_N$* (%)</th>
<th>Initial TCE mass (g)</th>
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<td>2.5</td>
<td>16</td>
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<tr>
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<td>15</td>
<td>11</td>
<td>4.0</td>
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</table>

*$S_N$ is defined as volume of NAPL in pore space divided by total volume of pore space.
Table 4. Experiments 1 and 3, column modeling results for varying model dimensions.

<table>
<thead>
<tr>
<th>Experiment/Dimensions</th>
<th>$K_{La}$ (hr$^{-1}$)</th>
<th>$\beta$</th>
<th>effective $S_N$ (%)</th>
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<tr>
<td>1/1-D</td>
<td>0.095</td>
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<td>0.07</td>
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<td>3/2-D</td>
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Table 5. Experiment 5, flow cell modeling results for varying model dimensions.

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>$K_{La}$ (hr$^{-1}$)</th>
<th>$\beta$</th>
<th>effective $S_N$ (%)</th>
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<tr>
<td>1-D</td>
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</tr>
<tr>
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<td>0.033</td>
<td>1.3</td>
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<tr>
<td>3-D</td>
<td>5.6</td>
<td>0.8</td>
<td>16</td>
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Figure 1. Ideal (dashed) and non-ideal (solid) mass transfer conditions exhibited as mass flux reduction versus percent mass removal
Figure 2. Schematic of 10 cm column with TCE zone. A coarser sand (724 µm) comprised the matrix while the TCE zone consisted of the same coarse sand, a lower-K sand (360 µm), or a ceramic cube.
Figure 3. Schematic of flow cell used for experiments. A coarser sand (724 µm) comprised the matrix. Either the same sand or two finer sands were used to create zones 1 (172 µm) and 2 (360 µm).
Figure 4. TCE dissolution for physically homogeneous systems.
Figure 5. TCE dissolution for physically heterogeneous systems.
Figure 6. TCE dissolution comparing physically homogeneous and heterogeneous systems.
Figure 7. Mass flux reduction versus percent mass removal for a 5 and 15 cm column with uniform NAPL distribution, a column with one local NAPL zone, and a flow cell with two local NAPL zones.
Figure 8. Mass flux versus percent mass recovery for the 5 and 15 cm columns with uniform NAPL distribution, column with lower-K NAPL zone, column with ceramic-cube NAPL zone, and flow cell with two lower-K NAPL zones.
Figure 9. Measured versus simulated elution comparing one local NAPL zone column experiment and a lower-K NAPL zone column experiment.
Figure 10. Measured versus simulated elution comparing uniform and non-uniform K for flow cell experiment with residual TCE in lower-K zones.
Figure 11. Two-dimensional model of flow cell experiment with lower-K zones (experiment 5) examining varying $K_{La}$ values.
APPENDIX B: IN SITU OXIDATION OF TRICHLOROETHENE LIQUID IN HETEROGENEOUS POROUS MEDIA: 2-D FLOW CELL EXPERIMENTS
IN SITU OXIDATION OF TRICHLOROETHENE LIQUID IN HETEROGENEOUS POROUS MEDIA: 2-D FLOW CELL EXPERIMENTS

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ABSTRACT

The effectiveness of potassium-permanganate in situ oxidation of immiscible-liquid trichloroethene (TCE) in heterogeneous porous media was examined in intermediate-scale flow cell experiments. Lower-permeability (K) zones contaminated with residual saturation of TCE were emplaced in a higher-permeability matrix. Potassium permanganate (KMnO$_4$) solution was flushed through the flow cell in a series of pulses. Water was flushed through the system after the KMnO$_4$ flush to evaluate long-term mass flux behavior, which was compared to a water-flush control experiment. TCE mass removal was monitored, and manganese-oxide precipitation was characterized. Precipitation occurred within and adjacent to the lower-K zones, and formed tails extending downgradient from the lower-K zones. During flow interruptions, precipitation formation extended from the lower-K zones into the surrounding matrix. TCE mass flux immediately after KMnO$_4$ flushing and at the start of the subsequent water flushing was greater than that of the control experiment. After 37 pore volumes of water flushing following the KMnO$_4$ flush, mass flux was similar to the control experiment. The pore volumes required to achieve complete TCE removal via water flushing was estimated to be reduced by half due to the KMnO$_4$ flush.
INTRODUCTION

The presence of immiscible-liquid contamination at a site can greatly impact the costs and time required for site remediation. Thus, there is great interest in remediation methods that can be used to achieve significant mass removal for DNAPL source zones. In-situ chemical oxidation (ISCO) using permanganate is one such method (Vella and Veronda, 1992; McKay et al., 1998; Siegrist et al., 1999; Moes et al., 2000; Mott-Smith et al., 2000). It has been shown that KMnO₄ can degrade a wide range of organic compounds (Schnarr et al., 1998). KMnO₄ has been used successfully in several field projects (Schnarr et al., 1998; Huang et al., 2000; Mott-Smith et al., 2000; Nelson et al., 2000; Seol et al., 2003).

The efficiency as well as some of the problems associated with KMnO₄-based ISCO have been examined in several laboratory studies (Li and Schwartz, 2000; Reitsma and Marshall, 2000; Conrad et al., 2002; MacKinnon and Thomson, 2002; Li and Schwartz, 2004b; Li and Schwartz, 2004c). The primary concerns associated with KMnO₄ use are pore clogging due to the formation of Mn-oxide precipitates and the formation of CO₂ gas, both of which could limit mass transfer (Li and Schwartz, 2000; Reitsma and Marshall, 2000; Thompson et al., 2000). However, it has been shown that diffusion of KMnO₄ into a lower-permeability zone contaminated with immiscible liquid can occur without having detrimental effects (Struse et al., 2003). It has recently been suggested that adding citric acid to the system could dissolve Mn-oxides precipitates, increasing KMnO₄ availability (Li and Schwartz, 2004a). Secondary concerns associated with KMnO₄ use involve impacts on redox conditions, which may for example affect the
distribution of metals such as manganese, chromium, and nickel (Crimi and Siegrist, 2003).

The distribution of immiscible liquid in subsurface environments is typically very nonuniform, and is affected greatly by physical material heterogeneity (e.g., Kueper and Frind, 1988; Kueper et al., 1993). Under certain conditions, immiscible liquid may become entrapped in lower-permeability zones (e.g., Oostrom et al., 2003). Mass removal via hydraulic-based methods is likely to be constrained in such cases due to the preferential flow and limited contact between the contaminants and water or reagent. The influences of subsurface heterogeneity on the efficacy of ISCO methods needs to be addressed (Seol et al., 2003).

The purpose of this research was to investigate the effectiveness of in-situ chemical oxidation with KMnO₄ for a physically heterogeneous porous medium contaminated with immiscible-liquid phase TCE. Two-dimensional intermediate scale flow cells that contained residual TCE in lower-K zones were flushed with KMnO₄ solution to investigate the ability of ISCO to degrade entrapped immiscible liquids. The flow cell was subsequently flushed with water to evaluate mass flux behavior after KMnO₄ flushing. The impact of remediation with KMnO₄ on mass flux was evaluated by comparison to the results obtained from a control experiment (water flushing).

MATERIALS AND METHODS

All experiments were conducted using a flow cell constructed of 1.78-cm thick Type 304 stainless steel. The inner flow cell dimensions were 39.5 cm long by 20.2 cm
high by 5.6 cm thick. Series 1100 0.1-cm thick stainless steel porous plates (Mott Corporation) with 0.22 micron pore diameter were welded into both ends of the flow cell. Four evenly spaced connectors (Swagelock, SS-200-7-2) were welded at both ends to serve as inlet and outlet ports. A tempered glass plate (Romanoski Glass, Tucson, AZ) was attached to the flow cell with 7.62-cm C-clamps (Wilton 540A-3). A 0.635-cm wide by 0.238-cm thick expanded-PTFE joint sealant (John Crane, Morton Grove, IL) was placed between the glass plate and the flow cell flange to prevent leaks. All tubing was stainless steel (Alltech), either 0.318-cm or 0.159-cm outer diameter. A schematic of the flow cell is shown in Figure 1.

All porous media used in the experiments are commercially available, natural sands obtained from Unimin Corporation (Le Sueur, MN). Three media with different mean particle diameters were used, 724 µm (20-30 mesh), 360 µm (40-50 mesh), and 172 µm (70-100 mesh). Relevant properties of the sands are reported in Table 1. The 724-µm sand was used as the flow-cell matrix, with the two finer media serving to create the lower-K zones.

A stock KMnO₄ solution (2 molar) was made from ACS reagent grade crystals (Aldrich Chemical Col, Inc., Milwaukee, WI), from which 15-mM (2370 mg/L) flushing solutions were created as needed. A stock 1-M sodium thiosulfate pentahydrate solution was made from ACS grade (Aldrich Chemical Col, Inc., Milwaukee, WI) to quench the effluent samples (Hood et al., 2000). TCE was ACS grade (Aldrich Chemical Col, Inc., Milwaukee, WI), and was dyed with certified Sudan IV (Aldrich Chemical Col, Inc., Milwaukee, WI) at a concentration of 100 mg/L. Dichloromethane (DCM) used in
extractions was ACS/HPLC certified solvent (Burdick and Jackson, Muskegon, MI).

A control experiment consisting of only water flushing was conducted to characterize TCE dissolution and mass flux. An initial KMnO₄ experiment was conducted to characterize TCE transformation behavior in the heterogeneous system. The second KMnO₄ flushing experiment consisted of a series of three KMnO₄ pulses totaling ~4.5 pore volumes (1.1, 0.9, and 2.5 pore volumes). This was followed by a water flush of 37 pore volumes to determine the impact of in-situ oxidation on effluent TCE concentrations and associated mass flux. The flow cell was sealed for 12 days between pulse 1 and 2, 21 days between pulse 2 and 3, and 6 days between pulse 3 and the water flush.

Prior to each experiment, the flow cell was thoroughly cleaned and then wet packed with sand, added in approximately 600 g lifts. The sides of the flow cell were tapped with a rubber mallet to ensure uniform packing and to remove air bubbles. This process continued until the media was flush with the edge of the flow cell, at which time the flow cell was sealed and the back side was tapped with a rubber mallet. If gaps appeared along the edge of the flow cell, the flow cell was opened and additional sand was added. This process was repeated until the desired porosity was attained and no gaps appeared along the edges of the flow cell.

After the flow cell was packed, it was connected to a single-piston HPLC pump (Gilson model 305) and water was flushed vertically through the flow cell for several pore volumes to saturate the system and remove entrapped air. The mass of the flow cell was periodically measured to check for complete saturation, which was assumed when a
constant mass was achieved. The flow cell was saturated with distilled, deionized water. The flowrate was gradually increased during the saturation process until the flowrate that was planned for the experiment was achieved.

Following media saturation, the glass plate was removed and stainless-steel forms (2.5 cm wide and 16 cm long) were inserted into the flow cell at designated locations. After the form had been fully emplaced into the flow cell, the media inside the form was removed and placed in a beaker for mass determination. In a separate beaker, the selected finer media was combined with aqueous TCE solution to create a moisture content of 10%. Sudan IV dyed TCE was then added to the beaker, mixed thoroughly, and immediately packed into the forms. Subsamples were collected during the procedure to determine initial TCE saturation. After the zones were emplaced, the stainless-steel forms were removed and the glass plate reattached. The water flush or KMnO₄ solution flush was then initiated.

Effluent samples were collected with a 1 mL glass syringe and injected into a 20-mL Kimble autosampler glass vial with 4 mL of 1M sodium thiosulfate pentahydrate solution for dilution and to quench the oxidation of TCE by KMnO₄. The samples were stored at 4°C until analyzed. All effluent samples were analyzed using gas chromatography (Shimadzu GC-17A) with an electron capture detector (ECD) and a Tekmar 7000 headspace sampler. Effluent flow rate was monitored during sample collection. Upon completion of the experiment, the flow cell was opened and subsamples of the porous media were collected for solvent-extraction analysis. Samples were also collected for later analysis by SEM. The subsamples were added to a vial containing
excess DCM. The samples were then sealed and shaken. Aliquots of the extractant were removed and analyzed for TCE using a gas chromatography (Shimadzu GC-14) with a flame ionization detector (FID). Digital photographs (Nikon Coolpix 885) were taken throughout each experiment for visual documentation.

Samples for SEM analysis were collected from three locations within the flow cell after the initial KMnO₄ experiment: (1) uncontaminated sand surrounding the lower-K zone where presumably no oxidation took place, (2) within the lower-K zone where KMnO₄ solution apparently did not penetrate, and (3) at the boundary between the lower-K zone and the matrix where precipitates formed. All scanning electron microscope images were obtained using a Hitachi S-2460N with an energy dispersive x-ray spectroscopy (EDS) detector, which provides qualitative elemental analysis. Two sets of samples were collected for SEM analysis. The first set of samples was coated with a gold-palladium mixture to obtain improved visual images. The second set of samples was left uncoated for analysis with the EDS detector. The samples were mounted on aluminum pin mounts with carbon conductive tape.

RESULTS

KMnO₄ transport and Manganese oxide formation

The initial flow cell experiment consisted of a continuous flush of 15 mM KMnO₄. The KMnO₄ solution exhibited plug flow until reaching the emplaced lower-K zones, at which point the solution bypassed the lower-K zones and continued to move downgradient toward the outlet of the flow cell. Precipitates initially formed at the
interface between the surrounding media and the lower-K zones, except at the
downgradient end. During the course of the flushing, KMnO$_4$ solution primarily
penetrated the upgradient edge of the lower-K zones as exhibited by precipitate
formation. Precipitates formed to a lesser degree on the top and bottom edges of the
lower-K zones, while not forming at all at the downgradient edge (Figure 2). “Shadow”
zones into which the KMnO$_4$ solution did not enter were observed immediately
downgradient of both lower-K zones (Figure 3). Precipitates formed on the top and
bottom edges of the shadow zones, forming tails. The formation of these precipitates
indicates the presence of aqueous TCE. The precipitate-affected zones increased in
thickness during the experiment, indicating a continuous flux of TCE from the lower-K
zones. This behavior was also noticed in experiments conducted by Reitsma and
Marshall, 2000. Precipitation also occurred outside of the lower-K zones, due
presumably to TCE emanating from the lower-K zones. It was noted during post-
experiment disassembly of the flow cell that precipitate formation at the interface of the
glass plate and porous-medium surface accurately represented KMnO$_4$ solution
penetration and precipitation within the porous medium. Following completion of the
KMnO$_4$ flushing, the flow cell was opened and subsamples were collected to determine
remaining TCE mass and for SEM analysis.

SEM images of samples collected from the matrix and from the center of the
lower-K zones indicated precipitates did not form at those locations during the single
flush. In addition, manganese was not detected with the EDS analysis. Conversely, the
samples collected from the interface between the matrix and lower-K zones had
noticeable precipitates (Figure 4). EDS analysis of the precipitates indicated the presence of manganese, chlorine, and potassium as well as silica and oxygen (Figure 5). This indicates that chlorine and potassium by-products of TCE oxidation were being incorporated into the manganese oxide structure. Therefore, chloride may not be a good quantitative indicator of TCE oxidation within the lower-K zones.

The second KMnO₄ experiment consisted of a series of three pulses totaling ~4.5 pore volumes, with no-flow periods between the pulses. The qualitative results during the initial pulse were similar to those of the first experiment. KMnO₄ solution exhibited plug flow until coming into contact with the lower-K zones, which were bypassed, and a “shadow” zone was formed downgradient of both lower-K zones. During the no-flow periods, KMnO₄ solution diffused into the “shadow” zones downgradient of the lower-K zones. Also, pore water in the matrix changed from purple to clear, indicating complete reaction of KMnO₄. It is assumed that KMnO₄ oxidized aqueous TCE that had diffused from the lower-K zones.

During the initial KMnO₄ flush, precipitates formed at the upgradient, top, and bottom edges for both zones. Precipitates were not observed at the downgradient edges. As expected, manganese oxide precipitation was not as pronounced for zone 1 compared to zone 2, consistent with zone 1 having a lower permeability than zone 2. Differences in precipitate formation likely reflect differences in advective penetration of the KMnO₄ solution. Both zones formed precipitate tails downgradient. The first no-flow period was 12 days long and precipitate streaks up to 6 cm in length formed below the bottom edge of zone 1. Precipitation also occurred upgradient of both zones in the surrounding
matrix. This likely indicates that TCE was diffusing from the lower-K zones during the flow interrupts. The second pulse had negligible amounts of additional precipitation within the lower-K zones and was followed by another flow interrupt for 21 days. Streaks that had formed during the first flow interrupt increased in size. Because precipitation in the lower-K zones was minimal, the last pulse was increased to 2.5 pore volumes.

Precipitation at the bottom edge of zone 2 dramatically increased during the final flush, and by the end of flushing precipitates had formed 2.5 cm into the upgradient edge. At the end of flushing, 54% of zone 2 had noticeable precipitates while only 21% of zone 1 did, which is consistent with the permeability differences between the two media. The thickness of the downgradient zone 2 precipitation tails increased to ~1.5 cm, indicating that TCE oxidation continued to occur downgradient from the lower-K zone (Figure 6).

To confirm that TCE was dissolving from the lower-K zones, extraction samples were collected upgradient and downgradient of the lower-K zones. Within the downgradient “shadow” zones, aqueous TCE concentrations ranged from 29 to 10 mg/L for zone 1 and 50 to 30 mg/L for zone 2. TCE was not detected upgradient of zone 2. The “shadow” zones directly downgradient of the lower-K zones account for the TCE effluent concentrations due to the small contact time with KMnO₄ solution.

Mass removal and Mass Flux

For these experiments, loss of TCE mass from the two lower-K zones could occur by dissolution and subsequent mass flux or by KMnO₄-induced oxidation. Final TCE
mass in the lower-K zones was determined using the results of the solvent-extraction analysis. Effluent samples were collected and analyzed to determine mass removed due to dissolution and subsequent transport.

During the KMnO₄ flush, 3.2 grams of TCE were eluted, and TCE mass eluted during the subsequent water flush was 26.5 grams. The remaining mass of TCE in both lower-K zones at the end of KMnO₄ and water flushing was 7.5 grams, and it was estimated that a total of 4.5 grams of TCE could have been oxidized by KMnO₄.

Examining TCE mass flux, the rate of contaminant discharge, is an important parameter for determining if ISCO was an effective source zone remediation technique. After multiple KMnO₄ pulses, water was flushed through the flow cell for an additional 37 pore volumes to characterize TCE mass flux following ISCO. Formation of precipitates immediately around the lower-K zones did not appear to affect mass transfer of residual TCE from the lower-K zones, based on increased aqueous TCE concentrations after no-flow conditions. Aqueous TCE effluent concentration initially increased to 750 mg/L before leveling off at 500 mg/L for the next 20 pore volumes. After ~42 pore volumes, effluent concentrations gradually decreased to 290 mg/L at the end of the water flushing.

In a control experiment with identical conditions but with water as the flushing agent, aqueous TCE effluent concentrations were 230 mg/L after 40 pore volume, which is slightly lower than 290 mg/L observed for the KMnO₄ multiple flush experiment (Figure 7). Thus, for a similar period of total pore volumes, the mass flux was similar for both experiments. Source zone TCE mass in the source zone was degraded based on
observed manganese oxides formation, but the mass flux was apparently not affected over
the range of pore volumes monitored. Effluent TCE concentrations during the
subsequent water flush were similar to concentrations observed during the control
experiment, also indicating that manganese oxide precipitates immediately around the
lower-K zones do not inhibit mass transfer from the residual TCE in the lower-K zones.

Relying on mass flux alone as an indicator of the effectiveness of ISCO can be
misleading depending on the time of analysis. Over the short term, mass flux from the
control experiment and the KMnO₄ flushing experiment appear to be similar, indicating
minimal effectiveness of the remedial action. However, the efficacy of ISCO becomes
apparent over the long term. Based on the amount of mass remaining after the KMnO₄
flush and assuming a similar mass flux as obtained for the water flush, the amount of pore
volumes required to remediate the system would be 53% less than the control experiment
consisting of only water flushing (140 pore volumes for a water-only flush and 67 pore
volumes for KMnO₄ flushing followed by water flushing). The impact of mass reduction
by the KMnO₄ was not apparent in the short term but would be conspicuous by reduced
water flushing required for complete mass removal over the long term.

CONCLUSIONS

A series of 2-D flow cell experiments was conducted to determine the
effectiveness of ISCO using KMnO₄ when the contaminant was located in a lower-K
zone. Despite heterogeneity affects, KMnO₄ was able to degrade residual TCE in the
lower-K zones as noted by the manganese oxides that formed within the lower-K zones.
Pore clogging did not appear to hinder KMnO₄ penetration in the lower-K zone for the multiple-pulse experiment. Likewise, pore clogging did not appear to inhibit TCE from diffusing from the lower-K zones between pulses. In the short term, a combination of KMnO₄ and water flushing versus solely water flushing appears to have had little affect on mass flux. However, over the long term, the degradation of source zone mass becomes apparent as mass flux would decrease sooner and the time required for complete mass removal via water flushing would be reduced.
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REFERENCES


Table 1. Physical properties of silica sand

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*NA - not available
Figure 1. Schematic of flow cell used for experiments. A coarser sand (724 µm) comprised the matrix, and two finer sands were used to create zones 1 and 2 (172 µm) and 2 (360 µm). Depth is 5.6 cm.
Figure 2a. KMnO$_4$ injections for zone 2 ($d_{50} = 360$ µm) at (A) 0.01 PV, (B) 0.03 PV, and (C) 0.14 PV.
Figure 2b. KMnO$_4$ injections for zone 2 (d50 = 360 µm) at (D) 1.0 PV, (E) 2.0 PV, and (F) 4.5 PV.
**Figure 3.** Zone 2 after the first KMnO$_4$ pulse exhibiting the downgradient shadow zone, downgradient manganese oxide tails, and manganese oxide formation around the lower-$K$ zone.
Figure 4. SEM image of fine grain sand ($d_{50} = 360 \mu m$) with noticeable manganese oxides.
Figure 5. Qualitative elemental analysis of precipitates on sand grains with noticeable amounts of Mn, K, and Cl.
Figure 6. Distance in centimeters that manganese oxides formed inside and outside of the lower-K zones in the second experiment.
Figure 7. Effluent TCE concentrations (1) water flush following multiple KMnO₄ pulses and (2) water flushing only.
APPENDIX C: FIELD APPLICATIONS OF IN-SITU CHEMICAL OXIDATION USING PERMANGANATE FOR DCE-CONTAMINATED HETEROGENEOUS PERCHED AQUIFER STUDY
FIELD APPLICATION OF IN-SITU CHEMICAL OXIDATION USING PERMANGANATE FOR A DCE-CONTAMINATED HETEROGENEOUS PERCHED AQUIFER SYSTEM

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ABSTRACT

1,1-Dichloroethene (DCE) contamination is present at the Samsonite Building Area (SBA), which is part of the airport property at the Tucson International Airport Area (TIAA) Superfund Site. Aqueous DCE concentrations average 31 µg/L for the local perched aquifer system. A significant fraction of DCE is thought to be located in lower permeability strata adjacent to the water table of the perched aquifer. In-situ chemical oxidation (ISCO) using potassium permanganate (KMnO₄) was implemented as a remedial technology for the site. Nine injection wells were emplaced in the source zone area, with well screens spanning the vadose and saturated zones (23 to 28 meters below ground surface). Core subsamples collected during the injection well drilling were analyzed for organic matter and extracted for DCE. Bench-scale studies using core material determined that DCE was readily degraded by KMnO₄, even at lower reagent concentrations (< 1 mM). The natural oxidant demand was determined to be 1.0 x 10⁻⁵ g of KMnO₄ per g of sediment. Eight of the nine injection wells (IW) were injected with ~250 kg of ~1.7% KMnO₄ solution; the downgradient injection well, IW-07, served as a monitoring well. Several groundwater parameters were measured pre- and post-injection. The paramount physical parameter was ORP which increased 431 mV to average 634 mV. DCE levels dropped below detection in IW-07 after KMnO₄ solution was present. KMnO₄ is still present in all IW’s including IW-07. Site monitoring continues in an effort to determine if DCE concentrations will rebound after KMnO₄ is no longer present in the system. The project provides an opportunity to examine questions of significant
importance to the field of subsurface remediation with reagent application in deep heterogeneous subsurface systems.

INTRODUCTION

1,1-Dichloroethene (DCE) is a synthetic clear, colorless liquid with a mild, sweet smell. DCE is used in the making of fire retardant fibers and polyvinylidene chloride (PVDC) polymers and is considered a possible human carcinogen (ATSDR, 1995). DCE enters the environment though release during its manufacture and use, from the breakdown of PVDC products, and from the biotic or abiotic breakdown of 1,1,1-trichloroethane, tetrachloroethene, 1,1,2-trichloroethene, and 1,1-dichloroethane (EPA, 2002).

DCE contamination at the Samsonite Building Area (SBA) in Tucson, Arizona was initially reported in 1988 when the engineering firm Hargis & Associates, Inc. conducted a soil-gas survey. Follow-up soil gas surveys by Daniel B. Stephens & Associates in 1993 and 2000 confirmed the presence of DCE and identified the potential DCE source area (a 30.5 by 18.3 meters zone near monitoring well S-31). In 1993 the source area had a soil gas screening level (SGSL) above 3.8 µg/L. A soil-gas survey conducted in 2000 determined that the source-zone concentrations had not increased but in fact decreased to below the SGSL. It is not know whether DCE contamination came from an immiscible liquid surface spill on the surface or the result of abiotic degradation of another immiscible liquid. When PCE or TCE are anaerobically biodegraded, cis- and trans-1,2 DCE are daughter products (Lorah et al., 2001) not 1,1-DCE, which can be an
abiotic daughter product of 1,1-trichloroethane (TCA) degradation (Vogel and McCarty, 1987).

Groundwater samples collected from monitoring wells (S-31 and S-42) in (S-31) and downgradient (S-42) from the source zone have measured DCE levels near or above the maximum contaminant level (MCL), which is 7 µg/L, and continue to be monitored. Subsequent boring and monitoring-well sampling have determined that concentrations of DCE above the MCL are confined to the Tucson Airport Property. It does not appear that the DCE is migrating off site, which could indicate either natural attenuation or simply dilution due to mixing with uncontaminated groundwater.

It has been hypothesized that DCE migrated downward due to water recharge infiltration and sorbed onto surrounding media (Sandberg, 2004). Additionally, when the purported immiscible liquid release occurred the water level was ~50 feet higher in elevation and it is possible that the declining water table has contributed to DCE migration (Brinker, 2004). It has also been proposed that DCE may be a transformation product of 1,1,1-trichloroethane (TCA) hydrolysis (Vogel and McCarty, 1987). Based on current data, it has been hypothesized that no DCE non-aqueous phase liquid (NAPL) is currently present. Rather, it is speculated that DCE has sorbed onto the soil material in both the saturated and vadose zone, and aqueous DCE phase could be present in the lower-K zones (Brinker, 2004; Whillier, 2004). The aqueous phase DCE concentrations observed for well S-31 since 1997 have averaged 31 µg/L (Figure 1). The screened interval for the monitor well is 24.8 to 29.4 meters below ground surface. This relatively wide screened interval and the sample method could result in dilution, which could mask
the presence of DCE NAPL.

In the draft design Technical memorandum for the SBA remedy (CRA, 2003), in-situ oxidation with KMnO$_4$ was proposed as a potential remediation technology. Since this technology was not included in the 1997 Record of Decision for the Airport Property, EPA requested that a field-scale pilot test be performed to validate the applicability of in-situ oxidation for the SBA site. KMnO$_4$ has been shown in the laboratory to readily degrade numerous chlorinated compounds including DCE, trichloroethene (TCE), and tetrachloroethene (PCE) (Yan and Schwartz, 1999). From one set of laboratory experiments the half-life of a 10 mg/L solution of DCE at 10 degrees C was reported as approximately 5 minutes (Huang et al., 2001).

The proposed mechanism for DCE degradation is as follows (Seol et al., 2003):

$$2 \text{MnO}_4^- + \text{C}_2\text{H}_2\text{Cl}_2 \rightarrow 2 \text{MnO}_2 (s) + 2 \text{CO}_2 + 2\text{H}^+ + 2 \text{Cl}^-$$

Two moles of KMnO$_4$ are needed for every mole of DCE. Both of the byproducts, manganese oxide and carbon dioxide, can have adverse effects on performance. Creating gas or precipitates can decrease permeability, thereby limiting contact of the KMnO$_4$ and DCE. Examples of this have been demonstrated in laboratory experiments (Conrad et al., 2002; Schroth et al., 2001). However, such observations have not been apparent in field experiments (Seol et al., 2003). Oxidizable aquifer material (OAM) would also be oxidized and would consume a portion of the applied KMnO$_4$.

$$\text{OAM C + MnO}_4^- \rightarrow \text{CO}_2 + \text{MnO}_2 (s)$$

Reported organic carbon in the upper unit 4 clay (UU4C) is ~1% (Sandberg, 2004). Thus, it is possible that the OAM at the site would act as a sink for the KMnO$_4$ in competition with
the DCE.

Previous pilot projects conducted in the field have had mixed results, with reported effects ranging from complete destruction to inconclusive (Seol et al, 2003). One field project with 1,2-dichloroethene contamination in a saturated sandy soil used dry KMnO₄ salt instead of aqueous KMnO₄ (Oberle and Schroder, 2000). The contamination was in the saturated zone, which was only 1.2 to 2.4 meters below ground surface. The top 1.2 meters of soil was removed so the KMnO₄ salt could be placed on top of the water table. This minimized concerns of excessive KMnO₄ spreading that could occur in an aqueous injection. Complete destruction of 1,2-Dichloroethene was achieved.

A pilot-scale study using ISCO with potassium permanganate has been proposed as a possible remedial technology for the SBA site. The purpose of this demonstration project was to determine the performance of ISCO using aqueous KMnO₄ in a heterogeneous perched low-K environment contaminated with DCE. The specific objectives of the project are as follows: determine the feasibility and optimization of ISCO application at the SBA site with bench scale experiments and investigate in-situ treatment of a DCE source zone in a heterogeneous perched “low-K” environment.

**MATERIALS AND METHODS**

KMnO₄ solution used in the bench-scale experiments and the pilot study was made from RemOx™-ISCO grade reagent obtained from Carus Chemical Company (Peru, IL). KMnO₄ was ≥98.8% pure with chromium concentrations typically 1.4 mg/kg (Carus Chemical Company, 2005). A stock 1 M sodium thiosulfate pentahydrate solution
was made from ACS grade (Aldrich Chemical Col, Inc., Milwaukee, WI) to quench the effluent samples used in bench-scale experiments (Hood et al., 2000). DCE used in bench-scale experiments was ACS grade (Aldrich Chemical Col, Inc., Milwaukee, WI). Synthetic groundwater with an ionic strength of 0.01 M and pH of 7.7 was used in all bench experiments (Table 1). The recipe is designed to represent natural groundwater and was used in previous laboratory research for the same geological area (Johnson et al., 2003).

The pre-characterized source zone area had nine injection wells drilled in a grid pattern with approximately 9.1-meter intervals (Figure 2). Wells were drilled by WDC Exploration and Wells (Phoenix, Arizona) with a hollow stem auger CME-85 (St Louis, Missouri). Continuous cores were collected in a 1.5 meter core barrel 21.3 to 29.0 meters below ground surface in clear 7.6 cm outer diameter x 152 cm long x 0.16 cm thick acrylic tubes.

Sediment subsamples were collected from the cores when noticeable changes in stratigraphy were apparent and averaged 2 subsamples per core. Holes of approximately 6 cm² were cut into the side of the acrylic tubes with an utility knife, and a plastic 10 mL syringe with the tip cut off was then pushed into the hole. Samples were then pushed from the syringe with the plunger.

Two separate analysis were conducted with the subsamples–DCE concentration and total organic matter. Soil extraction subsamples were placed in premassed 40 mL VWR traceclean clear borosilicate 0.125" septa lined vials, which contained 20 mL of Burdick and Jackson HPLC/ACS grade methanol. The samples were stored at 4° C.
Before analysis, samples were placed on a model 4152110 Labquake shaker rotisserie (Dubuque, Iowa) for 12 hours and centrifuged. Then 4.5 mL of subsample were removed and added to 0.5 mL of HPLC/ACS grade methanol in a 21 mL headspace vial which were then analyzed for 1,1-DCE on a Shimadzu GC-17A with an ECD detector and Tekmar 7000 headspace sampler. Subsamples were placed in vortex whirl bags and taken to the Water Quality Center Lab (Tucson, Arizona) for total organic carbon (TOC) analysis. The samples were dried, ground, and digested with acid before being analyzed on a Model NA 1500 N/C/S Analyzer (Carlo-Erba Strumatazione, Milan, Italy).

**Bench-Scale Experiments**

Representative core-sediment subsamples were used in a series of bench-scale experiments designed to determine the rate of DCE oxidation with and without sediments as well as to determine demand associated with the aquifer material. Triplicate samples were collected each sampling period. Approximately five grams of sediment were placed in a 20 mL VWR traceclean clear borosilicate 0.125” septa liner vial, then synthetic groundwater was added to the reactor. Depending on the experiment, stock DCE solution and/or KMnO₄ solution were added to the reactors and placed on the Labquake shaker rotisserie for the duration of the experiment. At scheduled times, the reactors were removed from the rotisserie and, if KMnO₄ was present, sodium thiosulphate was added to stop DCE oxidation (Hood et al., 2000). Aliquots were removed with a glass syringe and analyzed with a gas chromatography (Shimadzu GC-17A) with an electron capture detector (ECD) and Tekmar 7000 headspace sampler for DCE or a ultraviolet-visible
spectrophotometer (Shimadzu UV-VI Model 1501) for KMnO₄.

Bench-scale experiments consisted of five different conditions (Figure 6). The five bench-scale experiments can be broken down into two groups: with and without sediments. Experiments A and B did not contain sediments from the Samsonite cores. Experiment A examined aqueous DCE oxidation by KMnO₄ and experiment B served as the system control experiment determining possible mass loss from the reactors. Experiments C, D, and E contained sediments from core IW-05. Experiment C examined KMnO₄ OAM demand, experiment D examined the kinetics of the sediment system, and experiment E looked at DCE sorption onto the sediments.

Experiment A consisted of three sub-experiments (A, A2, and A3) examining the transformation kinetics of DCE and KMnO₄ at different initial KMnO₄ concentrations. Synthetic groundwater was added to the vial reactors followed by DCE stock solution and finally stock KMnO₄ solution. After the scheduled sampling time, subsamples were removed and transferred into a GC headspace vial with sodium thiosulphate and then analyzed. Experiment A and A2 were duplicate experiments that investigated DCE oxidation rate with a 0.99 mM KMnO₄ solution.

Experiment B also consisted of three sub-experiments (B, B2, B3) that investigated DCE loss from the reactors over time and served as the system control experiment. Synthetic groundwater was first added to the reactors, and then stock DCE solution was added. At the scheduled times, subsamples were removed and analyzed by GC. Reactors sample times varied from 1 minute up to 20 hours. A unitless Henry’s constants was calculated from the measured concentrations in the water, knowing the air
volume and total vial volume according to the following equation:

\[ H = \frac{M_{\text{air}}V_{\text{water}}}{M_{\text{water}}V_{\text{air}}} \]

Experiment C investigated the natural oxidant demand of core material from IW-05. A representative sediment was selected based on core logs from IW-05 23 to 24 meters below ground surface. Experiment C was essentially the same as experiment B except for the addition of core sediments.

Experiment D consisted of five sub-experiments and examined the kinetics of the sediment system. Experimental conditions were the same as experiment C except various KMnO\(_4\) solutions concentrations were added to the reactors. Four different KMnO\(_4\) concentrations were tested, 1.0, 3.8, 20, and 29 mM (0.02 to 0.5%). Initial DCE concentrations were \(\sim\)100 µg/L, which was double the average aqueous concentration from monitoring well S-31.

Experiment E examined sorption of DCE onto the sediment materials. Reactors with sediments, synthetic groundwater, and DCE were monitored for changes in DCE concentration that could not be attributed to DCE volatilization into the headspace of the reactors. Based on the total DCE mass added, the aqueous mass, and the volatilized mass, the sorbed phase could be determined. Once the sorbed mass was known, the sorption coefficient, \(K_d\), could be calculated according to the following equation:

\[ K_d = \frac{S}{C} \]

where \(S\) (µg/g) represents the mass sorbed and \(C\) (µg/mL) is the concentration in the
aqueous phase.

**Field Experiments**

Prior to KMnO₄ injection, groundwater samples were collected from existing monitoring wells S-31 and S-42 and analyzed for temperature, pH, oxidation reduction potential (ORP), total dissolved solids (TDS), and conductivity using a Myron L Company Ultrameter II 6P that was calibrated daily. Chloride, chromium (IV), and DCE samples were also collected and analyzed either in-house, at Turner Laboratories, Inc. (Tucson, Arizona), or Tranwest Geochem (Tucson, Arizona). S-31 and S-42 were purged for three well casing volume of water with dedicated Model QED Micropurge bladder pumps (Ann Arbor, MI) before samples were collected. Injection wells 3, 5, 7, and 8 were also sampled prior to KMnO₄ injection. Water samples were collected from injection wells before, during, and after injection.

The field injection system was supplied by Carus Chemical Company (Figure 3). The injection system consisted of 3 main parts--drum lifter, feeder, and mixer. KMnO₄ arrived in 55 gallon drums. Drums lids were removed and a funnel with a diaphragm was attached. Next, the drums were lifted and inverted into a Penn Process Technologies Omega volumetric feeder (Plumsteadville, PA). The amount of KMnO₄ feeding into the mixer was controlled by a dial on the feeder. Source water from a City of Tucson fire hydrant, which was piped ~274 meters, was added to the mixer chamber. KMnO₄ solution was pumped from the mixer to PVC piping mounted on the top of the injection wells (Figure 4).
RESULTS AND DISCUSSIONS

Core subsample analysis

A total of 66 solvent-extraction subsamples were collected from the nine injection well bore-hole cores in the source zone area ranging from 22.6 to 31.7 meters below ground surface (bgs). The quantifiable detection limit (QDL) for DCE was 4.5 µg of DCE per kg of sediment. Samples were reported as either detect (>4.5 µg/kg), below QDL (<4.5 µg/kg), or non-detect. Of the 66 samples, four had detections, 18 were below the QDL, and 44 were non-detect for DCE (Figure 5). DCE was detected in cores from injection wells 1, 3, and 9. DCE was detected but below the QDL for all cores except 5 and 6. Cores on the southwest edge of the injection well scheme (IW 5 and 6) did not have DCE detections, but the rest of the cores had some level of contamination. Extraction samples from IW-05 were used for the bench-scale experiments.

Total organic carbon (TOC) subsamples were collected from 47 core locations. Average TOC for all samples was 0.03%, which is consistent with previous research in the area (Johnson et al., 2003). Determining TOC was an important step in determining the natural oxidant demand of the site.

Bench-Scale Experiments

For experiments A and A2, DCE concentrations dropped below detection (0.003 mg/L) in the presence of 0.99 mM KMnO₄ between samples collected at 15 and 20 minutes. A3 contained 19.25 mM KMnO₄ solution and DCE concentrations dropped below detection after 10 minutes (Figure 7). Based on the calculations presented by Yan
and Schwartz (1999), pseudo-first-order kinetic rates were calculated for the different initial \( \text{KMnO}_4 \) concentrations of 5.2 h\(^{-1}\) and 23 h\(^{-1}\) for 0.99 mM and 19.25 mM, respectively. These results indicate that DCE is readily degraded even at low concentrations of \( \text{KMnO}_4 \).

Experiment B examined the mass loss of DCE in reactors (Figure 8). Based on the amount of DCE in the aqueous phase and in the headspace, Henry’s constant could be determined. The average value of \( H \) was 1.5 from the experiments. Reported literature values for DCE are similar, 1.4 and 1.1 in the Handbook of Hydrology (1993) and Gossett (1987), respectively.

Experiment C examined the natural oxidant demand associated with sediment, which is an important for determining the amount of \( \text{KMnO}_4 \) to inject into the subsurface. The natural oxidant demand from bench scale experiments was determined to be \( 1.0 \times 10^{-5} \) g of \( \text{KMnO}_4 \) per g of sediment. Total organic carbon in the samples from IW-05 yield an average TOC of 0.015\%. Based on the average DCE concentrations from monitoring well S-31 (31 µg/L) and assuming no immiscible liquid in the injection area, 99\% of the \( \text{KMnO}_4 \) injected into the system would be consumed by the natural oxidant demand.

Experiment D investigated the rate of DCE degradation for several concentrations of \( \text{KMnO}_4 \) with core sediments. For the \( \text{KMnO}_4 \) concentrations used in the experiments (0.99 mM, 3.75 mM, 19.9 mM, and 29 mM), DCE concentrations dropped below detection in all cases in less than 25 minutes. For \( \text{KMnO}_4 \) concentrations >1 mM, DCE was removed in less than 5 minutes (Figure 9). At an initial \( \text{KMnO}_4 \) concentration of 29 mM, DCE was removed from the system is less than 2 minutes. DCE was readily
degraded even in the presence of sediments, and aqueous DCE in the contaminated aquifer should be degrade even more quickly since the average injection concentration was 108 mM (1.7%).

The results of experiment E were used to determine the linear sorption coefficient, $K_d$, between DCE and sediment materials from IW-05, which were classified as silty-sand (65% sand, 15% silt, 5% clay, and 15% gravel). A mean $K_d$ of 1.0 mL/g was calculated from the experiments. This value appears to be larger than expected based on the measured $f_{oc}$ from IW-05 sediment (0.00015) and using reported $K_{oc}$ values of 65 and 150 l/kg from the Army Corp of Engineers (2002) and EPA (1995), respectively, to calculated $K_d$. Reported $K_d$ for TCE from Air Force Plant 44, south of the Samsonite Building, area was 0.04 ml/g (Zhang and Brusseau, 1999). Using literature values for $K_{oc}$ and experimentally $f_{oc}$ enables the calculation of $K_d$. For TCE $K_d$ ranges from 0.01 to 0.07 l/kg (Garbarini and Lion, 1986; Seip et al., 1986), and for PCE ranges from 0.02 to 0.08 l/kg (Seip et al., 1986; Zytner et al., 1989). From Seip et al. (1986), Soil B best matches Samsonite core samples and has a $K_d$ of 2.11 for TCE. The majority of DCE mass in the system should be in the aqueous phase versus the sorbed phased based on reported literature $K_{oc}$ values and experimental $f_{oc}$ values used to determine $K_d$.

**Groundwater Measurements**

Physical parameters (pH, T, ORP, Conductivity, and TDS), chloride, chromium (IV), and DCE were sampled pre-, during, and post-injection. Pre-injection data was not taken for IW-01. For all the other IW’s, pre- and post-injection data is available. IW-07
did not have KMnO₄ injected into it. Instead it served as a downgradient monitoring well.

The range of pH’s for IW’s pre-injection and post-injection were 6.8 to 7.5. The maximum change pre- and post-injection was an increase of 0.5 pH units in IW-04 and IW-05. The average pH pre-injection was 7.0 for all wells and 7.2 post-injection. Post-injection pH increased in four of the wells, decreased in three, and did not change in one. There did not appear to be any general trend (Figure 10). If pH was affected, it appeared to slightly increase.

ORP measurements appears to be the best indicator of KMnO₄ presence in the injection and monitoring wells. Pre-injection ORP averaged 203 mV while post-injection ORP average 634 mV, an increase of 431 mV. ORP in IW-07 increased to 450 mV and 550 mV 10 and 16 days, respectively, before KMnO₄ was visible on day 24 (Figure 11). ORP has been remaining steady in the IW’s and not showing any signs of decreasing after 78 days.

Conductivity measurement varied widely between IW’s and did not appear to be a good indicator of the movement and extent of KMnO₄ solution. Pre-injection conductivity values ranged from 826 µS in IW-09 to 2891 µS in IW-05 and averaged 2153 µS. Post-injection conductivity values increased up to a maximum of 11,880 µS in IW-08 twenty days post-injection. Average conductivity values post-injection were 9809 µS; however, IW-07 did not exhibit any noticeable change throughout the sampling period even with the arrival of KMnO₄ (Figure 12). Conductivity has decreased post-injection in IW-03 and 04 further exhibiting that conductivity was not a good indicator of the
presence of KMnO₄.

TDS measurements like conductivity varied greatly. Post-injection TDS levels in IW-03, 06, 08, and 09 increased dramatically while in IW-03 and 04 TDS decreased (Figure 13). IW-07 measurements increased slightly, 51 ppm. As with conductivity, the transport of KMnO₄ solution to IW-07 did not cause a noticeable change in TDS. TDS as well as conductivity appears to provide information regarding the interaction between KMnO₄ and the surrounding soils which can be important information, but does not provide insight to the transport of KMnO₄ or DCE degradation.

Chloride levels were monitored pre-injection to determine baseline groundwater values. Chloride concentration in IW-07 averaged 278 mg/L and monitoring well S-31 averaged 350 mg/L. Injection water was obtained from a city fire hydrant, which was chlorinated. Water samples collected from the influent had an average chlorine concentration of 32 mg/L. Therefore, chloride could not be used as an indicator of DCE degradation since any contribution of chloride to the groundwater would be minimum compared to the addition in the chlorinated influent water. Chromium (IV) samples were collected from IW-07 and S-31 and in all cases were below detection limits. One total organic carbon sample was collected from S-31 and was 0.57 mg/L.

DCE samples were collected from IW’s pre-injection and from IW-07 after injection until KMnO₄ was present in the solution. Sampling also occurred from S-42, a downgradient monitoring well. IW-07 was sampled three times pre-injection and three times post-injection before KMnO₄ solution was present on the fourth sample. Throughout the entire sampling period, concentrations remained relatively constant at 29 µg/L.
until dropping to non-detect when KMnO₄ was present. IW-08 averaged 28 µg/L for two sampling periods pre-injection. IW-03 and IW-04 were sampled once pre-injection and were 31 µg/L and 53 µg/L, respectively. After KMnO₄ reached IW-07, only S-42 was sampled for DCE. DCE sampling will resume when KMnO₄ is no longer present in any injection or monitoring well.

Currently, all injection and monitoring wells at the Samsonite Building Area are being sampled monthly. Six months after injection, a post-flush core is scheduled to be collected. The core will be analyzed for DCE, total organic carbon, and subsamples will be analyzed for Mn oxides using a scanning electron microscope. The effectiveness of the KMnO₄ injection will be determined by a combination of several factors including the following: aqueous DCE concentration in the downgradient monitoring well (S-42), aqueous DCE concentrations in S-31 after KMnO₄ is absent from the injection wells, the distribution of KMnO₄ and/or Mn oxides in the post-flush core, and DCE concentrations in post-core flush extraction samples. Monitoring well S-42 is approximately 67 meters downgradient of the injection wells and in the downgradient DCE plume. Aqueous DCE concentrations have averaged 2 µg/L in S-42, and if the DCE concentrations decrease it could indicate that KMnO₄ effectively degraded DCE mass in the source zone. It does not necessarily mean that all the mass was degraded since uncontaminated water could be diluting remaining DCE mass. Likewise, if DCE concentrations in S-31 and the injection wells do not rebound after KMnO₄ solution is no longer present after several quarters of sampling, then the injection could be deemed effective. Examining the post-flush core will clarify if KMnO₄ solution was able to transport through advection and
diffusion to regions of lower-K in the perched aquifer and permeate the source zone area. If regions do not contain either KMnO₄ solution or Mn oxides, DCE in sorbed or aqueous phase could still be present especially in lower-K regions. All regions will have extractions samples collected and be analyzed for DCE. Long term monitoring will be essential for determining the effectiveness of the KMnO₄ injection at the Samsonite Building Area.

CONCLUSIONS
A pilot-scale study using ISCO with KMnO₄ was undertaken at the Samsonite Building Area which is part of the Tucson International Airport Area Superfund Site. Exploratory data, NOM and DCE extraction, were gathered from core material. Core materials were also used in a series of bench-scale experiments to determine natural oxidant demand and DCE remediation rates. Pre- and post-injection groundwater sampling was undertaken to determine the effectiveness and areal extent of KMnO₄ flushing. About 250 kg of KMnO₄ were injected into each injection well. KMnO₄ migrated ~10 meters to IW-07 within 30 days and DCE concentrations dropped to below detection. KMnO₄ solution is currently in all injection wells 72 days after injection. ORP measurements are above 600 mV for all the injections wells. ORP proved to be a positive indicator of KMnO₄ transport as levels increased before KMnO₄ was detected in IW-07. Other physical parameters i.e. pH, conductivity, and TDS were not acceptable indicators of KMnO₄ presence. KMnO₄ has persisted in the environment and migrated from the injection wells
showing promise of remediating the DCE source zone at the Samsonite Building Area.

Monitoring will continue to determine the long-term effectiveness of ISCO with \( \text{KMnO}_4 \).
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REFERENCES


Table 1. Synthetic groundwater used in bench experiments.

<table>
<thead>
<tr>
<th>Ionic Species</th>
<th>Concentration (mg/L)</th>
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</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>50</td>
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<tr>
<td>Ca$^{2+}$</td>
<td>36</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>25</td>
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<tr>
<td>NO$_3^-$</td>
<td>6</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>60</td>
</tr>
<tr>
<td>CO$_3^{2-}$/HCO$_3^-$</td>
<td>133</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>99</td>
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</tbody>
</table>
Figure 1. 1,1-Dichloroethene concentrations from monitoring well S-31
Figure 2. Areal view of injection wells at the Samsonite Building Area. KMnO₄ injection occurred in all except IW-07 which served as a downgradient monitoring well.
Figure 3. Carus Corporation KMnO₄ injection system.
Figure 4. PVC pipe fittings mounted to IW-01.
Figure 5. DCE extraction grid in µg/kg of sediment.
Figure 6. Flow diagram of bench-scale experiments A through E.
Figure 7. Experiment A, DCE degradation for two different initial KMnO₄ concentrations. Lines represent pseudo-first order rate constants.
Figure 8. Experiment B control experiments.
Figure 9. Experiment D, DCE aqueous concentration decreasing in the presence of varying KMnO₄ concentrations.
Figure 10. Pre- and post-injection pH measurements for IW-01 to 09.
Figure 11. ORP measurements pre- and post-injection for IW-01 to 09.
Figure 12. Conductivity measurements for IW-01 to 09.
Figure 13. TDS measurements pre- and post-injection for IW-01 to 09.
Figure 14. DCE concentrations in IW’s pre- and post-injection.