IN SITU CHEMICAL OXIDATION SCHEMES FOR THE REMEDIATION OF GROUND WATER AND SOILS CONTAMINATED BY CHLORINATED SOLVENTS

DISSERTATION

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By

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* * * * *

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ABSTRACT

This study investigates various aspects of in situ chemical oxidation (ISCO) schemes based on MnO$_4^-$ Batch experiments show that the interaction between MnO$_4^-$ and sediment solids will not only consume the reactant, but also can release toxic metals into ground water. Various column and flow tank experiments were conducted to examine the capacity and efficiency of the oxidation scheme. Oxidation was capable of destroying chlorinated ethylenes in aqueous phase. MnO$_4^-$ oxidation performs better in removal of residual DNAPL than pooled DNAPL. In zones of high NAPL saturation, Mn oxide precipitates causing pore plugging and permeability reduction. These changes potentially could cause the remedial action to fail. In an effort to mitigate the precipitation, experiments have been carried out to investigate possibilities of delaying the formation of colloidal Mn oxide and to remove the precipitates once formed. The investigation begins with the identification of the Mn oxide mineral structure and the determination of the chemical properties of the solid. Phosphate ion was added to the reaction in an attempt to slowdown colloidal formation due to its high charge and the tendency to sorb on surfaces. The results indicate that the presence of phosphate ion can lower the rate of colloid formation. However, the magnitude of effects due to the addition
of phosphate is limited by the ionic strength increase and the pzc (point of zero charge) of the mineral. The dissolution kinetics of birnessite was evaluated using solutions of citric acid, oxalic acid, and EDTA. The results showed that the addition of an organic acid could greatly increase the dissolution rate of birnessite. The dissolution mechanism involves proton and ligand-promoted dissolution and reductive dissolution. A permanganate reactive barrier system (PRBS) was designed and a proof-of-concept experiment was carried out in the laboratory. The experiment demonstrated how the PRBS could deliver MnO$_4^-$ at a stable, constant, and controllable rate. This idea could be developed as a long-term reactive barrier for the remediation of chlorinated solvents in plume.
Dedicated to Yijie and Olivia
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CHAPTER 1

INTRODUCTION

1. Background and significance of this study

Since the 1980s, ground-water contamination by organic chemicals has raised serious concerns in industrialized countries around the world. The most common of these contaminants are chlorinated organic solvents, like tetrachloroethylene (PCE) and trichloroethylene (TCE), which are usually used as degreasers in metal fabricating. Those compounds were first produced in Germany at the end of the last century and were introduced into the United States in about 1906 (Wiseman, 1979). In the early to middle twentieth century, they were used for a wide variety of purposes. Meanwhile, their toxicology and environmental behaviors were not thoroughly understood, leading to improper handling and disposal practices. Due to their widespread uses and historical mishandling, chlorinated solvents are at the top of the list of contaminants found in the United State and Europe. At approximately 400,000 sites in the United States alone, soil and ground water are contaminated by chlorinated solvents (Sutfin, 1996).
Once they enter the subsurface, chlorinated solvents pose an immediate threat to ground water quality. Their solubility in water is generally large, on the order of several hundred or thousand milligrams per liter. However, their maximum contaminant levels (MCL) determined by the Safe Drinking Water Act are much lower. The difference between the solubility and the MCL is in many cases more than two orders-of-magnitude. Thus, even a small amount of dissolved solvent can pollute a large volume of ground water. Because they are immiscible in water, chlorinated solvents often exist in the subsurface as a separate phase, called a non-aqueous-phase liquid (NAPL). Because most chlorinated solvents are denser than water, they are called DNAPLs, dense non-aqueous-phase liquids. DNAPLs occur as residual droplets along the migration pathway or pools at the bottom of an aquifer. The mass transfer rate from some DNAPL to the aqueous phase (i.e., the dissolution rate) is often small with relatively low ground-water flow velocities. In addition, natural degradation rates for DNAPLs are very small in aerobic settings. These two features cause DNAPLs to persist in the subsurface for centuries. Therefore, DNAPLs are a long-term source of ground-water contamination. Moreover, DNAPLs typically do not move along the flow gradient in aquifers because they are denser than water and tend to move downward under a separate hydraulic head. The presence of DNAPL causes extreme difficulty in site characterization and remediation.

2. Review of the remediation technologies

Remediation techniques for ground-water contamination can generally be categorized as either ex situ or in situ, based on the operational procedure. Ex situ
approaches, including pump-and-treat, soil vapor extraction (SVE), air sparging, steam flooding, six-phase heating, etc, involve bringing contaminants to the surface and treating them there. SVE and air sparging can only work well in geological formations with high air permeability. Heating methods usually are costly and when the electricity is applied, they require a relatively homogenous field setting. Conventional pump-and-treat methods generally relegate the treatment to an effort in hydraulic plume control rather than mass removal of the DNAPL from the site. To improve the efficiency of contaminant removal, cosolvents or surfactants are added to increase the solubility of DNAPL. However, these approaches are usually very expensive and some of them are not environmentally safe. Meanwhile, field demonstration has shown that surfactants do not completely remove the DNAPL (USNRC, 1994).

Examples of in situ treatment schemes include bioremediation and abiotic chemical destruction. Intrinsic bioremediation, as an in situ treatment approach, is efficient for soils containing polycyclic hydrocarbons, light petroleum oils, and other organic contaminants (Gen-Hsung et al., 1996). However, bioremediation suffers from a drawback that aerobic bacteria cannot use chlorinated aliphatic compounds as a primary substrate. In addition, bioremediation does not work directly on the DNAPL even when the bacteria can consume the compound as a secondary substrate. Enhanced biodegradation requires the addition of the nitrogen, phosphorous and some electron acceptors, so that chlorinated ethylenes can be biodegraded through a sequential reductive pathway (Semprini et al., 1995; McCarty and Wilson, 1992). In the case of PCE, the pathway is PCE → TCE → DCE → vinyl chloride → ethylene. Complete
dechlorination is slow and is characterized by a complicated reaction pathway, which make this technology less practical for remediating chlorinated ethylenes in the field.

In recent years, both oxidative and reductive schemes have been developed as in situ remedial technologies. Chlorinated solvents can be destroyed through reductive dechlorination, catalyzed by zero-valent iron (Gillham and O'Hannesin, 1994). This strategy is mainly applied in the field using a reactive barrier or treatment wall. A five-year field experiment has provided encouraging results. However, the rate of reductive dechlorination is slower with a decreasing number of chlorines attached to the compound. It is also a passive technology, which is not appropriate for source zone remediation.

Oxidative dechlorination can be achieved through advanced oxidation processes (AOPs), which have been employed to the treatment of drinking water. AOPs rely on reactive hydroxyl radicals released from the oxidants to oxidize chlorinated solvents. Ozone, hydrogen peroxide are often used in the AOPs, sometime under ultraviolet radiation or in the presence of other chemicals. The most common field applications so far have utilized Fenton's reagent, a mixture of hydrogen peroxide and ferrous iron. Hydrogen peroxide reacts to become a hydroxyl free radical under iron catalyst. The hydroxyl free radical is capable of oxidizing complex organic compounds. This technique has a history of application in wastewater treatment. It has been applied in in situ schemes, but appears to be less effective than MnO$_4^-$ and is extremely reactive with the medium.

Recently, oxidation of the chlorinated solvents by potassium permanganate (KMnO$_4$) has emerged as a viable scheme for treating subsurface contamination, and has received wide attention. KMnO$_4$ is a powerful oxidant for organic synthesis and its
oxidation mechanism is different from other AOPs. Batch scale experiments have shown a rapid, completed mineralization of contaminants with final products that are environmentally safe (Yan and Schwartz, 1999). Researchers at the University of Waterloo (Schnarr et al., 1998) and Oak Ridge National Lab (West et al., 1997) have conducted experiments to investigate permanganate-oxidation schemes in field and laboratory tests. Even though these pilot experiments were not well controlled, the results suggested that MnO$_4^-$ oxidation is a promising technology for the remediation of chlorinated solvents. This approach also has been implemented at several sites around the nation even though its efficiency and factors that impact success of the scheme were not well understood. History in the development of remedial technologies has shown time and time again that there is a rush to move promising technologies into the field before fundamental scientific work has been completed.

Problems remain to be solved in order to achieve complete removal of DNAPLs from a contaminated aquifer. This study specifically addresses topics that bear on the realistic use of MnO$_4^-$ oxidation schemes for DNAPL clean ups including mass removal rate, and the geochemistry of Mn oxide. The study also addresses perceived weaknesses of the MnO$_4^-$ oxidation scheme – flooding inefficiencies, and pore plugging, related to reaction products. The results of this investigation will provide fundamental information for the implementation of oxidation schemes in the field.
3. Brief summary of subsequent chapters

This research uses laboratory experiments to investigate various aspects of in situ chemical oxidation (ISCO) schemes with MnO$_4^-$ for the remediation of chlorinated ethylenes. Chapters 2 through 7 are each devoted to one specific problem that might be encountered during site remediation. The chapters are written in the form of complete research papers. Some of the materials in Chapters 2, 3, 6, and 7 have been presented at conferences presentations and several technical papers.

Chapter 2 focuses the non-specific reactions between MnO$_4^-$ and natural sediments. Such reactions not only consume the oxidant and lower the flushing efficiency, but also can release harmful metals to the ground water. However, the effect of mobilized metals is expected to be localized and short-term. In Chapter 3, results from various column and flow tank experiments demonstrate the capabilities of the powerful oxidant, MnO$_4^-$ in removing and destroying DNAPL in porous media. These experiments also showed that reaction products (Mn oxide, CO$_2$ gas) can cause pore plugging and reduce the permeability of the porous medium. There is a need for basic data to understand and to solve problems caused by Mn oxide precipitation encountered during remediation. Chapter 4 provides useful information on the mineral structure and chemical composition of the Mn oxide, as well as its surface chemical properties.

Chapter 5 investigates the possibility of adding phosphate to delay and to control colloidal Mn oxide growth in MnO$_4^-$ oxidation schemes. The results show a limited effect of phosphate on delaying the formation of colloids. A different approach to mitigate the problem of Mn oxide precipitation was developed and tested through a series of batch
and flow tank experiments in Chapter 6. It was discovered that Mn oxide solid can be dissolved quickly by certain organic acids like citric, oxalic, and EDTA, via various reaction mechanisms such as ligand-promoted, and reductive dissolution. By imposing ligand-promoted dissolution, the precipitates of Mn oxide formed in the oxidation of TCE by MnO$_4^-$ were dissolved and removed from the porous medium. Eventually, all the DNAPLs and precipitates were dissolved out of the porous medium.

In Chapter 7, a semi-passive permanganate reactive barrier system (PRBS) was designed and tested in laboratory conditions. It may be developed as a field technology for the remediation of the contaminant plume. Chapter 8 summarizes the results from this research, outlines the major findings of the study, and discusses the direction for future work on this subject.
CHAPTER 2

RELEASE OF METALS FROM THE OXIDATION OF SUBSURFACE SEDIMENTS

1. Introduction

The \textit{in situ} destruction of the chlorinated solvents, using oxidants like potassium permanganate (KMnO$_4$), is receiving considerable commercial interest. MnO$_4^-$ is a powerful oxidant that has been used for a long time in wastewater treatment. Batch scale experiments show that this oxidant rapidly destroys chlorinated ethylenes with final products that are environmentally safe (Yan and Schwartz, 1999). Researchers at the University of Waterloo (Schnarr et al., 1998) and Oak Ridge National Laboratory have conducted field demonstrations as proof-of-concept for MnO$_4^-$ oxidation schemes. All these results point to oxidation using MnO$_4^-$ as a promising technology for the remediation of chlorinated solvents. This approach also has been implemented by consultants at several sites in Florida and California.
Indications from these field studies and my preliminary work (Li and Schwartz, 2000) are that in situ chemical oxidation (ISCO) schemes using MnO$_4^-$ have inherent problems that could severely limit their applicability. As a powerful oxidant, MnO$_4^-$ is not only capable of oxidizing chlorinated ethylenes, but also inorganic compounds in ground water and solid sediments. For example, Drescher et al (1998) reported significant consumption of MnO$_4^-$ by humic acid in a system consisting of sand, TCE, MnO$_4^-$ and humic acid. With sediments consuming some of the MnO$_4^-$, the overall efficiency of the cleanup is reduced and costs are increased.

It has been noted that MnO$_4^-$ reaction with sediment can release metals (e.g. Cr$^{3+}$) to the aqueous phase at a concentration of regulatory concern. Column and batch experiments show that both KMnO$_4$ and MnO$_2$ can oxidize trivalent chromium to toxic hexavalent chromium (Chambers et al., 2000). Given the present, relative limited understanding of the oxidation reactions, there is a need for studies to understand these problems and to improve the efficiency of MnO$_4^-$ delivery. The objective of this study is to examine the competition in MnO$_4^-$ utilization provided by geologic media, and to determine what other products might be liberated by oxidation. It is also the intent to propose a possible oxidation mechanism for the sediments to explain the sources of chemical changes. The hypothesis is that MnO$_4^-$ will react with the minerals that comprise the porous medium. The study here will focus on elements of environmental concern, like chromium, selenium, arsenic, etc.
2. Materials and methods

Batch studies were utilized to investigate the consumption of MnO$_4^-$ by sediments and the release of potentially hazardous metals. Batch experiments provide a basis for examining the interaction of MnO$_4^-$ with natural sediment and the extent to which metals are released. Twenty-three samples were collected from various media, such as, alluvium, glacial till, glacial outwash, and carbonate sand (Table 2.1). Samples were collected at depth, away from soil horizons. Analytic grade KMnO$_4$ used in this study was obtained from Fisher Scientific Co..

Sediment samples were placed in an aluminum pan to air dry for two to three days. Experiments were conducted at room temperature in 25 mL vials. 15 g of each sediment sample was mixed with 15 mL of 2.5 g/L KMnO$_4$ solution. A control was prepared with the same KMnO$_4$ solution, but without the sediment. After the MnO$_4^-$ solution was added to the solid medium, the vials were covered with aluminum foil and black cloth, and kept in the dark to avoid photo-induced degradation of KMnO$_4$. Sample vials were shaken by hand once a day to ensure mixing during the experiment. At predetermined time steps, 5 mL of solution was removed from the vial and filtered through a 0.22 μm glass fiber membrane to remove any suspended solids immediately prior to the concentration measurement. MnO$_4^-$ concentrations were measured with a Varian Cary 1 UV–visible spectrophotometer at a wavelength of 525 nm.

The study of metals released by the oxidation of sediments followed a similar procedure. The controls (untreated with MnO$_4^-$) in this case were mixtures of 15 mL
Milli-Q deionized water and sediments. By comparing the differences between metals released from the control experiments and oxidized materials, the effect of MnO₄⁻ treatment could be established. After 10 days, once the MnO₄⁻ had mostly been consumed, both the untreated controls and samples with oxidant were separated from large solid particles and filtered to remove suspended solids. The samples were analyzed by a Perkin-Elmer Sciex ELAN 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). As a first stage, a semi-quantitative screening analysis was performed to identify the elements with the most dramatic change in concentration. This step was followed by a quantitative analysis with specific external standards. In all, 12 elements were analyzed quantitatively. The results were converted to the pore water concentration, based on the porosity of the media. The KMnO₄ was also analyzed by ICP-MS at the same concentration as used in the experiment, to assess the possibility that impurities could be present in the oxidant.

In order to understand the possible source of metals released into the aqueous phase and possibly to understand the reaction mechanism between sediment and MnO₄⁻, the chemical compositions of three aquifer sediment samples were determined. Whole sample chemistries were determined for samples DC1, MS, and RB. The samples were prepared for analysis by ICP-MS. About 100 mg of each solid sample were mixed with lithium metaborate (LiBO₂) in 1:6 ratio in a platinum crucible. These materials were placed in an oven at a temperature of 1000 °C for 30 minutes to fuse the sample mixtures. Then, after cooling, the mixture was dissolved in 10 % HNO₃ and diluted to 100 mL. This process assures that all elements in the solid materials are dissolved in the final
solution. The ICP-MS analysis determined the concentration of elements in the solution based on external standards.

Solid sediments were also examined by scanning electron microscopy (SEM) to observe directly any details in the solid that might influence their reaction with MnO$_4^-$.

The examination was conducted using JEOL JSM-820 SEM equipped with Oxford eXL energy dispersive X-ray analyzer for element analysis. Images of interesting particle were taken for subsequent analysis. In some cases, the chemical composition of selected areas within particles was determined using the element analyzer on the SEM.

3. Results

Results of batch experiments are plotted in Figure 2.1. After 10 days, for more than half the samples of natural sediment, irrespective of type, MnO$_4^-$ concentrations dropped to near zero, with more than 99% of MnO$_4^-$ consumed. Nineteen out of 23 samples tested consumed more than 50% of MnO$_4^-$.

The remaining four samples indicated a much smaller change in MnO$_4^-$ concentration. One sample, NEUSDA, from an alluvial aquifer, consumed less than 6% of the MnO$_4^-$ after 10 days. Careful visual examination discovered this sample contained mostly quartz. The change in MnO$_4^-$ concentration in all the samples can also be seen from Figure 2.2, where MnO$_4^-$ concentrations before and after 10 days of treatment are presented. The decrease in the MnO$_4^-$ concentration follows a first order kinetic rate law for more than half of the samples (Figure 2.1). Because MnO$_4^-$ is likely conservative in the aqueous phase, it is unlikely concentration reductions were caused by sorption onto the solids.
The reduction in MnO$_4^-$ concentration implies oxidation reactions with the solids. Results of the ICP-MS analysis of the pore water MnO$_4^-$ treatment (Figure 2.3 - 2.14) confirmed this conclusion. In spite of the variability among the samples, there are common features among the results. Of the 12 elements that were quantitatively analyzed, zinc (Zn), chromium (Cr), rubidium (Rb), selenium (Se), and mercury (Hg) generally increased in concentration; molybdenum (Mo), and lead (Pb) decreased. The remaining elements (titanium (Ti), arsenic (As), vanadium (V), and cesium (Cs)) generally showed no significant change. While the pattern of change is relatively consistent, the magnitude of change is variable. In some cases, the concentration could change several-hundred fold. Table 2.2 presents the element concentrations of the solutions with and without the MnO$_4^-$ treatment, and concentrations, ranges for national waters reported by U.S. EPA, together with the drinking water standards as Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs). Element concentrations measured in this study, with or without MnO$_4^-$ treatment, are within the ranges of the national observed values.

Among all the elements tested, Zn has the largest increase, an average of 1548 µg/L for all samples. The increase is consistent in all samples (Figure 2.3). Zn concentrations are generally high for all samples without MnO$_4^-$ treatment. This result suggests that Zn is available in a soluble form. For several samples, the Zn concentrations before the treatment are higher than 1 mg/L. After the treatment one sample (Sample RB) has a Zn concentration close to 10 mg/L. Zn is not regulated in the National Primary Drinking Water Regulations, but in the National Secondary Drinking Water Regulations, which provide guidance for nuisance chemicals (USEPA, 2001). The secondary standards
are non-enforceable guidelines regulating contaminants that may cause cosmetic effects or aesthetic effects in drinking water. The standard for Zn is 5 mg/L. None of the samples without the MnO₄⁻ treatment had a Zn concentration exceeding the standard, but 7 samples had Zn concentrations close to or surpassing the standard with the treatment.

Cr showed the second largest increase among all the elements tested, averaging 504 µg/L for all. Every sample tested has an increase in Cr concentration (Figure 2.4). The concentration in an aqueous solution without oxidation treatment is low, around 10 µg/L, but the treatment increased the concentration to close to 1000 µg/L for most samples. Cr is regulated with both the MCLG and the MCL at 0.1 mg/L (100 µg/L). Some states, such as California, have an even lower MCL of 0.05 mg/L. Most solid samples treated with the oxidant provide Cr concentrations above the MCL. Given the adverse environmental and health effects related to Cr, it will be of concern in MnO₄⁻ treatments.

Rb concentration also increased in almost all samples following 10 days of treatment with MnO₄⁻ (Figure 2.5). The average increase was 369 µg/L. Rb concentration in solution without treatment is low, ranging from about 2 to 90 µg/L. However, following 10 days of treatment, the concentration jumps to as high as about 1000 µg/L for some samples. Rb is not nationally regulated, but an increase due to MnO₄⁻ is definitely marked.

Se concentrations also exhibit an across the board increase, averaging 198 µg/L (Figure 2.6). The concentration of the untreated solution varies from below detection to just > 100 µg/L. However, with the treatment several samples showed an increase of
more than 500 µg/L in concentration. Se is regulated with both MCLG and MCL at 0.05 mg/L (50 µg/L). With its potential for impacts, the mobilization of Se during the MnO$_4^-$ treatment could be a concern.

The concentration of Hg before the treatment is low, mostly below 5 µg/L, concentrations in several samples were below detection limit (Figure 2.7). The MnO$_4^-$ treatment increases the Hg concentrations in almost all samples, by an average of 19.4 µg/L. Several samples show concentrations at about 100 µg/L. Hg is a metal that can have direct human health impacts, like kidney damage. It is regulated with both the MCLG and MCL at 0.002 mg/L (2 µg/L). Given this low standard, Hg should be closely monitored in ISCO schemes employing MnO$_4^-$.

Cs is barely detectable in the untreated aqueous samples, and only slightly elevated afterward (Figure 2.8). Although some release of Cs by the oxidation is common to almost all the sediments tested, the small increase and the fact that it is unregulated make it less of a concern in MnO$_4^-$ schemes.

In most of the experiments, Cd is below detection for samples both treated and untreated with MnO$_4^-$ (Figure 2.9). The effect of the MnO$_4^-$ oxidation on Cd concentrations is mixed and relatively insignificant. However, this element has a MCL standard at 0.005 mg/L (µg/L). For several samples, the treatment raises the concentration slightly over regulatory limits.

V and Ti behave similarly in response to MnO$_4^-$ oxidation. They both have almost unchanged average concentration for all the samples with and without the treatment (Table 2.2). Their concentration changes in individual samples were mixed and minor (Figure 2.10 and 2.11). They also both are not regulated.
The concentrations of As at the start of treatment ranges from below the detection limit to 120 µg/L with a mean of 16 µg/L (Figure 2.12). MnO₄⁻ oxidation lowered the As concentration to average 4.3 µg/L (Table 2.2). However, As is regulated with an MCL of 0.01 mg/L (10 µg/L). Thus, samples, both treated and untreated, have concentrations higher than the regulation standard. As a potential carcinogen, As should be closely monitored during remediation action, even though MnO₄⁻ treatment appears to reduce its concentration in ground water.

The consequence of oxidation on the Pb concentration is mixed (Figure 2.13). Results vary from a 246 µg/L increase to a 348 µg/L decrease. On average, the changes in all the samples is a decrease of 49 µg/L. The MnO₄⁻ treatment generally reduces the Pb concentration in ground water. Pb in drinking water has an MCL of 0.015 mg/L (15 µg/L). More than half of the samples exceeded the MCL, with and without the treatment, or both.

Of all the elements tested, Mo exhibits the largest reduction in the concentration due to the MnO₄⁻ treatment, an average of 121 µg/L. This reduction was apparent in almost all of the samples (Figure 2.14). Mo concentrations in drinking water are not regulated.

The change in solution composition can either due to the addition of KMnO₄, or be caused by water-solid interactions. An analysis of the chemical impurities has revealed that some of the element concentration changes may be attributed to the KMnO₄ reagent. Figure 2.15 summarizes the ICP-MS measurements for the same 12 elements discussed earlier for the KMnO₄ solution at the concentration of 2.5 g/L, the same as used in the metal release experiments. The result shows that the major impurities of the reagents are
Zn, Rb and Pb, with Ti, Cr, Se, and Cs at lower but detectable level. V, As, Mo, Cd, and Hg are not detectable. The KMnO$_4$ solution can contribute approximately 1000 µg/L of Zn and Pb, and more than 100 µg/L of Rb, but the impurities from reagent solution could not produce the concentration increases in the metals observed in the experiment for the rest of the samples.

The chemical compositions for the solid sediments were measured for three samples (Figure 2.16 – 2.18). The concentrations used for the figures are µg/L for solution and µg/kg for the solid, which is equivalent to µg/L. In Table 2.3, data measured in this study were compared with the national values for surficial deposits. Samples in this study generally have a smaller average elemental concentration than the national data, but metals are all within the range of the national data values. An important feature common to all the samples tested is that the solution element concentration is always smaller than that of the solid respectively, no matter whether treated with MnO$_4^-$ or not. This result generally indicated the potentials for the solids to be the source of the solution chemical change. The concentration data were converted to the elemental mass content, which were presented in Table 2.4. Though some variation is evident for different samples and elements, the elemental mass content in the solution is only a fraction of that in the solid for most of the elements. This confirms the earlier suggestion that the solid sediments are capable of being the major source of the solution chemical changes.

Figure 2.19 is an SEM image of a solid particle from sample MS. Apparently the particle has a coating that could have developed through weathering or some other surface reaction. This example suggests a heterogeneous and more chemically complex material, which could be the source of the metals that have released. The concentration of
the trace elements determined by SEM is low, and below the detection limit of 0.1% of the quantitative chemical microanalysis. No trace element was detected with this method.

4. Discussion

In the batch experiment, the dramatic disappearance of MnO$_4^-$ the change in chemistry of the aqueous phase point to significant interactions between porous media and MnO$_4^-$. Given the variability in mineralogy and grain coatings, it is not possible to propose a reaction mechanism. The results of the element source analysis suggest that the sediment solids are capable of releasing these chemicals to ground water for all the samples tested. Furthermore, impurities in the KMnO$_4$ reagent can contribute to the increase. However, not all of the elements that were analyzed experienced a concentration increase in solution. For example, Mo had a significant reduction, as did Pb, even with a large concentration (almost 1000 µg/L) from the KMnO$_4$ solution. Obviously, the change of the solution compositions not only relies on the source of the elements but also the chemical process that governing the speciation of the elements.

The addition of KMnO$_4$ to an aqueous solution dramatically increases the redox potential, measured as $E_H$. If a contaminant like TCE is present, the reaction can also reduce the pH (Equation 2.1).

\[
C_2HCl_3 + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2 + 2\text{CO}_2 + 3\text{Cl}^- + \text{H}^+ \quad (2.1)
\]
Natural ground water has pH in a range roughly from 5 to 9, and \(E_H\) from -100 mV to 600 mV, estimated from Domenico and Schwartz (1997), Pourbaix (1974), and Christensen et al. (2000), which can be represented in the circled area of Figure 2.20. In the figure, Mn stability field for \(\text{MnO}_4^-\) is above the water oxidation dissociation line, so \(\text{MnO}_4^-\) will certainly increase the \(E_H\) of the solution. The addition of \(\text{MnO}_4^-\) will increase \(E_H\) in the direction shown by the solid arrow in Figure 2.20. If the pH also changes, then the dashed arrow is an estimate of the direction of change in \(E_H\)-pH. A change in \(E_H\)-pH will affect the speciation. If the re-speciation involves phase change between solid and dissolved species, the mobility of the elements changes.

In the following discussion, I will rely mainly on Pourbaix (1974) and Brookins (1988) for information about the speciation of different elements under different \(E_H\), and pH. The \(E_H\)-pH diagrams in these books are based on a simple chemical system and standard state (1 atm, 25 \(^\circ\)C). In more complicated real environments, there should be some variations. However, this will have little influence on the discussion here.

The increase in Zn concentration is definitely caused by impurity of the \(\text{KMnO}_4\). In a system of Zn-O-H-S-C, the stability diagram (Brookins, 1988) shows all vertical lines within the water stable area, except at very reducing condition when sulfide exists. This means that under most conditions a change in redox potential alone will not change the Zn concentration in ground water, unless the change is away from very reducing condition when ZnS exist. Under this condition an increase in \(E_H\) will increase Zn concentration. However, as a major impurity of \(\text{KMnO}_4\), Zn should be monitored during the oxidation remediation action, considering it is regulated in drinking water.
Cr concentrations exhibit a large increase due to MnO$_4^-$ oxidation. Because Cr is not a significant impurity in KMnO$_4$ (< 10 µg/L in my solutions), The increase in Cr should come from reaction with the solid sediments. Across wide pH and E$_H$ ranges, Cr is a stable solid either as Cr(OH)$_3$ or Cr$_2$O$_3$ at oxidation state (III), or trivalent chromium. Only in strong oxidizing conditions, does Cr exist as dissolved species CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$, or HCrO$_4^-$ at oxidation (VI), or hexavalent chromium. Cr(III) is the most environmentally stable species of Cr. Virtually all naturally existing Cr occurs as Cr(III). Other forms of Cr tend to be converted to Cr(III) in natural environments (Barnhart, 1997), because Cr(III) is at the most thermodynamically stable oxidation state. Cr can potentially cause many adverse environment and health effects, especially in the hexavalent state, because it is more toxic and mobile. As the oxidation state changes with the addition of MnO$_4^-$, E$_H$ changes in the direction indicated by the solid arrow in Figure 2.20. Solid Cr(III) presented in the sediments will be oxidized according to one of the following equations (Equations 2.2-2.4), releasing Cr(VI) into the ground water in a mobile form.

\[
\begin{align*}
\text{Cr}_2\text{O}_3 + 5\text{H}_2\text{O} & = 2\text{HCrO}_4^- + 8\text{H}^+ + 6\text{e}^- \quad (2.2) \\
\text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O} & = \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 6\text{e}^- \quad (2.3) \\
\text{Cr}_2\text{O}_3 + 5\text{H}_2\text{O} & = 2\text{CrO}_4^{2-} + 10\text{H}^+ + 6\text{e}^- \quad (2.4)
\end{align*}
\]

Not only can MnO$_4^-$ oxidize Cr(III) to Cr(VI), but can MnO$_2$ too, at a slower rate. Through a heterogeneous surface reaction, Cr(III) can be oxidized to Cr(VI) effectively by various forms of Mn oxide or hydroxide like β-MnO$_2$ (Guha et al., 2001), γ-MnOOH (Johnson and Xyla, 1991), and birnessite (Banerjee and Nesbitt, 1999). The Mn oxide
formed in the MnO$_4^-$ oxidation is likely to continue to oxidize the Cr(III) after MnO$_4^-$ remediation action has stopped.

Because Cr(III) is the most stable oxidation state across a large range of $E_H$ and pH, there is a tendency for Cr(VI), which has been mobilized by the MnO$_4^-$ oxidation, to be converted back to Cr(III), once the Cr(VI) migrates to more normal conditions away from the MnO$_4^-$ treatment area. A field study has confirmed this suggestion. In a pilot field MnO$_4^-$ remediation experiment (Chambers et al., 2000), elevated concentrations of hexavalent chromium started to decline two weeks after the injection of MnO$_4^-$, and returned back to pre-treatment condition within three months. This process is natural attenuation, which has been listed as possible remediation technologies for Cr contamination (USEPA, 2000). Thus, the extent of mobilized Cr(VI) at a real contaminant site is probably limited to a relatively small area, due to natural attenuation process.

Rb and Cs are both alkali metals, like Na and K, and have very similar chemical features. From the published stability diagrams, the solid phase can only exist under strong reducing condition as native metals, or solid hydride like RbH, CsH. In the natural environments, they can only present as ions like Rb$^+$, and Cs$^+$. Changes in $E_H$, and pH within the range of natural environments should have no significant effect on their concentration. However, it is possible for them to form co-precipitates or impurities with other metal oxides, which should be only at trace levels. In my experiments, the increase in Rb is due to impurities in the KMnO$_4$ reagents.

In natural environments, native selenium is stable under reducing conditions, so are metal salts of selenide, Se(-II), which can both be oxidized to soluble HSeO$_3^-$, SeO$_3^{2-}$,
or SeO$_4^{2-}$. Se can often substitute for S due to their similar chemical nature, so it can occur with metal sulfides (Brookins, 1988). Selenium tends to be much more mobile in oxic as compared to reducing condition (Alloway, 1995). The treatment with MnO$_4^-$ should release Se from the solid sediments and increase its concentration in ground water.

Hg exhibited a slight, but significant increase in concentration due to oxidation. Even these small increases are of concern because of the low MCL (2 µg/L). The KMnO$_4$ contains no detectable Hg as an impurity. Thus, increases in Hg concentration should be from the oxidation of metals. The main species of Hg, which are stable over a large range of E$_H$ and pH, are all solids, HgS under reducing condition, HgO under oxidizing condition, and native Hg in between. Within the pH range of normal environment, variation of E$_H$ alone does not change the mobility of this element. However, the existence of some species, for instance, Cl$^-$ can increase its solubility by forming complexes (Alloway, 1995). The increase of Hg following oxidation does not seem to be caused by the impurity in the KMnO$_4$ or the adjustment of E$_H$. It is likely associated with other chemical changes in the system that were not quantified in this study. However, the increase in Hg concentration is relatively small and only important because of its health sensitive nature.

Cd has a mixed response to oxidation, but all changes are minor. In natural ground water, it exists as Cd$^{2+}$ or solid Cd oxide/hydroxide. The lines on the appropriate E$_H$-pH diagram are vertical, indicating that its phase composition should not be sensitive to changes in E$_H$. The changes observed in this study are insignificant.

V is soluble except under strongly reducing condition at neutral pH. However, V concentration does not increase in most of the samples treated, although the solid
sediments apparently contain abundant V. Likely, V in the solid is the poorly soluble mineral vanadate, which does not respond to the $E_H$ change.

Ti is stable as a solid phase over large $E_H$ and pH ranges, in the form of oxides and hydroxides. At very low pH, the stable phase is TiO$^{2+}$. Increasing the $E_H$ does not appear to mobilize Ti. The small variation of Ti detected in the study could be related to its association with other mineral. KMnO$_4$ likely contributes a small amount of Ti, as well.

According to the stability diagram (Brookins, 1988) for system of As-O-H, As is stable as a native element or oxide under reducing condition. It can be oxidized to various forms of soluble arsenic acid. In natural environment, As is commonly present as arsenopyrite, FeArS (Alloway, 1995). It seems that MnO$_4^-$ oxidation should enhance its concentration. However, this was not the case with the experimental result from this study. As is also associated with iron oxide/hydroxide through adsorption or co-precipitation. When this happens, the mobility of As is often controlled by the stability of iron oxide/hydroxide. The binding of As with iron oxide/hydroxide is stronger in oxidizing conditions than in reducing conditions. This mode of occurrence was proposed as a possible mechanism contributing to the arsenic pollution of ground water in Bangladesh. One suggested scheme for the treatment was through co-precipitation with iron oxide/hydroxide by aerating the polluted water (Nickson et al., 1998; Nickson et al, 2000). The decrease of As concentration in this study may be explained by the same mechanism, considering iron is a very common element. However, without further understanding of the mineral composition of each sample, it is difficult to fully identify the release mechanism.
On average, the concentration of Pb is lower after oxidation. However analysis of KMnO$_4$ reagent reveals that Pb is a major impurity with concentrations at about 1000 µg/L. The loss of Pb must have taken place after the KMnO$_4$ came in contact with the solid sediments. In most normal environments, Pb is stable as an oxide, carbonate, sulfite, or sulfate, all solids. In the pH range near neutral, solid lead carbonate is the stable phase. Because carbonate is widespread in the natural environment, it is possible that Pb contributed from KMnO$_4$ reacts with the carbonate from the sediments, forms PbCO$_3$ and precipitates as a solid.

Mo concentration in all the samples declines after the MnO$_4^-$ treatment. It is not clear what caused the decrease. Mo is stable as Mo(IV) and Mo(VI). Under reducing conditions, it is a cation, and occurs in solids like, MoS$_2$. Under oxidizing conditions, it is an anion, present as various forms of molybdate acid, such as HMoO$_4^-$, or MoO$_4^{2-}$, depending on pH. Thus, it seems that increasing E$_{H}$ by applying MnO$_4^-$ treatment would increase the mobility and solubility of the element. A possible explanation is the Mo(IV) is oxidized to Mo(VI) by MnO$_4^-$, and mobilized Mo anions form insoluble salt or co-precipitated by cation of other metals, which is similar to a pathway reported by Alloway (1995).

The process of metal speciation in natural environments can be complicated by the activity of microorganisms and natural organic matter (NOM). The presence of microorganisms and NOM will increase the consumption of MnO$_4^-$, and possibly release metals bound onto the NOM. The change of chemical concentration can be more complicated when contaminants like TCE are present, which are capable of shifting the equilibria of dissolved-precipitated phase, sorbed-solution phase and complexes by
changing the pH, and $E_H$ as well as the addition of Cl. The reaction between MnO$_4^-$ and chlorinated ethylenes can drop the pH from neutral to 2-3, under which conditions calcareous minerals will dissolve and release heavy metals. The MnO$_4^-$ destruction of chlorinated solvents is achieved by dechlorination, a process that liberates the Cl. Mobilization of several metals (Hg, Cd, Pb) was found to be sensitive to the concentration of chloride ion, which facilitates the formation of complexes with Cl (Alloway, 1995). The interaction between the sediment solids and MnO$_4^-$ should happen primarily at the surface of the solid. The SEM image (Figure 2.19) indicates that the surface coating of the solid particle has a more complex texture and chemical composition. The coating contacts MnO$_4^-$ solution directly, therefore, it is more important in contributing on the releasing of metals.

The control solution in this study, which is designed to represent conditions before the MnO$_4^-$ treatment, was exposed to the air and the solution was prepared with Milli-Q water that contains dissolved oxygen. In natural systems, conditions are likely more reducing than this, especially in areas close to a contaminant plume, which represented by the area located in the lower portion the circle in Figure 2.20. The controls in this study might be located in the area a little above the circle in the same figure. Therefore, under natural conditions, metal releases may be more significant than the result from this study suggested, because of the larger change in $E_H$. 
5. Conclusions

The consumption of MnO$_4^-$ is significant for most sediments tested. This process will lower the delivery efficiency of MnO$_4^-$ in remedial schemes. However, the ability for most natural sediments to consume MnO$_4^-$ reduces concern that MnO$_4^-$ itself would emerge as a major contaminant at most sites.

MnO$_4^-$ likely oxidizes solid metal oxide and mobilizes some metals during the treatment. For example, chromium, Cr (III), which often exists as a Cr$_2$O$_3$ solid, was oxidized to Cr (VI), a dissolved species of chromium. Metals bound to organic compounds would also be added to the solution as MnO$_4^-$ oxidizes organic materials. Clearly, MnO$_4^-$ is a powerful oxidant that is capable of oxidizing solids and organic contaminants indiscriminately. The heavy metal loading is of regulatory concern, although it is not clear how mobile these constituents might be.

The MnO$_4^-$ change in redox condition is limited to the zone where MnO$_4^-$ contacts the sediments. At the edge of the treatment zone, the $E_H$ should remain close to the pre-treatment condition. Therefore, as the metal species released by the MnO$_4^-$ oxidation move out of the treatment zone, they again will revert to their pre-treatment forms. It would be likely that most metals would be immobilized again. The mobilization of the metal species should be a localized, short-term effect.

Each element and related species will likely respond to the MnO$_4^-$ treatment differently. $E_H$-$pH$ diagram seems to provide a useful tool to analysis speciation under oxidation. An analysis involving stability diagram will help to design a monitoring plan before a remedial action is conducted. The results suggest caution in the application of
oxidation schemes to environmentally sensitive areas and aquifers containing high concentrations of metal oxides at lower oxidation states.
<table>
<thead>
<tr>
<th>Samples</th>
<th>Description</th>
<th>Sedimentary phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC1</td>
<td>Light yellowish brown silty fine sand</td>
<td>Glacial outwash</td>
</tr>
<tr>
<td>DC2</td>
<td>Gray brown sand and gravel</td>
<td>Glacial till</td>
</tr>
<tr>
<td>JPD</td>
<td>Gray brown medium sand and silt</td>
<td>Glacial till</td>
</tr>
<tr>
<td>JP2</td>
<td>Dark brown gray sand</td>
<td>Glacial till</td>
</tr>
<tr>
<td>JP3</td>
<td>Light brown gray silt with dark sand and gravel</td>
<td>Glacial till</td>
</tr>
<tr>
<td>MT1</td>
<td>Gray brown silty sand with light color sand and gravel</td>
<td>Glacial till</td>
</tr>
<tr>
<td>MT2</td>
<td>Dark brown sand</td>
<td>Glacial outwash</td>
</tr>
<tr>
<td>MS</td>
<td>Yellow brown silty sand</td>
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</tr>
<tr>
<td>OS1</td>
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<td>Alluvium</td>
</tr>
<tr>
<td>RB</td>
<td>Light brown sand</td>
<td>Alluvium</td>
</tr>
<tr>
<td>CBS</td>
<td>Light gray sand</td>
<td>Carbonate beach</td>
</tr>
<tr>
<td>OSD1</td>
<td>Dark brown sandy gravel</td>
<td>Glacial outwash</td>
</tr>
<tr>
<td>OSD2</td>
<td>Brown sandy gravel</td>
<td>Glacial outwash</td>
</tr>
<tr>
<td>KI1</td>
<td>Light white gray crashed limestone</td>
<td>Carbonate rock</td>
</tr>
<tr>
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<td>Light white gray crashed limestone</td>
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</tr>
<tr>
<td>KI3</td>
<td>White gray crashed limestone</td>
<td>Carbonate rock</td>
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<tr>
<td>MRB1</td>
<td>Brown gray sand and gravel</td>
<td>Glacial till</td>
</tr>
<tr>
<td>MRB2</td>
<td>Brown gray silty sand</td>
<td>Glacial till</td>
</tr>
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<tr>
<td>MRB4</td>
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<tr>
<td>VDOE</td>
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<td>Alluvium</td>
</tr>
<tr>
<td>NEUSDA</td>
<td>Brown gray fine sand</td>
<td>Alluvium</td>
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</table>

Table 2.1. Description of samples and their sedimentary origin.
Table 2.2. Average and range of concentration levels for sediment solutions with and without MnO$_4^-$ treatment, and MCLG and MCL levels. 0 indicates concentration below detection limit.

* National water quality data from EPA public domain STORET database, adapted from Newcomb and Rimstidt (2002).


MCLG: Maximum Contaminant Level Goals; MCL: Maximum Contaminant Level.

n/r means not regulated.

^^ Recently, U.S. EPA has reset the As MCL to 0.01 mg/L.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Solution concentration without MnO$_4^-$ treatment</th>
<th>Solution concentration with MnO$_4^-$ treatment</th>
<th>National ground water element concentration*</th>
<th>USEPA drinking water regulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average (mg/L)</td>
<td>Range (mg/L)</td>
<td>Average (mg/L)</td>
<td>Range (mg/L)</td>
</tr>
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<td>Ti</td>
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<td>0.28</td>
<td>0.007-4.73</td>
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<tr>
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<td>0.0005-0.12</td>
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<td>Samples in this study</td>
<td>National sample values</td>
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<tr>
<td></td>
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<td>Range (mg/km)</td>
<td>Average * (mg/km)</td>
<td>Range * (mg/km)</td>
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<tr>
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<td>7.2</td>
<td>&lt;0.1 - 97</td>
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<td>0.10 - 0.26</td>
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<td>19</td>
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Table 2.3. Average and range for elements in three sediment samples and reported value of national samples.

* Average or median contents, and range in contents, reported for elements in soils and other surficial materials (Shacklette and Boerngen, 1984). n/a means data not available.
Table 2.4. Element mass contents of the solution of selected samples with and without \( \text{MnO}_4^- \) treatment, in percentage of that of the sediments. 0 indicates concentration below detection limit.
Figure 2.1 Utilization of MnO$_4^-$ through oxidation of various sediments. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.2 KMnO$_4$ concentrations before and after 10 days of treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.3. Zn concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.4. Cr concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.5. Rb concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.6. Se concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.7. Hg concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.8. Cs concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.9. Cd concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.10. V concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.11. Ti concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.12. As concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.13. Pb concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.

Figure 2.14. Mo concentrations with and without the oxidation treatment. The initial KMnO$_4$ concentration is 2.5 g/L.
Figure 2.15. Trace impurity of the KMnO$_4$ solution of 2.5 g/L

Figure 2.16. Solid and solution element concentrations before and after 10 days of the MnO$_4^-$ treatment for sample DC1.
Figure 2.17. Solid and solution element concentrations with and without the MnO$_4^-$ treatment for sample MS.

Figure 2.18. Solid and solution element concentrations with and without the MnO$_4^-$ treatment for sample RB.
Figure 2.19. SEM image of sediment solid particle of sample MS. Apparently the particle has a coating that could have developed through weathering or other surface reaction. It shows more heterogeneous and more chemically complex, which could be the source of the metals that have released. See text for more discussion.
Figure 2.20. Simplified $E_{H}$-pH diagram showing the $E_{H}$ and pH change for MnO$_4^-$ treatment. Diagram constructed based on manganese-water system, at 25 °C. Two dashed lines are the limits of water at oxidizing and reducing conditions. The solid line is the MnO$_4^-$ and MnO$_2$ phase divider. The circle represents the $E_{H}$, pH range of normal ground water. Solid arrow is the $E_{H}$, pH change when MnO$_4^-$ treatment applied, while the dashed arrow is the change when MnO$_4^-$ reacted with TCE, releasing H$^+$ from the reaction. Information of the $E_{H}$-pH diagram is adapted from Pourbaix (1974). The normal ground water range was estimated based on Domenico and Schwartz (1997), Pourbaix (1974), and Christensen et al. (2000).
CHAPTER 3

PERMANGANATE OXIDATION SCHEMES FOR THE REMEDIATION OF
SOURCE ZONE DNAPLS: PROBLEMS OF REACTION PRODUCTS

1. Introduction

Subsurface contamination by chlorinated organic solvents presents a serious threat to the nation’s soil and ground-water quality. The most common contaminants are chlorinated ethylenes, like tetrachloroethylene (PCE) and trichloroethylene (TCE), which are listed at the top of the national priority list for environment clean up (USNRC, 1994). Contamination in source areas commonly is found as dense non-aqueous phase liquid (DNAPL). A plume of dissolved contaminants also would develop down gradient. The DNAPL source area contains the majority of the total mass of the contaminant, and is main concern in the remediation.

The \textit{in situ} destruction of chlorinated ethylenes by potassium permanganate has been studied by many researchers as a potential sources zone remediation technology (West et al., 1997; Schnarr et al., 1998; Yan and Schwartz, 1999; Thomson et al., 2000; Reitsma and Marshall, 2000). Yan and Schwartz (1999) elucidated the reaction pathway
and the products of TCE oxidation by MnO$_4^–$. Using isotopically labeled materials, they found that MnO$_4^–$ oxidized TCE to CO$_2$ with carboxylic acids as intermediate products. Another key product in this reaction is manganese dioxide (MnO$_2$), which precipitates as a solid.

Based on mass balance considerations from laboratory experiments, Schnarr et al. (1998) proposed the following general equation for the reaction of MnO$_4^–$ with chlorinated TCE

$$C_2HCl_3 + 2\text{MnO}_4^– \rightarrow 2\text{MnO}_2 + 2\text{CO}_2 + 3\text{Cl}^- + \text{H}^+ \quad (3.1)$$

From the stoichiometric relationships in Equation 3.1, the destruction of TCE can be monitored by tracking the accumulation of the Cl$^-$ over time.

Previous studies have shown that permanganate is efficient in oxidizing chlorinated ethylenes in the aqueous phase, with half-lives on the order of tens of minutes. Ultimately, all of the chlorinated compounds and intermediates are mineralized to produce harmless products. With these obvious advantages, this technology has been rushed into field applications concerned with the removal of source-zone DNAPLs at various sites around the nation (Mott-Smith et al., 2000; McKay et al., 2000). At these field sites, investigators reported a dramatic decrease in the contaminant concentrations when permanganate flushing was applied. However, in some cases, concentrations rebounded after the treatment was stopped. Without detailed and careful observations, it is difficult to determine whether this rebound was caused by the remaining DNAPL or simply by the re-establishment of the contaminant plume from upstream.
A potential problem is that key reaction products, MnO₂ and CO₂, can cause plugging and flow diversion. Schroth et al. (2001) reported permeability reduction during the \textit{in situ} MnO₄⁻ oxidation in a 1-D column experiment. There is little research on the impact of these problems on mass removal rate and possible fixes through the inhibition of precipitation. Clearly, there is a need to better understand the \textit{in situ} oxidation process, especially with respect to the behavior of the solid reaction products and their effects on the porous medium. This study specifically addresses gaps in knowledge that bear on the realistic use of permanganate-oxidation schemes for DNAPL clean ups. Visualization-type experiments were used to evaluate the \textit{in situ} oxidation process. Experience has shown visualization approaches to be useful in understanding processes in the subsurface (Reitsma and Marshall, 2000). I also discuss the results of various column and flow tank experiments that elucidate problems of flooding inefficiencies, and pore plugging, related to reaction products. Thus, the objective of the study is to assess the extent to which the precipitation of MnO₂ impacts the oxidant flood.

2. Methods

A 1-D column experiment was conducted using a glass column with Teflon end fittings and packed with medium silica sand (45 micron) (US Silica, Ottawa, IL) (Figure 3.1). Details of the experimental set up are summarized in Table 1. Once the column was packed, it was positioned upside down. One mL of TCE was added to the column evenly across the opening to create a zone of residual DNAPL saturation. The column was returned to an upright position and fluid was pumped upward through the column using
an Ismatec tubing bed pump (Cole Parmer Instrument Co. Vernon Hills, IL). Effluent samples were collected periodically for chemical analysis. After the experiment finished, several porous medium samples were taken along the column. The samples were treated with thiosulfate to dissolve the Mn oxide. The resulting solution was analyzed by ICP-MS to quantify the distribution of Mn oxide along the column.

Two dimensional, tank experiments were conducted using a thin, small 2-D glass flow tank, outfitted with Teflon end fittings (Table 3.1). The flow tank was filled with transparent borosilicate glass beads with a mean grain size of 1 mm. Two PTFE (polytetrafluoroethylene) tubes with an inside diameter of 1.32 mm were installed in the two ends of the tank to function as recharge and discharge wells. Both tubes had ends open at a depth of 0.5 cm from the bottom of column.

Once the column was packed, it was saturated with Milli-Q water. A Spectroflow 400 solvent delivery system (Kratos Analytic, NJ) provided flow into the tank. An Ismatec pump removed fluid at the outlet (Figure 3.2). With both pumps running at the same steady rate, the ambient flow was horizontal along the length of the tank. One mL of the TCE was added to the tank from the top to form a zone of residual DNAPL saturation across the vertical depth of the tank and a small DNAPL pool at the bottom. The tank was flushed for about two weeks with KMnO₄. Effluent samples were taken three times a day for chemical analysis. Images of the column were taken with a digital camera to monitor the development of MnO₂ precipitation.

During the 2-D flow tank experiment, digital photography was used to monitor the flooding and plugging with MnO₂. With either the glass beads or the silica sand, the flow tank transmits some light from the back of the tank. The formation of the reaction
product could be monitored by the digital images as a function of time using a Nikon 950 digital camera. The visual monitoring was carried out inside a dark room to avoid interference from ambient light. After the experiment was completed, the images were downloaded to a PC, and were processed with Photoshop to correct the slight size differences among the images collected during the extended experiment.

The effluent from the column and flow tank was collected periodically for chemical analysis to monitor TCE degradation. Concentrations of TCE, Cl\(^{-}\) and MnO\(_{4}^{-}\) were monitored during the entire experimental period. Cl\(^{-}\) concentration was utilized to estimate the quantity of TCE that was oxidized, and the overall efficiency of the cleanup scheme. TCE concentration was measured with a Fisons Instruments 8060 gas chromatograph equipped with a Ni\(^{63}\) electron capture detector and a DB-5 capillary column (JandW Scientific, Rancho Cordova, CA). Pentane was used for liquid-liquid extract of TCE. Cl\(^{-}\) ion concentration was measured with a Buchler Digital Chlorodometer. Permanganate concentrations were measured with a Varian Cary 1 UV-visible spectrophotometer at a wavelength 525 nm. Samples of MnO\(_2\) were dissolved and analyzed by a Perkin-Elmer Sciex ELAN 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

3. Results

The 1-D column experiment confirms the ability of MnO\(_{4}^{-}\) to oxidize the TCE present in the column. Mass balance calculations, based on the measured TCE and Cl\(^{-}\) concentration in the effluent from the column, indicated the nearly complete removal of
the pure TCE in a relatively short time (Figure 3.3). Integrating the TCE removal curve shows that after 365 hours of permanganate flushing, 96.9% of the initial TCE was removed from the column. The rate of TCE removal was highest at early time when MnO$_4^-$ first entered the column, and decreased significantly with time. Ninety percent of the TCE was removed in the first 115 hours of the experiment, while another 250 hours was required to remove the last 7%. Flushing by MnO$_4^-$ was halted when Cl measurements suggested that TCE had been removed from the column. Flushing continued with Milli-Q water pumped through the column. Interestingly, TCE concentrations rebounded to about 130 mg/L. Apparently, the Cl measurements were not sensitive at the lower level of detection to the small quantities of Cl produced by the oxidation of TCE that remained in the column. It is estimated that several hundred additional hours would be needed to bring TCE concentration below 5 mg/L, the regulatory limit.

The distribution of MnO$_2$ in the column at the end of the experiment is shown in Figure 3.4. The majority of the Mn oxide was located at or closely adjacent to the original DNAPL zone. These precipitates tended to plug the column toward the end of the experiment, making flushing increasingly difficult.

The results from the 2-D flow tank experiment (Figure 3.5) were similar to the 1-D experiment, except that the removal efficiency was noticeably less. After 313 hours of flushing with MnO$_4^-$, only 34.9% of the initial TCE was removed from the tank. Half of the TCE was removed in the first 25% of the elapsed time. Figure 3.6 shows that at the end of the experiment the TCE concentration rebounded, once the injection of MnO$_4^-$
stopped. With increased TCE concentration, the residual permanganate in the flow tank reacted and produced an increase in Cl\(^{-}\) concentration at the end of the experiment.

The digital imaging system provided a useful way to monitor the growth in the zone of MnO\(_2\) precipitation (Figure 3.7). Precipitation started once MnO\(_4\)\(^{-}\) came in contact with dissolved TCE that occurred in close proximity to the zone with pure TCE DNAPL. The zone of MnO\(_2\) precipitation was evident in a zone with a light brown color, located down gradient of where the residual DNAPL occurred (Figure 3.7(b)). There was a tendency for the MnO\(_4\)\(^{-}\) flood to bypass the zone with the highest DNAPL saturation, moving instead through a much less saturated zone in the upper portion of the tank (Figure 3.7(c)). With time, the precipitation of MnO\(_2\) reduced the permeability across most of the tank. MnO\(_2\) rapidly formed a precipitation rind above the small DNAPL pool, which was located near the bottom of the tank (Figure 3.7(d), (e), (f)). A greater injection pressure was required to maintain the flow near the end of the experiment. The experiment was halted when Mn oxide plugged the tank nearly completely and MnO\(_4\)\(^{-}\) could no longer be injected. Careful examination of the tank after the experiment indicated the presence of tiny CO\(_2\) bubbles, produced from the oxidation reaction. The gas bubbles likely played a role in reducing the permeability and the flow in the system. Flushing with MnO\(_4\)\(^{-}\) appears effective in removing residual DNAPL. However, much of the original volume of the pool of DNAPL at the bottom of the tank was evident at the end of the experiment.
4. Discussion

Results from both the 1-D and 2-D experiments indicate that early in the flushing process, DNAPL mass removal rate was greatest. As the treatment proceeded, the rate decreased dramatically. Conducting experiments to achieve complete DNAPL removal was frustrated by the tailing effect in the TCE concentration toward the end of the treatment. This tailing effect had been noted by researchers studying DNAPL dissolution (Powers et al., 1992; Imhoff et al., 1994). Towards the end of their experiments, when a large proportion of the initial DNAPL was dissolved, small droplets remained in hydraulically stagnant zones in the medium. The stagnant zones are not flushed because preferential flow paths develop even within the homogeneous media. With MnO$_4^-$ oxidation schemes, the tendency for preferential flow paths to develop will be further promoted as MnO$_2$ precipitates in the zones of higher DNAPL saturation or CO$_2$ bubbles are trapped in the porous medium. The rapid oxidation and relatively slow mass transfer rate from the DNAPL to the aqueous phase means that MnO$_2$ would tend to precipitate at or immediately adjacent to the DNAPL, which results in a zone of more concentrated precipitates around the zones of greatest saturation. Flow tended to bypass these zones and follow a more permeable flow path, causing the DNAPL oxidation process to become diffusion controlled. Although CO$_2$ bubbles in the subsurface can dissolve in the aqueous phase according to Equation 3.2, the rapid accumulation of CO$_2$ early in the flushing led to the production of the bubbles. Flow bypassing also reduced the possibility for water to contact and dissolve the bubbles. Thus, the effect of the bubbles in reducing the permeability is persistent.
\[ \text{CO}_2 + \text{H}_2\text{O} \Leftrightarrow \text{HCO}_3^- + \text{H}^+ \quad (3.2) \]

These effects are most obvious in the 2-D tank experiment where DNAPL is present at high residual saturation as a small pool. The pooled DNAPL persisted because the interfacial area was relatively small and \( \text{MnO}_4^- \) moved around but not through these zones. In zones of lower residual saturation, TCE oxidation was more efficient because \( \text{MnO}_4^- \) could move through the zones. With the opportunities for \( \text{MnO}_4^- \) to move around zones of DNAPL saturation in a two-dimensional system, the destruction rate of TCE was significantly less overall than that with a one-dimensional system. Similar observations have been reported by other researchers (Thomson et al., 2000). These results suggest that with 3-D flow conditions, evident at actual contaminated sites, the efficiency of removal would probably be even smaller. It appears that \( \text{MnO}_4^- \) oxidation is more effective in cleaning up residually saturated DNAPLs rather than pools of DNAPL. Clearly, in actual field settings, the issue of flushing efficiency will be of concern in the design. Experiments are underway to find an effective additive that minimizes the precipitation effects.

5. Conclusions

This study utilized a series of laboratory experiments to explore the feasibility of applying oxidation techniques to clean up ground water and soil contaminated by chlorinated ethylenes. I investigated problems that could potentially impact the oxidation
of TCE with permanganate, such as precipitation of MnO$_2$ around zones of high DNAPL saturation, and permeability-related flow bypassing. 1-D column and 2-D flow tank experiments provided data on mass removal rates and related flushing efficiencies. The column and flow tank experiments continue to indicate that the oxidation of chlorinated ethylenes by MnO$_4^-$ is a useful remediation technology. The kinetics of the oxidation reaction are generally fast and capable of reducing the mass of pure-phase product, especially early in the treatment. However, MnO$_2$ precipitates and CO$_2$ gas bubbles present significant delivery problems. The rapid buildup of these reaction products in zones with high DNAPL saturation leads to pore plugging, which lowers the permeability, and causes flow bypassing. The flushing efficiency will be reduced without controlling this problem. It is anticipated that in actual field settings, the issue of flushing efficiency needs to be considered in the design. For this technology to be practical, there is a critical need to find a solution that would control or remove the MnO$_2$. 


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<th>Dimension (mm)</th>
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<th>$Q$ (mL/min)</th>
<th>KMnO$_4$ (g/L)</th>
<th>Porosity</th>
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<td>Glass beads</td>
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Table 3.1. Experimental setups for the 1-D column and 2-D flow tank experiments
Figure 3.2. 1–D column experimental setup

Figure 3.3. 2–D flow tank experimental setup
Figure 3.4. Variation in TCE concentration with time in the effluent of the 1-D column and the calculated removal based on Cl\textsuperscript{-} stoichiometry.

Figure 3.5. Distribution of Mn along the column after \textit{in situ} oxidation of DNAPL.
Figure 3.6. Effluent TCE concentration change with time in the 2 – D column experiment.
(a) Time: 0. Two-dimensional sand tank at the beginning of the experiment. The arrow shows the flow direction.

(b) Time: 3.5 hours after pumping started. A zone of Mn oxide precipitation is formed immediately downstream of where the residually saturated TCE is present.

(c) Time: 12 hours after pumping started. Much more extensive Mn oxide precipitation is observed. A small pool of TCE has became evident at the bottom of the tank.

(d) Time: 48 hours after pumping started. The more intensive precipitates indicated that TCE is being oxidized. However, the DNAPL pool is relatively unaffected.

(e) Time: 7 days after pumping started. Flow of MnO$_4^-$ is now mainly occurring at the top of the tank.

(f) Time: 14 days after pumping started. The tank is now plugged with Mn oxide. Note how the TCE pool has been sequestered.

Figure 3.7. DNAPL removal in the 2-D flow tank experiment. The dark brown color indicates the presence of Mn oxide(s), and the light color at the mid-bottom of the image (f) is the remaining pool of DNAPL after flushing had stopped.
CHAPTER 4

MINERALOGY OF MANGANESE OXIDE FORMED IN THE
OXIDATION OF CHLORINATED ETHYLENES BY PERMANGANATE

1. Introduction

The feasibility of in situ chemical oxidization (ISCO) to remediate DNAPLs (dense non-aqueous phase liquids) in the subsurface has been investigated in a variety of studies (Vella and Veronda, 1992; Schnarr et al., 1998; Yan and Schwartz, 1999). When permanganate is used, chlorinated ethylenes breakdown to CO$_2$, Cl$^-$, while MnO$_4^-$ reduces to MnO$_2$, a solid precipitate (Yan and Schwartz, 2000). For example, the reaction of dichloroethylene (DCE), trichloroethylene (TCE), or tetrachloroethylene (PCE) can be written as

\[ \text{C}_2\text{H}_2\text{Cl}_2 \text{ (DCE)} + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2(s) + 2\text{CO}_2 + 2\text{Cl}^- + 2\text{H}^+ \]  \hspace{1cm} (4.1)

\[ \text{C}_2\text{HCl}_3\text{ (TCE)} + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2(s) + 2\text{CO}_2 + 3\text{Cl}^- + \text{H}^+ \]  \hspace{1cm} (4.2)
The precipitation of $\text{MnO}_2(s)$ and the formation of $\text{CO}_2$ bubbles near the zones of high DNAPL saturation can cause pore plugging of the porous media, which contributes to low flushing efficiency, and reduces rate of DNAPL removal (Li and Schwartz, 2000; Reitsma and Marshall 2000; Thomson et al, 2000). Li and Schwartz (2002) presented results of visualization experiments which how the precipitation of $\text{MnO}_2$ causes a rind to form around zone of high DNAPL saturation. This process essentially sequestered the DNAPL and virtually eliminated further oxidation.

Clearly, for ISCO scheme to be effective remediation of chlorinated ethylenes, the precipitation of $\text{MnO}_2$ must be controlled or the precipitates have to be removed. Although $\text{MnO}_2$ is a natural mineral, that is common in geological systems, there is a concern that precipitates might dissolve and be mobilized in these scheme, to produce elevated manganese concentration in ground water.

To date, there is no study on the mineral structure and the environment fate of the $\text{MnO}_2$ precipitates that formed in ISCO schemes. It is possible that knowledge of the mineralogical structure of this oxide can help to solve the problem of pore plugging and related permeability reductions.

Thus, the goal of this study is to investigate the solid reaction product formed from the oxidation of common chlorinated ethylenes by $\text{MnO}_4^-$. Various techniques will be applied to identify the mineral, determine its chemical composition, and measure the chemical properties of the surface. The specific objectives are
1. to study the mineral structure of the manganese oxide formed as a consequence of oxidation of chlorinated ethylenes with MnO$_4^-$, determine its mineral type and chemical composition; and

2. to measure the surface chemical properties of the MnO$_2$.

The identification of the structure of MnO$_2$ mineral, together with the determination of the chemical composition will lay the foundation for further studies on how MnO$_2$ precipitation can be controlled or removed once it has formed. Specific surface area is an indicator of the adsorption capacity of the mineral. It is usually measured using nitrogen adsorption method (BET). Point of zero charge (pzc) is an important surface charge property that provides information of surface charge change with pH, or other chemical conditions. Study of the Mn oxide formed in the permanganate oxidation has two folders of the significances. First, it helps to understand the mechanism of the permanganate oxidation reaction. Second, it will be vital to solve the precipitation related permeability change which is vital to the future of this technology.

2. Manganese oxide mineral type and structure

There are more than 30 different types of Mn oxide/hydroxide minerals, with different structures and compositions. Because mineral type influences the chemical reactivity, it is helpful to identify the type and mineral structure of Mn oxide that formed
in the oxidation reaction. Post (1999) presents a comprehensive review of the structures of these minerals and their interaction with the environment. Generally, there are two different major structural types for these minerals: layer structures, and chain or tunnel structures, which are all made up from the MnO₆ octahedras (Figure 4.1, 4.2). Mn oxides having a layer structure consisting of stacks of sheets, or layers, of edge-sharing MnO₆ octahedra. Water molecules and various cations can exist in the interlayers between the sheets. Mn oxides with a tunnel structure are formed with single, double, or triple chains of edge-sharing MnO₆ octahedra. The chains share corners with each other to produce a framework that has tunnel with square or rectangular cross sections. The larger tunnels are partially filled with water molecules and/or other cations (Post, 1999). Identifying the type of Mn oxide mineral is not straightforward because the samples are usually not crystallized well enough for single-crystal diffraction study, especially with synthetic oxides of the type formed here. In most cases, however, powder x-ray diffraction is still the main technique for the sample identification, with other techniques like, transmission electron microscopy (TEM), IR spectroscopy, and electron microprobe analysis, providing supplementary information.

3. Materials and methods

Preparation of the manganese dioxide

A single batch of manganese dioxide was prepared by the following method and used in all experiments. 75 g TCE was added to a 6 L flask. 30 g/L of KMnO₄ is added slowly into the flask with a peristaltic pump at a controlled rate, and mixed with a
magnetic stir bar. A total of 185 g of KMnO₄, which is in excess compared with the TCE stoichiometry (Equation 4.2), is added. The complete mixing process took about 2 days. After all the KMnO₄ was added, the solution was stirred for one more day to allow the reaction between the TCE and KMnO₄ to be completed. The solution was aged for one additional day. The final purple color of solution indicated an excess of KMnO₄ as expected. Precipitates from the solution were filtered and stored in a dialysis bag (Spectral/Por Cellulose Ester Membrane, 3500 Dalton). The dialysis bag containing the Mn oxide precipitates was placed in a glass column with Milli-Q water to remove the soluble impurities. Water was changed once a day until the conductivity of the solution reached the value of fresh Milli-Q water. The conductivity was measured with a conductivity dip cell (K=10.2) connected to a digital conductivity meter (1481-90 model, Cole-Parmer Instrumental Company). The entire dialysis process took four weeks. After dialysis, the solid sample was placed in a plastic container and was quick frozen in the liquid nitrogen, in order to preserve the mineral structure (Wang, 1996). A freeze drying technique was applied to remove the water (ice) from the sample. Finally, a clean brown powder of manganese dioxide was obtained. After the preparation of the Mn oxide powder, a series of measurements was conducted to determine its mineral structure, chemical composition, and solid surface properties.

Thermal analysis

Thermal analysis was used to determine the quantity of structural water in the mineral. SEIKO SSC 5020 instrument (Haake Inst., Paramus, NJ) with a TG/DTA simultaneous analysis module, model 200 was used for thermal gravimetric (TG) and
differentiated thermal analysis (DTA). An aliquot of manganese oxide powder sample was heated in the analyzer from 25 °C to 930.4 °C. The weight loss in the sample at temperatures above 125 °C is considered due to the loss of structural water. The instrument uses a differential method to measure the change in sample weight with time and temperature.

Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Analysis

Chemical analysis with ICP-MS was used to determine the content of the manganese and potassium within the Mn oxide. 50 mg of Mn oxide power was dissolved in a solution of 100 mg/L citric acid in 1 L flask stirring for two days. The resulting solution then was diluted 1000 times for elemental analysis by the ICP-MS. The instrument was calibrated with external standards. A Perkin-Elmer Sciex ELAN 6000 DRC Inductively Coupled Plasma Mass Spectrometer (ICP-MS) housed in the MARC facility at The Ohio State University was used for this purpose.

TEM (transmission electron microscope) analysis

TEM analysis provides a direct examination of the fine structure of a mineral. A small sample of Mn oxide (e.g. 1-5 mg) was placed into an 8 mL vial filled with methanol. Alcohol is used instead of water because alcohol has a smaller tension that can disperse the sample. Ultrasound was applied to the vial in order to break down the particle into suspension. A drop of sample was put on the holey carbon grid for the TEM analysis. A Philips CM-200 TEM with best resolution at 2.7 Å analyzed the sample. It provided image of the structural details of the mineral.
XRD (X-ray diffraction) analysis

X-ray diffraction powder analysis can provide information on mineral structure and help to determine the mineral type. The sample was ground in a ceramic mortar and pestle for a random-oriented topfill powder mount. The analysis was performed with a Philips diffractometer (Philips Elec. Inst., Mahwah, NJ) using CuKα-radiation and vertical, wide-range goniometer equipped with a diffracted beam monochromator and a theta-compensating slit. Measurements were made by step scanning with a counting time of 4 second increments of 0.05° 2θ from 5 to 70° 2θ.

Specific surface area

Specific surface area of the Mn oxide powder is measured using the liquid nitrogen adsorption (BET) method. Before analysis, the sample was vacuum desiccated with P2O5 and degassed at 60 °C. Analysis was conducted using Micromeritics FlowSorb II 2300 surface area analyzer.

Measurement of point of zero charge (PZC)

The pzc of the Mn oxide was determined by potentiometric titration inside an argon filled glove box. All solutions were prepared from Milli-Q water that was bubbled with argon gas to remove CO2 gas before moving into the glove box. 100 ml solution of solid Mn oxide concentration at 2 g/L was used for the titration. The Mn oxide powder was rehydrated for more than a week before being placed into the reaction solution. NaOH was used as background electrolyte with solution concentrations at 0.005, 0.01,
0.05, 0.01 mM. A magnetic stirrer kept the solution agitated during the experiment. A pH probe was placed in the solution to monitor pH. The proper amount of HNO₃ or NaOH was added with a micro-pipette to control pH of the solution. The change of pH after adding the HNO₃ or NaOH each time was recorded. Using equation 4.4, which involves the method described by Sigg and Stumm (1981), the quantity of H absorbed onto the solid could be obtained. Thus, pzc can be determined when the experimentally determined surface charge is zero.

\[
\sigma_0 = \left( C_A - C_B - [H^+] + [OH^-] \right) \frac{F}{a \cdot S}
\]  

(4.4)

where F is the Faraday constant (C mol⁻¹), S is the specific surface area (m² g⁻¹) of the solid. C_A and C_B are the concentrations of the strong acid and base (mol L⁻¹) added, respectively, and a is the concentration of solid in the suspension (g/L)

4. Results

Figure 4.3 presents the result of X-ray diffraction powder (XRD) analysis for the synthetic Mn oxide. There is no very prominent peak in the spectrum, which indicates that the powder is not well crystallized. However, the pattern of the XRD spectrum matched that of the birnessite in the database in general, and has a clear but not very intense peak at 7.3 Å. Among all the Mn oxide minerals, the birnessite family has layer spacings of approximately 7 Å, with Na, Ca or K as the interlayer elements. Varentsov
and Grasselly (1980) gave XRD of birnessite d (Å) = 7.27, 7.37, 7.40 Å. Post (1992, and 1999), and Post and Veblen (1990) think that the 7 Å interlayer spacing is the typical birnessite spacing, and identify it as the characteristic feature for birnessite. Because the mineral is formed in the potassium rich environment, I believe the mineral formed in the oxidation of chlorinate ethylenes by MnO$_4^-$ is semi-amorphous potassium-rich birnessite. The basic structural unit for birnessite is a sheet of MnO$_6$ octahedra. The interlayer cations and water molecules generally are known to occupy different positions in each of the three phases. The H$_2$O molecules in the mineral should mostly exist at the interlayer (Post, 1999), however some of them can be present as OH. Sometimes, this birnessite is called manganese (hydro)oxide.

Transmission electron microscopy (TEM) analysis found that the Mn oxide crystal is a cluster of small needles (Figure 4.4). The findings from TEM analysis confirm earlier XRD results that the crystal structure of Mn oxide is poorly developed. TEM chemical composition analysis also identified K and Mn as the only major metal cations in the mineral.

Thermal analysis established that structural water in the mineral was 12.49% by weight of the total solid. The ratio of K and Mn in the mineral was determined by ICP-MS analysis of the dissolved Mn oxide. From a charge balance of the different elements, the formula of the Mn oxide mineral was identified as $\text{K}_{0.854}\text{Mn}_{1.786}\text{O}_4\cdot1.55\text{H}_2\text{O}$. This result assumes that the oxidation state for all the Mn inside the mineral is IV. It is widely believed (Post and Veblen, 1990) that Mn in synthetic birnessite has a mix of oxidation states of III and IV, even II. While there is no way to determine the exact oxidation state of the Mn, the chemical composition based on this assumption seems reasonable, and
comparable with others result (Post and Veblen, 1990). Post and Veblen (1990) studied synthetic Na-birnessite and Mg-birnessite, and give them the formulas $Na_{0.54}Mn^{4+}{_1.87}O_4\cdot{1.4}H_2O$, and $Mg_{0.27}Mn^{4+}{_1.87}O_4\cdot{1.6}H_2O$, respectively. They assumed that the charge deficiency of the crystal was caused solely by the vacancy of the Mn at approximately one out of every 16 Mn sites. Alternatively, $Mn^{3+}$ can also cause a charge deficiency. Then, these same minerals might be given formulas $Na_{0.58}Mn^{4+}{_{1.42}}Mn^{3+}_{0.58}O_4\cdot{1.5}H_2O$, and $Mg_{0.29}Mn^{4+}{_{1.42}}Mn^{3+}_{0.58}O_4\cdot{1.7}H_2O$.

The results of specific surface area measurement are listed in Table 4.1. The mean value of four independent measurements using the BET method yield a specific surface area for Mn oxide of 23.55 m$^2$/g, which is relatively small as compared to similar minerals.

Ideally, potentiometric titration of the Mn oxide solid at four different ionic strengths should yield a series that cross each other at the point of zero charge. Though not a significant deviation, the measurement of the pzc did not generate a perfect cross of the series that had been performed. One possible cause for this variation is that the slow but continuous dissolution of the solid during titration, which can change the total surface area of the solid, and the concentration of H$^+$ in the solution. Another possible explanation is the slow response of the pH probe to the addition of the strong acid or base. A delay in the response might also produce some error. The measured pzc for the Mn oxide is $3.7 \pm 0.4$, which is comparable to other reported values, for example, $2.8 \pm 0.3$ for a synthetic MnO$_2$ (Morgan and Stumm, 1964), and 2.0 to 4.5 for different forms of MnO$_2$ (Faure, 1998). An even wider range of pzc values for various forms of MnO$_2$ between 1.5 – 7.1 was reported by Ardizzone and Trasatti (1996).
5. Discussion and summary

The solid reaction product from the oxidation of chlorinated ethylene by permanganate is identified as semi-amorphous potassium-rich birnessite, which has a layered mineral structure with an interlayer spacing of 7.3 Å. Its chemical formula was determined as $\text{K}_{0.854}\text{Mn}_{1.786}\text{O}_4\text{•}1.55\text{H}_2\text{O}$. It has a relatively small specific surface area at $23.55 \text{ m}^2/\text{g}$.

The pzc is related to the colloid coagulation process. At pHs above the pzc, the Mn oxide particles are negatively charged, below the pzc they are positively charged. At pHs close to the pzc, the net charge on the surface of the particles approaches zero. Thus, the mutual repulsion of the colloids is reduced sufficiently to permit the inter-particle collisions, agglomeration, and subsequent sedimentation. Colloids agglomerate when their concentration exceeds the critical coagulation concentration (CCC), which can happen over a spectrum of pHs. However, at pHs close to pzc, the coagulation happens at a lower CCC and is more severe. During the ISCO schemes with chlorinated ethylenes, the release of $\text{H}^+$ from the reaction drops the pH of the solution from neutral into the acidic range. Sometimes the pH falls below 2, as was evident in some of my experiments. Because the pzc of the manganese oxide is $3.7 \pm 0.4$, this change of pH can definitely enhance colloid coagulation. Thus, the combination of the acidification of the reaction condition and the pzc of the reaction product, Mn oxide, being at $3.7 \pm 0.4$ makes the precipitation from the oxidation treatment a severe, inherent problem.
Mn oxide itself is an oxidant and can be involved in reactions with a variety of organic and inorganic compounds. Shindo and Huang (1984) studied the reaction of birnessite, cryptomelane, and pyrolusite with hydroquinone, and found that the rate of reaction was in the order of birnessite > cryptomelane > pyrolusite. Pissigallo et al. (1995) reported similar results when they studied the reaction between chlorophenols and Mn oxides. Differences in the reactivity of the different Mn oxides were attributed to differences in the specific surface area, pzc, and the level of crystallization, which related to the specific surface area. Various reports have shown that naturally existing Cr(III) being oxidized to toxic, mobile Cr(VI) effectively by $\beta$-MnO$_2$ (Guha et al., 2001), by $\gamma$-MnOOH (Johnson and Xyla, 1991), and birnessite (Banerjee and Nesbitt, 1999). Perez-Bineto and Arias (1991) and Sumichrast et al. (1994) reported the oxidation of organic compound by MnO$_4^-$ is autocatalytic. Mn oxide catalyzes the reaction through a surface reaction. The birnessite, which formed from the oxidation of chlorinated ethylenes with MnO$_4^-$ has a relatively high reactivity.

Once formed in the subsurface, birnessite could participate in the various reactions with existing organic and inorganic matter, making it relatively unstable in natural settings. These reactions may be slow as compared with the MnO$_4^-$ oxidation reaction, but in the long term, or over geological times, it may add dissolved Mn back into the ground water at levels above regulatory standards. Thus, additional work is needed to look at the long-term behavior of Mn oxide in subsurface.
Test | Specific surface area
--- | ---
1 | 23.8 (m²/g)
2 | 22.8 (m²/g)
3 | 24.6 (m²/g)
4 | 23.0 (m²/g)
**Average** | **23.6 (m²/g)**

Table 4.1. Results of specific surface area measured using BET method.
Figure 4.1 Polyhedral representations of crystal structures of Mn oxide minerals with chain or tunnel structures. (A) Pyrolusite. (B) Ramsdellite. (C) Hollandite. (D) Romanechite. (E) Todorokite. Adapted from Post (1999).
Figure 4.2. Polyhedral representations of crystal structures of Mn oxide minerals with layer structures. (A) Lithiophorite. (B) Chalcophanite. (C) Na-rich birnessite-like phase showing disordered $\text{H}_2\text{O}/\text{Na}$ (light color ball) sandwiched between the Mn octahedral sheets. Adapted from Post (1999).
Figure 4.3. Spectrum of X-ray diffraction analysis of the Mn oxide. Peak at 7.3 Å indicates the interlayer spacing of the mineral.
Figure 4.4. Results of the TEM analysis for the Mn oxide powder. The white fibrous material in the picture is cluster of small needle crystal of the mineral.
CHAPTER 5

PHOSPHATE AS AN INHIBITOR OF THE FORMATION OF COLLOIDAL MANGANESE OXIDE IN THE OXIDATION OF CHLORINATED ETHYLENES WITH PERMANGANATE

1. Introduction

Oxidation schemes using permanganate (MnO$_4^-$) for the remediation of subsurface contamination by chlorinated ethylenes have been developed and tested at various sites around the nation (Vella and Veronda, 1992; West et al, 1997; Schnarr et al., 1998; Yan and Schwartz, 1999; Mott-Smith et al., 2000; McKay et al., 2000). Results from these tests have shown that \textit{in situ} chemical oxidation (ISCO) is capable of destroying the contaminants quickly, with relatively harmless and safe reaction products. In the case of trichloroethylene (TCE), the oxidation reaction can be written as:

\[ \text{C}_2\text{HCl}_3(\text{TCE}) + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2(s) + 2\text{CO}_2 + 3\text{Cl}^- + \text{H}^+ \] (5.1)
Studies (Li and Schwartz, 2000; Reitsma and Marshall 2000; Thomson et al, 2000) have revealed that the solid product of Equation 5.1, MnO$_2$, cause the plugging of the pore space. This can dramatically lower the flushing efficiency, and the DNAPL removal rate, especially later in the treatment period. My latest research results (Li and Schwartz 2001), have shown that during the MnO$_4^-$ flushing of a DNAPL source zone in a homogeneous medium, the precipitation of MnO$_2$ formed a rind around the DNAPL pool. Effectively, this process sequestered the TCE from further oxidation. The decrease in flushing efficiency due to the permeability changes is obviously a concern in practical implementations of this technology.

The Mn oxide produced during the oxidation reaction forms initially as colloids before more visible precipitates are evident. Coagulation of colloids leads to pore plugging. However, colloids can be transported by ground water through the porous medium. So if the process of colloid coagulation was controlled or delayed, Mn oxide colloids could be transported further away from the treatment zone, to avoid local plugging in the DNAPL zone. The stability of the colloidal solution is a function of the repulsive force of the colloid particles, which is directly related to the surface charge of the colloid particles. When the surface charge is high, no matter whether it is positive or negative, the repulsive force of the colloid particles is large. Under this condition the colloid solution is more stable. When surface charge is close to zero, the repulsive force of the colloids is diminished, and the attractive force coalesce the particles into larger ones and sedimentation occurs.
Change to the surface charge of colloidal particles can be created by adding chemicals that have large charge and also can adsorb onto the colloids. Posselt et al (1968) added polydiallyldimethyl ammonium (PDADMA) to a colloidal hydrous Mn dioxide solution and causing the surface charge be reversed and the colloids to be restabilized. Due to environment concerns, chemicals like PDADMA could not be used at an actual site. Other additives need to be found and tested. Phosphate ions have large charge and easily binds to colloids. Manganese dioxide ($\delta\text{MnO}_2$) is an important adsorbent of phosphate in natural waters (Yao and Millero, 1996). Mata-Perez and Perez-Benito (1985) found that in aqueous phosphate buffers, the rate of conversion of the soluble Mn (IV) species into MnO$_2$ is retarded when they studied the reduction of permanganate by trimethylamine using UV-vis spectrophotometer analysis. They also found that the delay of the colloid formation is dependant on the concentration of the phosphate buffers, temperature and ionic strength. Stewart (1965) indicated the rather slow precipitation of Mn oxide in the presence of phosphate ion. Schroth et al. (2001) found that colloid precipitation is somewhat slowed in a 1-D column experiment to oxide TCE with a mixture of KMnO$_4$ and Na$_2$HPO$_4$ buffer solution. The possible control of the colloid formation by phosphate ion will be investigated in this study.

There are more than 30 different types of Mn oxide/hydroxide minerals, with different structure and compositions. Differences in the reactivity of the different types of Mn oxides are caused by difference in the specific surface area, point of zone charge (pzc), and level of crystallization, which related to the specific surface area. It is helpful to identify the type and mineral structure of Mn oxide that formed via oxidation. The identification of the structure of Mn oxide mineral, together with the determination of the
chemical composition will lay the foundation for further study of this mineral and help to quantify its physical and chemical properties, which relate to the environmental reactivity and the fate of the mineral.

This study investigates the reaction products from the oxidation of the chlorinated ethylene by MnO₄⁻. Several methods will be tested in order to control the growth of the colloid. The objective of this study is to investigate the factors that control the growth of Mn oxide colloids, and possible approaches to control the rate of the growth.

2. Methods

Colloid growth measurements

Various studies of MnO₄⁻ oxidation (Steward, 1965; Insausti et al., 1995) have shown how to apply a UV-vis spectrophotometer to monitor the reaction. MnO₄⁻ has a distinct, characteristic peak at a wavelength of 525 nm, while transparent at 418 nm. Thus, the product from the oxidation reaction Mn oxide, as a colloid, can be measured at a wavelength of 418 nm. UV-vis spectrophotometry method can provide qualitative information on the colloid growth. To examine the delay effect of phosphate buffer on colloid coagulation, experiments were conducted to examine colloid formation using a Varian Cary 1 UV-vis spectrophotometer and continuously scanning at wavelengths of 418 nm and 525 nm. Reactions occurred in the capped cuvette inside the spectrophotometer. All experiments were conducted in aqueous solution at 22 °C. The reactants were potassium permanganate and trichloroethylene (TCE), with the latter in excess. The concentrations of KMnO₄ and TCE were 0.158 mM and 3.8 mM for all the
experiments. A buffer comprised of equal mixture of \(\text{KH}_2\text{PO}_4\) and \(\text{K}_2\text{HPO}_4\) was used as the source of phosphate. The concentration of this buffer mixture was varied in each experiment. One experiment with no phosphate buffer added provided a baseline for comparison. KCl was added to maintain all solutions at the same ionic strength. Details of the collection of experiments are listed in Table 5.1.

UV-vis spectrophotometer only provides qualitative information on colloid particle growth. In order to provide more insight on this process, experiments have been conducted to measure the size of the growing colloid particles and their zeta potential, a property that reflects the surface charge of the colloids. Zeta potential has been used to evaluate the stability of the colloid. The value of the inner potential at the plane of shear is defined as zeta potential, which shows repulsive forces of the colloid particles and can be indirectly measured experimentally.

The purpose of these experiments is to measure directly particle size as the colloids grow and their surface charges. Finally, I wanted to compare the rates of particle growth as a function of different phosphate species. Colloid growth under different conditions was monitored using photon correlation spectroscopy, which measures the size of submicron particles. It operates on the basis of electrophoretic light scattering. Colloid particle size is determined statistically from the intensity of the light scattering. When measuring the zeta potential, an electrical field is applied to the sample, and the scattered light is compared with a reference beam thus allowing the determination of the sign and value of the zeta potential, which are related to the electrophoretic mobility. The zeta potential is calculated automatically from the experimentally determined electrophoretic mobility via Smoluchowski’s equation (5.2).
\[ \mu_e = \frac{e \zeta}{\eta} \]  

(5.2)

where \( \mu_e \) is the electrophoretic mobility, \( \varepsilon \) is permittivity of liquid, \( \zeta \) is zeta potential, \( \eta \) is the viscosity of the liquid.

The size of colloid particles during the growth process was measured with 90 Plus particle sizer (Brookhaven Instrument Co. Holtsville, NY), and the zeta potentials were determined with ZetaPlus (Brookhaven Instrument Co. Holtsville, NY). The reactions were conducted inside the cuvettes supplied with the instruments. The experiments were run under conditions listed in the Table 5.2. Measurements were made automatically by the instruments at pre-set times. KCl was added to the reaction solution to maintain the same ionic strength for all runs.

3. Results

Spectrometric studies of the colloidal growth with and without phosphate show clear differences as presented in the Figure 5.1 and 5.2. In TCE oxidation by MnO\(_4^-\) without phosphate, colloids formed immediately, as indicated by an elevated absorbance across all the wavelengths scanned (Figure 5.1). With the addition of phosphate, the absorbance spectrum shows a gradual decrease in the MnO\(_4^-\) peak until almost all the MnO\(_4^-\) has been consumed. The spectrum also shows an increase in absorbance at all wavelengths, suggesting the presence of colloids.
This pattern of response can also be illustrated by showing the absorbance at wavelengths of 418 nm and 525 nm. Figure 5.3 shows the closely synchronized change of absorbance at 418 nm and 525 nm for the reaction without the phosphate. The synchronized change at absorbances at 418 nm and 515 nm is the result of the colloid existence. The starting point for the increase at wavelength 525 nm coincides with the start of colloid formation. Thus, I can identify that without phosphate in the solution, the spectrum of the absorbance has only two steps: Step 1: colloid growth; Step 2: formation of visible precipitates. Figures 5.4 and 5.5 illustrate results of similar experiments with phosphate at varying concentration. There is a distinct difference between the spectrums in the reaction with and without phosphate, especially at early times. Based on the absorbance variation at a wavelength of 418 nm, four steps in the reaction pathway with the addition of phosphate were identified:

1. Aqueous reaction step: a decrease of MnO$_4^-$ concentration as indicated by the absorbance at 525 nm, and an increase of the absorbance at 418 nm, which is probably because of a soluble Mn (IV) species.

2. Phosphate delay step: MnO$_4^-$ continuously decreases, but at a lower rate according to a first order kinetic rate law. Phosphate starts to influence the soluble MnO$_2$ species, possibly by forming MnO$_2$-H$_2$PO$_4^{-1}$ and MnO$_2$-HPO$_4^{-2}$ complexes, which reduces the rate of colloid formation. As a result, UV absorbance at wavelength 418 nm is lower;

3. Coagulation step: MnO$_4^-$ has been consumed and the influence of phosphate is reduced with time, probably by the dissociation of MnO$_2$-H$_2$PO$_4^{-1}$ and

4. Precipitation step: the final transition to precipitated MnO$_2$ via the MnO$_2$-HPO$_4^{-2}$ complex, leading to a further increase in absorbance at 525 nm.
MnO$_2$-HPO$_4^{-2}$ complexes. Colloids start to form, as is implied by the synchronized increase in absorbance at both 418 nm and 525 nm.

4. Precipitation step: after the colloid formation peaks, as seen from UV absorbance, colloids are coagulated and precipitate out of the suspension. Eventually, most of the Mn oxide precipitates.

The above analysis suggests that phosphate probably reacts with the soluble forms of Mn(IV). Thus, the effect of phosphate in delaying the coagulation occurs in steps 2 and 3. This suggestion explains the results of other researchers who show phosphate stabilizes Mn oxide colloids, and a soluble Mn oxide species has been identified (Mata-Perez and Perez-Benito, 1985).

From Figure 5.6, the peak concentration of colloids is lower with an increase in the concentration of the phosphate buffer. Also, the peak comes at a later time, meaning that the process of coagulation is extended by the presence of phosphate and that colloid particles are suspended in the solution for a longer time. Meanwhile, the rate of particle growth is lower as compared to solutions with a low concentration of phosphate or no buffer at all. Precipitation of particles also extends over a longer time. Results in Figure 5.6 suggest that as the concentration of phosphate increases to a certain point, the four-step process might become a two-step process.

The time elapsed from the beginning of the oxidation reaction to the precipitation point, the start of step 4, is defined as $T_p$, and $1/T_p$ is defined as the rate of the colloid growth. From Figure 5.6, $T_p$, the time when colloid concentration peaked was determined. Figure 5.7 is the plot of phosphate concentration versus $1/T_p$. The solid line in the figure provides an excellent least squares fit to the data, indicating an almost linear
relationship between the $T_p$ and phosphate concentration. The rate of colloid growth in
the experiment without phosphate is not included here because the pH of the reaction
solution was not fixed. The oxidation reaction can drop the pH 2 to 3 scale due to the
release of proton in the reaction. The pzc of the Mn oxide is 3.7. The reaction proceeding
toward the pzc would increase the coagulation process.

The results of colloid size measurements from photon correlation spectroscopy
are shown in Figure 5.8. A distinct feature of this figure is that the colloid growth rate
under conditions where no salts were added to the background solution is much smaller
than that was evident with the addition of either KCl or other phosphate ions. This result
indicates that ionic strength influences the colloid growth rate greatly. As expected, the
starting point for colloid growth to form in the solution is delayed by the phosphate, 35
minutes later for reaction with phosphate than without. The results show that although the
presence of phosphate ions can slowdown the coagulation process, especially at early
times, in general increasing of the ionic strength also increases the rate of colloid growth.

The zeta potential measurement results are presented in Figure 5.9 and 5.10. For
experiments run with no background electrolyte, the surface charges of the colloids are
always positive. The experiment run with KCl as background electrolyte but without any
phosphate addition produced similar results in terms of surface charge. However, when
phosphate was added to the reaction solution, the surface charge of the colloids became
negative shortly after the reaction started (Figure 5.10). The reversal of charge on
particles should be caused by phosphate attachment to the solid. However, this change in
surface charge does not have a long-term effect on the coagulation of colloids.
4. Discussion

During the MnO$_4^-$ treatment of chlorinated ethylenes, the release of H$^+$ from the reaction (Equation 5.1) drops the pH of the solution from neutral to the acidic range in unbuffered solution. Occasionally, the pH falls below 2, as observed in some experiments. Because the pzc of the manganese oxide is 3.7 ± 0.4, this change in pH can definitely enhance the coagulation of colloids. For pHs close to the pzc, the net charge on the surface of the particles approaches zero. The mutual repulsion of the colloids reduced sufficiently to permit the inter-particle collisions, agglomeration, and subsequent sedimentation. Thus, the combination of H$^+$ production and a pzc for Mn oxide of 3.7 ± 0.4 enhances the precipitation.

Phosphate ion can react with the soluble Mn(IV) species and slowdown the formation of colloid by tens of minutes. The extent of Mn oxide precipitation control provided by phosphate may not be helpful in field problems. The addition of phosphate also increases ionic strength, which in turn increases the rate of colloidal formation. Another reason that the delay effect of the phosphate is not sufficient might be that the pzc of Mn oxide from the MnO$_4^-$ oxidation is around 3.7. At a neutral range of pH, the surface charge of the particles is negative, and the negative charged phosphate ion does not adsorb on the particles well. Finally, the relatively unstable complex of phosphate and soluble Mn(IV) species leads to Mn oxide coagulation and precipitation.

Researchers, using UV-vis spectrophotometry to study the oxidation of double carbon bond organic acids with MnO$_4^-$, reported that the decomposition of MnO$_4^-$ formed a chemical intermediate before finally producing Mn oxide. Wiberg et al. (1973) believed
that the intermediate is cyclic hypomanganate ester. Lee and Brownridge (1973) reached a similar conclusion and also detected of Mn(VI) during the reaction. Simandi and Jaky (1976), and Freeman et al. (1981) actually determined the oxidation state of the dissolved species as IV using iodometric titration. They concluded that a soluble Mn(IV) species, possibly MnO₃²⁻ formed and slowly precipitated. Because both Mn(V) and Mn(VI) absorb at wavelength of 418 nm, the intermediate theory provides a possible explanation of the existence for step 2 in the UV-vis spectrum where the absorbance is decreased. However, I believe that step 2 is caused by a soluble Mn species, but not Mn(V) or Mn(VI). It is also probably not a colloidal form. There are two reasons. First, the intermediates of Mn(V) and Mn(VI) reportedly have a transitory existence, of just seconds. The time scale in my experiment is much larger. Secondly, UV-vis absorbances at 418 nm and 525 nm both decrease, which is not the behavior that growing colloids would produce. The existence of step 2 suggested the presence of a soluble reaction product, probably Mn(IV), that led to the colloidal Mn oxide. This process is caused by a phosphate ion reacting with the soluble Mn(IV) species that caused the delay of the colloid formation. This idea is consistent with results from the direct measurement of the colloid particle size (Figure 5.8). The phosphate delay effect occurs at an early stage before the any detectable colloid formed in the solution. The effect shown in Figure 5.8 could be caused by phosphate reactions with soluble Mn(IV) species, forming MnO₂⁻H₂PO₄⁻¹ or MnO₂⁻HPO₄⁻² complexes. This process exist in the framework of the model proposed here. Equation 5.1 can be rewritten as a three-step process as equation 5.3, 5.4, and 5.5. The phosphate ion reaction with soluble Mn(IV) is represented with equation 5.6 and 5.7.
\[ C_2HCl_3(TCE) + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2(\text{aq}) + 2\text{CO}_2 + 3\text{Cl}^- + \text{H}^+ \]  
(5.3)

\[ \text{MnO}_2(\text{aq}) \rightarrow \text{MnO}_2(\text{c}) \]  
(5.4)

\[ \text{MnO}_2(\text{c}) \rightarrow \text{MnO}_2(\text{s}) \]  
(5.5)

\[ \text{MnO}_2(\text{aq}) + \text{H}_2\text{PO}_4^{-1} \leftrightarrow \text{MnO}_2(\text{aq})-\text{H}_2\text{PO}_4^{-1} \]  
(5.6)

\[ \text{MnO}_2(\text{aq}) + \text{HPO}_4^{-2} \leftrightarrow \text{MnO}_2(\text{aq})-\text{HPO}_4^{-2} \]  
(5.7)

where \( \text{MnO}_2(\text{aq}) \) is dissolved Mn(IV) species; \( \text{MnO}_2(\text{c}) \) is colloidal Mn oxide; \( \text{MnO}_2(\text{s}) \) is the Mn oxide precipitates. \( \text{MnO}_2(\text{aq})-\text{H}_2\text{PO}_4^{-1} \) and \( \text{MnO}_2(\text{aq})-\text{HPO}_4^{-2} \) are phosphate complexes. As oxidation of TCE begins, dissolved Mn oxide (\( \text{MnO}_2(\text{aq}) \)) is first produced. Then \( \text{MnO}_2(\text{aq})-\text{H}_2\text{PO}_4^{-1} \) and \( \text{MnO}_2(\text{aq})-\text{HPO}_4^{-2} \) are formed. Because \( \text{MnO}_2(\text{aq})-\text{H}_2\text{PO}_4^{-1} \) and \( \text{MnO}_2(\text{aq})-\text{HPO}_4^{-2} \) are not very stable and later dissociate, the colloids coagulate and precipitate. The existence of soluble Mn(VI) species in phosphoric solutions has also been reported by other researchers (Jaky and Zrinyi, 1993; Perez-Benito et al., 1996).

Study of products of the reduction of \( \text{MnO}_4^- \) ion by trimethylamine in aqueous phosphate buffers by Mata-Perez and Perez-Benito (1984) found phosphate slowed down the process of precipitation. However, only the two steps were identified, a delayed colloid coagulation step, and a precipitation step. Similar results were presented by Insausti et al. (1995). I carefully examined their data and concluded that the difference...
between the two sets of experiment results was probably caused by a difference in the kinetic rate of the reduction reactions involving MnO$_4^-$ and two different compounds, TCE and trimethylamine. When the reaction rate is slower, the production rate of Mn oxide colloids from the trimethylamine reaction is also slower, even at a much higher MnO$_4^-$ initial concentration as compared with my experiment. Thus, the concentration of the colloids in the solution did not start precipitating before the reaction stopped, which leads to a two-step process. However, the reaction between MnO$_4^-$ and TCE has a higher rate, which let the Mn oxide colloids form before the MnO$_4^-$ oxidation reaction stopped. This case leads to a four-step process. There are clearly two parallel processes that determine the concentration and the growth of the colloids in solution. One is the colloid production from the MnO$_4^-$ oxidation reaction and subsequently the colloid coagulation process after it reaches the CCC (critical coagulation concentration). The other is the delay due to phosphate ion reacting with the soluble Mn(IV) species. The result of the two parallel pathways can be different depending on the relative reaction rate of the two processes.

The four-step process indicated that the rate of Mn(IV) production in the MnO$_4^-$ oxidation reaction is greater than the rate of phosphate forming complexes with soluble Mn(IV) species. With the increase of the concentration of the phosphate buffer, slopes of curve at step 2 become smaller, and the peaks at the end of step 3 are smaller. These results indicate that with an increase in the concentration of the phosphate buffer in the solution, the rate for phosphate to form complexes with soluble Mn(IV) species becomes bigger, as compared with the same rate of MnO$_4^-$ oxidation reaction of which the initial concentrations were kept the same. As one can see from these data, even in the laboratory
condition, it would need a very high concentration of phosphate for the colloid growth process to be controlled to a realistic extent.

5. Conclusions

My studies indicate that phosphate ion can slow down the formation of colloidal Mn oxide from TCE oxidation with MnO$_4^-$ ion. Phosphate ion delays the formation of Mn oxide colloids by forming a soluble Mn(IV)-phosphate species. The rate of the colloid formation decreases with increasing concentrations of phosphate ion for the range of concentrations in my experiments. However, the effect of phosphate in delaying colloid formation is limited by three factors. First, Mn oxide colloids form after the concentration of the soluble Mn(IV) species reaches its CCC. The rapid reaction rate of the oxidation by MnO$_4^-$ quickly produces enough Mn (IV) to exceed the rate of phosphate-Mn(IV) complex formation. Second, the effect of phosphate in delaying Mn oxide precipitation is diminished by increasing ionic strength. When phosphate is added to the solution, it increases the ionic strength, which is unfavorable to the effort in slowing down colloid formation. The third reason is because of the low pzc of the Mn oxide. Phosphate does not sorb on the Mn oxide colloids well because at the pH range where phosphate has a strong surface charge (-), Mn oxide colloid also negatively charged, due to its low pzc.

It is not likely phosphate can be applied to control Mn oxide formation in ISCO schemes. A different approach to the problem of precipitation related permeability change is needed. I am now in the process of developing a method to remove precipitates once formed.
<table>
<thead>
<tr>
<th>Run</th>
<th>[KMnO₄] (mM)</th>
<th>[TCE] (mM)</th>
<th>Buffer (M) [KH₂PO₄] = [K₂HPO₄]</th>
<th>Ionic Strength (KCl) (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.158</td>
<td>3.8</td>
<td>0</td>
<td>0.23</td>
<td>varies</td>
</tr>
<tr>
<td>2</td>
<td>0.158</td>
<td>3.8</td>
<td>0.02</td>
<td>0.23</td>
<td>6.81</td>
</tr>
<tr>
<td>3</td>
<td>0.158</td>
<td>3.8</td>
<td>0.03</td>
<td>0.23</td>
<td>6.81</td>
</tr>
<tr>
<td>4</td>
<td>0.158</td>
<td>3.8</td>
<td>0.04</td>
<td>0.23</td>
<td>6.81</td>
</tr>
<tr>
<td>5</td>
<td>0.158</td>
<td>3.8</td>
<td>0.05</td>
<td>0.23</td>
<td>6.81</td>
</tr>
</tbody>
</table>

Table 5.1. Experimental conditions for the colloid growth experiment involving the UV-vis spectrophotometer.

<table>
<thead>
<tr>
<th>Runs</th>
<th>[KMnO₄] (mM)</th>
<th>[TCE] (mM)</th>
<th>[KH₂PO₄] (M)</th>
<th>[K₂HPO₄] (M)</th>
<th>[K₃PO₄] (M)</th>
<th>I (KCl) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.63</td>
<td>6.09</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.63</td>
<td>6.09</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.24</td>
</tr>
<tr>
<td>3</td>
<td>0.63</td>
<td>6.09</td>
<td>0.02</td>
<td>0.02</td>
<td>0</td>
<td>0.24</td>
</tr>
<tr>
<td>4</td>
<td>0.63</td>
<td>6.09</td>
<td>0</td>
<td>0</td>
<td>0.04</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 5.2. Experimental conditions for monitoring colloid particle size growth and surface charge with photon correlation spectroscopy and zeta-plus.
Figure 5.1. Sequential scanning of the reaction from 350 nm to 700 nm during the MnO$_4^-$ reaction with TCE at conditions [KMnO$_4$] = 0.158 mM, [TCE] = 3.8 mM, I = 0.23 M(KCl), no phosphate added.
Figure 5.2. Sequential scanning of the reaction from 350 nm to 700 nm during the MnO$_4^-$ reaction with TCE at conditions [KMnO$_4$] = 0.158 mM, [TCE] = 3.8 mM, I = 0.23 M(KCl), [KH$_2$PO$_4$] = [K$_2$HPO$_4$] = 0.05 M.
Figure 5.3. Time variation in UV-VIS absorbance at 418 nm and 525 nm during MnO$_4^-$ reaction with TCE at conditions [KMnO$_4$] = 0.158 mM, [TCE] = 3.8 mM, I = 0.23 M(KCl), no phosphate added.
Figure 5.4. Time variation in UV-VIS absorbance at 418 nm and 525 nm during MnO$_4^-$ reaction with TCE at conditions [KMnO$_4$] = 0.158 mM, [TCE] = 3.8 mM, I = 0.23 M(KCl), [KH$_2$PO$_4$] = [K$_2$HPO$_4$] = 0.03 M.
Figure 5.5. Time variation in UV-VIS absorbance at 418 nm and 525 nm during MnO$_4^-$ reaction with TCE at conditions [KMnO$_4$] = 0.158 mM, [TCE] = 3.8 mM, I = 0.23 M(KCl), [KH$_2$PO$_4$] = [K$_2$HPO$_4$] = 0.05 M.
Figure 5.6. Time variation in UV-VIS absorbance at 418 nm during MnO$_4^-$ reaction with TCE at conditions [KMnO$_4$] = 0.158 mM, [TCE] = 3.8 mM, I = 0.23 M(KCl), phosphate concentration various from 0 to 0.05 M.
Figure 5.7. Colloid growth rate ($1/T_p$) versus phosphate concentration ($[\text{K}_2\text{HPO}_4]=[\text{KH}_2\text{PO}_4]$).
Figure 5.8. Result of the colloidal particle growth with time as monitored by the particle sizer.
Figure 5.9. Zeta potential measurement of colloidal particles at run 1. No background electrolyte added.
Figure 5.10. Zeta potential measurement of colloidal particles in run 4 with $[\text{K}_3\text{PO}_4] = 0.04$ M.
CHAPTER 6

TREATMENT OF THE MANGANESE OXIDE PRECIPITATION FROM
PERMANGANATE OXIDATION OF CHLORINATED ETHYLENES IN THE
SUBSURFACE: BATCH AND 2-D FLOW TANK EXPERIMENTS

1. Introduction

Since early 1990’s, in situ chemical oxidation (ISCO) has emerged as a new approach to solve problems of ground water contamination. Oxidation schemes using MnO$_4^-$ to destroy chlorinated ethylenes have been developed and tested at various sites around the nation (Vella and Veronda, 1992; West et al, 1997; Schnarr et al., 1998; Yan and Schwartz, 1999; Mott-Smith et al., 2000; McKay et al., 2000). Results from these tests have shown that in situ oxidation is capable of destroying chlorinated solvents quickly, and of producing reaction products that are relatively harmless and safe (Equation 6.1, 6.2, 6.3).
Usually in field applications, the aqueous concentration of contaminant decreases dramatically when the oxidation treatment is applied. However, in some cases concentration of contaminant rebounded shortly after the treatment stopped. Some studies (Li and Schwartz, 2000; Reitsma and Marshall 2000; Thomson et al, 2000) have revealed that the precipitation of MnO$_2$ leads to the plugging of the pore space, which results in a low flushing efficiency, and a lowered DNAPL removal rate, especially late in the treatment period. My latest research results (Li and Schwartz 2001), using a small flow tank and high resolution imaging, show that during the flushing of a TCE DNAPL source zone in a homogeneous medium with MnO$_4^-$, the precipitation of MnO$_2$ formed a rind around the zone of high DNAPL saturation. This process sequestered the TCE and effectively prevented further oxidation of the contaminant. Flushing efficiency decreased greatly due to the reduction in permeability caused by the formation of Mn oxide precipitates and CO$_2$ bubbles.

During subsurface soil flushing, the heterogeneity of the porous media can greatly influence the pattern of flow. Ibaraki and Schwartz (2001) have demonstrated, with numerical modeling, that heterogeneity can create fast flow zones in the porous media, which can cause treatment chemicals to bypass zone of contamination and failure of the
treatment. Precipitation produced by chemical remediation will change the permeability of porous media, which leads to the increase of heterogeneity of media and unsuccessful remediation action.

There is relatively little research on the impact of physical and chemical heterogeneity on mass removal rate and fixes through inhibition of precipitation. Previous studies have led investigators to the position that the problem of precipitation has to be solved before ISCO schemes can be useful in the field for site remediation. Clearly, to achieve remediation goals with DNAPL contamination, the precipitation of Mn oxide must not occur in the zone of DNAPL saturation. One possible strategy is to delay the formation of precipitates so that the plugging occurs further away from the DNAPL zone, which I have discussed in the previous chapter. A second strategy is to find ways of removing the precipitates once they are formed.

Let me discuss the first strategy in more details. The Mn oxide formed during the oxidation of chlorinated ethylenes initially forms colloids. Coagulation of colloids leads to precipitates that are notable by inspection. Colloids sometimes can be transported by ground water through the porous medium. So if the process of colloid coagulation was controlled or delayed, Mn oxide colloids might be transported further away from the treatment zone. Thus, solids might not cause problems in the DNAPL zone. The possible control of the colloid formation by phosphate ion was investigated in my earlier study. The results showed that the phosphate ion has a limited effect on delaying of the formation of Mn oxide colloids. It is thought that the additives slow down the formation of colloids by forming a soluble Mn(IV)-phosphate complex. However, the suppression of precipitation is diminished by increased ionic strength. Phosphate also does not sorb
onto the Mn oxide colloids well. In the typical pH range, phosphate has a strong negative surface charge (-), as does Mn oxide, due to its low pzc.

Even if control of the colloid formation was successful, precipitates will still form in the subsurface, at a distant location from the DNAPLs. From a regulatory point of view, this is still not acceptable. Although Mn oxide is a harmless mineral, in some cases, over long time, the precipitates may be remobilized, adding manganese above regulatory levels into ground water.

If the control of colloid formation was not viable, there is a second approach, namely the removal of Mn oxide precipitates from the area surrounding the high DNAPL saturation. A successful approach to the removal of the precipitates will not only solve the problem of plugging, but also the removal of the precipitates from the subsurface, in order to address environmental concerns of excess Mn.

Dissolution of sparsely soluble oxide mineral

There are four ways to increase the solubility of a metal oxide: changes to the pH, E₄, media composition, or ionic strength. The alteration of the pH and E₄ in the subsurface to values that can dramatically change the solubility of a Mn oxide is not realistic, because it is only at very extreme pH and E₄ values that Mn oxide can be soluble. Ionic strength adjustment is also not feasible, because only a reduction in the ionic strength can possibly increase solubility. In reactive natural systems, it is not realistic to expect that minerals would not dissolve. The third alternative finding an appropriate additive seems to be the only viable possibility.
The dissolution of sparsely soluble metal oxides has been studied by many researchers. Stumm and his colleagues (Furrer and Stumm, 1986; Zinder et al., 1986; Wieland et al., 1988; Biber et al., 1994) have proposed a series of surface reaction models to describe these kind of dissolution reactions. Because an ISCO based on MnO$_4^-$ produces hydrogen ions, the reaction usually occurs under acidic conditions. Under such a condition, the dissolution reaction can take place through surface protonation. Furrer and Stumm (1986) described this process, for a trivalent oxide, in a model of stepwise protonation reactions (Equation 6.4, 6.5, 6.6, 6.7).
The first three steps involve the adsorption of protons onto the surface of the solid, and weakening of the metal-OH bond. This process is fast and the reactions can be considered equilibrium. The last step (Equation 6.7) is the detachment of metal species, which is the rate limiting process. The dissolution rate \( R_H \) \( \text{mol m}^{-2} \text{ h}^{-1} \) is proportional to the third power of the surface protonation in the case of trivalent oxide.

\[
R_H = k_H' [\equiv \text{MeOH}_2^+]^3
\]  

(6.8)

Where \( k_H' \) is the rate constant of proton-promoted dissolution reaction; \( \equiv \text{MeOH}_2^+ \) is the active site available for protonation, or the surface concentration of protons. A more general empirical rate law for proton-promoted dissolution is

\[
R_H = k_H' [H^+]^n
\]  

(6.9)

Where \( n \) is usually between 0.0 and 0.5.

When other constituents exist in the solution, a more complex set of reactions can occur. Ligands can sorb on the surface of the solid, shifting the charge distribution inside the metal-(hydro)oxide core, and cause the detachment of metal. Furrer and Stumm (1986) provided a model of the ligand-promoted dissolution reaction where the dissolution a trivalent oxide \( (\text{M}_2\text{O}_3) \) with hydrogen oxalate ion \( (\text{C}_2\text{O}_4\text{H}^-) \) can be described by three elementary steps: (a) an equilibrium reaction involving the formation of a ligand surface complex, a fast surface adsorption step (Equation 6.10); (b) the slow detachment
of the metal from the solid to the aqueous phase (this is the rate limiting step) (Equation 6.11); and (c) a fast subsequent protonation step restoring the original surface configuration (Equation 6.12). The product in equation (6.12) should be the same as the solid reactant of the equation (10)

\[ M \text{OH}_2 + \text{OH}^- \xrightleftharpoons[k_1']{k_1} M \text{OH}_2 \text{OH}^- \]

\[ M \text{OH}^- + n\text{H}_2\text{O} \xrightarrow[k_{\text{slow}}]{k} M \text{OH}^- + \text{ML}^+ \text{(aq)} \]

\[ M \text{OH}^- + 2\text{H}^+ \xrightarrow[k_{\text{fast}}]{k} M \text{OH}_2 \]

The rate of dissolution can be expressed as

\[ R_L = k_L' \langle \equiv \text{ML} \rangle = k_L' C_L^s \]

where \( k_L' \) is the rate constant of the ligand-promoted dissolution reaction; ML is the metal-ligand complex; and \( C_L^s \) is the surface concentration of ligands.

If ligands are available under acidic conditions, then both ligand and proton promoted dissolution will occur. Furrer and Stumm (1986) illustrate this combined
process using the following equations (Equation 6.14, 6.15, 6.16, 6.17). However, it is not necessary to assume that the general reaction rates are the superposition of the two processes, which requires that the two processes are parallel reactions.

\[
\begin{align*}
&M\overset{\text{OH}}{O}H + H_2O \overset{k}{\underset{k_1}{\rightleftharpoons}} M\overset{\text{OH}}{O}H^- \\
&M\overset{\text{OH}}{O}H^- + H \overset{k}{\underset{k_2}{\rightleftharpoons}} M\overset{\text{OH}}{O}H
\end{align*}
\] (6.14)

\[
\begin{align*}
&M\overset{\text{OH}}{O}H^- + nH_2O \overset{k_3}{\text{slow}} \rightarrow M\overset{\text{OH}}{O}H^- + ML^{(aq)}
\end{align*}
\] (6.16)

\[
\begin{align*}
&M\overset{\text{OH}}{O}H^- + H^+ \overset{k_4}{\text{fast}} \rightarrow M\overset{\text{OH}}{O}H
\end{align*}
\] (6.17)

Dissolution reactions can also involve electron transfer at the solid surface. This reductive dissolution reaction was described by Zinder et al. (1986). Equations 6.18 to 6.22 illustrate the proton-promoted dissolution of metal oxide under reducing conditions. The first two steps (Equation 6.18, 6.19) of protonation are similar to that for non-
reducing condition, which causes polarization and weakening of the metal-oxygen bonds. The third step (Equation 6.20) is a redox reaction, when electrons are transferred from the reducing agent to metal core at the solid surface. The outgoing metal ion is reduced and become an activated complex. The fourth step (Equation 6.21) is the detachment of the metal group, which is the rate limiting step. The final step (Equation 6.22) restores the original solid surface by another protonation.
The reaction rate is

\[ R_{e, H} = k_4 \{E\} \]  \hfill (6.23)

where \( k_4 \) is the rate constant in equation 6.21, and \( E \) is the surface concentration of the surface species, which is the statistically determined number of potentially detachable surface metal species per unit area.

Ligand-promoted dissolution of metal oxides under reducing conditions is explained in a model shown in equations 6.24 to 6.28 (Zinder et al., 1986). A surface chelating (Equation 6.24) reaction is followed by protonation (Equation 6.25). Then at the same site, electron transfer occurs (Equation 6.26). The first three reaction steps weaken the metal-oxygen bonds and lead to the detachment step (Equation 6.27), which it the rate-limiting step. The solid surface reverts back to the initial state by another protonation (Equation 6.28).
The reaction rate for this system is given as

$$R_{e,H} = k_4 \{EL\}$$  \hspace{1cm} (6.29)

where $k_4$ is the rate constant of the slowest reaction (Equation 6.27), detachment process; EL is the surface concentration of the surface species, a statistically determined number.

With the dissolution inhibition theory, a more general dissolution reaction rate is presented by Biber et al (1994) as:
\[ R_{\text{tot}} = k_H(C_H^s)^n + \sum k_{Li}C_{Li}^s + \sum k_{Hi}C_{Hi}^s + \sum k_{Ri}C_{Ri}^s + k_{OH}(C_{OH}^s)^m + \sum k_{Mi}C_{Mi}^s + k_{aq} \]  

(6.30)

where \( \sum k_{Li}C_{Li}^s \), \( \sum k_{Hi}C_{Hi}^s \), \( \sum k_{Ri}C_{Ri}^s \), \( \sum k_{Mi}C_{Mi}^s \) represent the contribution to the dissolution made by ligand, inhibitor, reductant, and metal ion; \( k_H(C_H^s)^n \), \( k_{OH}(C_{OH}^s)^m \) represent the acid and basic dissolution, respectively; the last term, \( k_{aq} \) is considered the effect of hydration. Usually, under a given condition only one or two mechanisms are dominant. Thus, equation 6.30 can often be simplified to one or two terms.

Furrer and Stumm (1986) and Biber et al. (1994) found that some ligands, like dicarboxylic acids, hydroxy carboxylates, diphenols, EDTA, NTA, can effectively promote dissolution, because they have two or more donor atoms as functional group, or can form bidentate or multidentate mononuclear surface chelates, which weaken the metal-oxygen (or hydroxy) bond, causing the metal center group to leave the solid surface. Previous studies of \( \beta \)-MnOOH (Mn(III, IV)) dissolution (Stone, 1987; Stone and Morgan, 1984b) found that oxalate and EDTA can enhance the dissolution rate sufficiently. Perez-Benito et al., (1996) reported reduction of colloidal manganese dioxide by oxalic acid. It remains to be determined whether the dissolution of Mn oxide from the oxidation of chlorinated ethlyenes by MnO \(_4^-\) can be enhanced by organic chelating agents.

These questions can be examined with batch experiments. Li and Schwartz (2001) used 2-D flow tank experiment in a homogenous medium, to illustrate how precipitation caused plugging problem in ISCO schemes. Here, I intend to test the prototype treatment method with a 2-D flow tank setup that provides more realistic flow conditions.
Objectives

This study investigates the use of chemical additives to control the formation of Mn oxides and to remove them in porous media. The specific objectives of this study are

1. to investigate with batch experiments the possibility of removing the Mn (hydro)oxide from the porous media by chemical modifications to the aqueous phase; and

2. to test, by flow tank experiments, the most promising strategy form (1) above.

2. Methods

In an earlier section, I reported how the Mn oxide mineral was prepared and its solid surface properties were measured. The X-ray diffraction powder (XRD) analysis shows the mineral formed in the oxidation of chlorinated ethylenes with MnO$_4^-$ is semi-amorphous potassium-rich birnessite. Based on whole-mineral analysis, using charge balance of the different elements, the Mn oxide mineral has the formula $K_{0.854}Mn_{1.786}O_4\cdot1.55H_2O$. The specific surface area of the Mn oxide mineral is 23.55 m$^2$/g, which is relatively small among similar minerals. The measured pzc for the manganese dioxide is 3.7 ± 0.4.
Batch experiment to determine dissolution rates

The possibility of using chemical additives to dissolve Mn oxide was examined with batch experiments. Citric acid, oxalic acid and ethylenediaminetetraacetic acid (EDTA), all used as received from Fisher Scientific, were used for the experiment. The Mn oxide powder prepared earlier was rehydrated for at least a week before the experiment. The concentration of Mn oxide was 0.1 g/L, and the acid strength was 0.1 Mm. 0.1 M NaNO$_3$ used as a background electrolyte. A controlled experiment using no organic acid, with the same pH maintained by adding nitric acid was used for comparison. The experiment conditions are listed in Table 6.1. Strong acid (HNO$_3$) or base (NaOH) was added with a micro-pipette to maintain the pH at a specified value. The experiment was carried out in a 100 mL vial, and the solution was stirred magnetically throughout the 25-hour experiment. The vial was wrapped in aluminum foil to minimize possible photo-enhanced reactions. At predetermined intervals, a 2 mL sample was taken from the vial with a syringe, and filtered using a 0.1µm syringe filter to remove the undissolved solids. The filtrate was transferred into a vial and diluted for ICP-MS and ICP-OEM analysis. The time-course data were later used to determine the rate of dissolution.

Similar experiments were conducted with citric acid, which showed good dissolution rate, an environmentally friendly solute, to examine the effect of concentration on dissolution rate. The concentration range was 0.05 mM, 0.1 mM and 0.2 mM with one control experiment with no citric acid. All experiments were pH controlled at pH = 2. The experimental conditions are listed in Table 6.2. A strong acid (HNO$_3$) and base (NaOH) were used to maintain the pH value not to exceed ± 0.03 of the pre-set
value. The rest of the experiment condition followed the same procedure as mentioned in the previous section.

2-D flow tank with dissolution of Mn oxide from heterogeneous medium

To test the effect of additives under more realistic conditions, a flow tank experiment with a heterogeneous medium was conducted. A thin, small 2-D glass flow tank with Teflon end fittings was constructed for the experiment (Table 6.3). The flow tank was filled with medium silica sand (US Silica, Ottawa, IL) with lenses constructed of fine glass beads, which acted as low permeability zones. Two PTFE tubes with inside diameter of 1.32 mm were installed in the two ends of the column to function as recharge and discharge wells. Both tubes had ends open at a depth of 0.5 cm from the bottom of column. Once the column was packed, it was saturated with Milli-Q water. A Spectroflow 400 solvent delivery system (Kratos Analytic, NJ) was used to maintain inflow to the tank, the Ismatec pump removed fluid at the outlet (Figure 6.1). With both pumps running at the same steady rate, flow was horizontal along the length of the tank. After the system was set up, a tracer test was run to examine the heterogeneity of the media. The results showed that the heterogeneity achieved its design purpose.

Two grams of the blue dyed TCE was added to the tank from the top to form a zone of residual DNAPL saturation across the vertical depth of the tank and small DNAPL pools perched on the low permeability lens and on the bottom of the tank. The tank was flushed with KMnO₄ solution of 200 mg/L at 0.5 mL/min. Once the pore plugging caused a reduction in flow, the pumping rate was reduced to 0.1 mL/min in order to reduce the pore pressures of pumping on the glass flow tank and to allow the
dissolution reaction to be completed. Once plugging was essentially complete, treatment began to remove the solids. The flushing to remove the precipitates would continue until the whole flow tank was clean. The KMnO$_4$ flushing would resume to continue the oxidation of the remaining DNAPL in the tank. This process was repeated until all the DNAPLs in the flow tank were cleaned up. Both citric acid and oxalic acid were used to dissolve the Mn oxide precipitates. EDTA was not used in the flow tank experiment, due to its toxicity, even though batch experiments showed it to have the highest dissolution rate among the three chemical additives.

Effluent samples were collected three times a day and were analyzed as before. Pictures of the flow tank were taken with a digital camera to monitor the development of the growing zone of Mn oxide precipitation and the removal of the DNAPLs.

Visualization

The thin glass flow tank was designed for visualization. During the 2-D flow tank experiments, formation and removal of the Mn oxide phase was monitored photographically. Packed with either glass beads or silica sand, with light box shining from the back of the tank, the flow tank is semi-transparent to the light. A Nikon 950 digital camera was used for this purpose. The visual monitoring was carried out inside dark room to avoid interference from unnecessary light source. After the experiment completed, the images were downloaded to a PC, and were processed with Photoshop image software to provide consistent image sizes.
Chemical analysis

The effluent from the flow tank was collected periodically and analyzed for TCE, Cl, and MnO$_4^-$ based on the Cl concentration, the TCE that has been oxidized was calculated. With all the TCE accounted for, it is possible to calculate total mass of the contaminant that was removed. TCE was measured with a Fisons Instruments 8060 gas chromatograph equipped with a Ni$^{63}$ electron capture detector and a DB-5 capillary column (JandW Scientific, Rancho Cordova, CA). Pentane was used for the liquid-liquid extraction of TCE. Cl ion concentration was measured with a Buchler Digital Chlorodometer. Permanganate concentrations were measured with a Varian Cary 1 UV-visible spectrophotometer at a wavelength 525 nm.

3. Results

The results of batch experiments of the Mn oxide dissolution are present in Figure 6.2 and 6.3. From Figure 6.2, dissolved Mn concentrations reached a plateau for all the experiment after a few hours of reaction. By comparing with the total Mn oxides added to the solutions, all solids were dissolved in the experiment with EDTA and citric acid at the end of 25 hour period, producing a dissolved Mn concentration of 5000 µg/L. Oxalic acid has a lower plateau value at about 2500 µg/L. The solution comprised of added nitric acid only dissolved a little of the solids. During the experiment, visual observation of the color confirmed the result from chemical analysis. The solution became clear soon after the reaction started during the experiment with the organic acids, while the color
remained almost unchanged for the experiment using nitric acid. A light red color in the solution was observed for a few minutes after the reaction started during the experiment with EDTA. The solution became colorless after the disappearing of the red color.

All solids were dissolved in the experiments with different concentrations of citric acid (Figure 6.3). The control in the experiment, with no citric acid added, yields dissolved Mn concentration less than 70 µg/L. Citric acid can improve the solubility of Mn oxide dramatically, even at relatively small concentration.

If a dissolution reaction mechanism has been clearly determined, equation 6.30 should be used to determine the reaction rate. In reality, the dissolution reactions probably will not be parallel with each other. Rather, the reactions likely interfere with each other competing for the active reaction sites on the solid surface. Therefore, I will not differentiate the individual dissolution processes, and only a general reaction rate will be determined.

The time series data do not fit in the first order dissolution rates that other researchers have proposed for ligand-promoted dissolution of Fe oxide (Furrer and Stumm, 1986; Wieland et al., 1988), even in the early time of the reaction (Figure 6.2, 6.3). The initial rate method was used to make the calculation. The data for the first hour were used and a polynomial function was fitted to the data. The first derivative was taken and its value at time zero was the initial dissolution rate. This method is the same as used by Liang et al. (2000) in a study of the ligand-induced dissolution of ferrihydrite colloids by citrate. The results (Table 6.4.) show that EDTA has the highest initial rate, while nitric acid has the lowest. The initial rate of dissolution increases with the increasing concentration of citric acid (Figure 6.3), although later all the reactions reached the same
limit by dissolve all the solid. The dissolution rate increasing with the concentration of the citric acid is listed in Table 6.5.

Flow tank experiment

The first experiment conducted with the flow tank was a simple tracer test. It was run to examine the pattern of displacement given the heterogeneous character of the medium (Figure 6.4). The flow tank was first saturated with water. Then, MnO$_4^-$ was added as a tracer at a constant concentration of 0.5 g/L. The MnO$_4^-$ solution moved rapidly through coarser grained units, around the low permeable lenses (Figure 6.4(b, c)). Eventually, the tracer moved into the low permeability lenses (Figure 6.4(d, e)).

After the entire tank was filled with the tracer (Figure 6.4(f)), Milli-Q water was pumped into the tank to displace the tracer. Water replaced the tracer in the zones of high permeability first (Figure 6.4(g, h)). Only after the water had displaced most of the tracer, did it begin to become noticeable in low permeable lenses (Figure 6.4(i)). Finally, all of the tracer was displaced from the flow tank. The tracer test showed that the porous medium had a clearly heterogeneous character.

After the tracer test was finished, the flow tank was flushed with Milli-Q water to remove any residual tracer. Then, blue-dyed TCE was injected into the flow tank as a source of DNAPL contamination. The flow tank experiment would be carried out until the DNAPL inside was completely removed over the next four weeks. As MnO$_4^-$ solution was pumped through the tank, precipitates formed and eventually plugged the tank. Organic acids were added to restore the permeability by removing the Mn oxide. There were four cycles of MnO$_4^-$ flushing before all the DNAPL was removed from the tank. Of
the three flushing with organic acids, the first and third were with oxalic acid, and the second was with citric acid.

The progress of the flushing cycles can be seen clearly from TCE concentration monitoring in the effluent from the tank (Figure 6.5). The quantity of oxidized TCE is calculated from the Cl concentration based on equation 6.2. It is evident that the dissolved TCE concentration decreased dramatically shortly after flushing by MnO$_4^-$ began, at the beginning of the experiment, 220 hours, 350 hours, and at the end of the experiment. The concentration of dissolved TCE gradually rebounded during the subsequent flushing with organic acid and Milli-Q water. The estimated quantity of TCE oxidized essentially goes to zero during flushing with organic acid and Milli-Q water. Peaks on the curve match with times when the tank is being flushed with MnO$_4^-$. The quantity of TCE oxidized was at a maximum early in the MnO$_4^-$ flushing and declined with time when the Mn oxide formed and limited the interfacial contact between the DNAPL and oxidant. A mass balance calculation based on the total TCE measured at the effluent, and the amount destroyed indicated that 94.1% of the initial TCE was removed from the tank. This amount represents nearly complete removal of the DNAPL from the tank.

The purpose of this experiment was to test the efficacy of removing solid Mn oxide by organic acid. Thus, for each cycle of flushing, the addition of the specific organic acid was not halted until all of the visible Mn oxide was removed from the tank. Thus, high concentrations of TCE were evident in the effluent during the latter part of the flushing with organic acid and Milli-Q water. Also, the low pumping rate maintained
during the organic acid flush increased the concentration of TCE because the slow flow around the DNAPL promotes TCE concentrations close to saturation.

The changes in the medium during the first MnO₄⁻ flush are recorded in the images of Figure 6.6. The sequence of images begins by showing heterogeneous medium consisted of fine grain glass beads lens embedded in the coarser-grained silica sand (Figure 6.6(a)). Blue-dyed TCE was added as DNAPL before MnO₄⁻ flushing started (Figure 6.6(b)). As the image shows, TCE accumulates above the low permeability boundaries. As flushing began, MnO₄⁻ (light purple color) entered the tank (Figure 6.6(c)). Brown colored MnO₂ precipitates formed and kept growing as MnO₄⁻ flushing continued (Figure 6.6(d, e, f)). Eventually, dark brown and black colored Mn oxide precipitates filled most of the flow tank. Notice how the DNAPL at the bottom of the tank was displaced as the Mn oxide precipitates formed and pumping continued. Flushing eventually was stopped due to the extent of plugging. After the first MnO₄⁻ flush, most of the residually saturated and perched DNAPL was cleaned out of the tank. Only the pooled DNAPL remained in the bottom of the tank (Figure 6.6(g)).

An oxalic acid solution of 2 g/L initially was used to remove the Mn oxide precipitate from the flow tank (Figure 6.7). After flushing with oxalic acid started, a clear zone (white) formed at the corner where the inlet is located (Figure 6.7(a)). The clear zone enlarged as the oxalic acid dissolved Mn oxide precipitates. The oxalic acid front initially moved along the top half of the flow tank where the precipitates were less concentrated (Figure 6.7(b)). By the time of Figure 6.7(c), the precipitates in the upper right corner of the tank were completely dissolved as well as those at the bottom of the flow tank. Precipitates in the finer grained lenses dissolved more slowly and later. The
dissolution front moved forward, leaving zones of more intensive precipitates as islands (Figure 6.7(d)). As the dissolution front moved forward, dissolution was faster in the zone of high permeability (Figure 6.7(e, f, g, h, i, j, k, l, m)). Dissolution of the Mn oxide continued, until only a small zone remained in the flow tank (Figure 6.7(n)). Eventually, all the precipitates were removed from the tank (Figure 6.7(o)). After the first full cycle of flushing by both MnO$_4^-$ and oxalic acid, all the residual and perched DNAPL was destroyed. Only pooled DNAPL was present at the bottom of the flow tank. This result confirms my earlier conclusion that oxidation with MnO$_4^-$ is a better technique for cleaning up residual rather than pooled DNAPL (Li and Schwartz, 2000).

After the oxalic acid flush removed the precipitates, a second flushing cycle was started (Figure 6.8). MnO$_4^-$ flushing is evidenced again by the light purple fluid in the lower right corner (Figure 6.8(a)). MnO$_4^-$ moved quickly through the right half of the flow tank. Again the flush moved quickly in zones of high permeability, bypassing the low permeability lenses. The DNAPL was situated on the left side of the tank. At this stage, there was not yet contact between MnO$_4^-$ and the TCE (Figure 6.8(b)). Once MnO$_4^-$ reached the TCE pool, the oxidation reaction began as indicated by the brown colored Mn oxide precipitates. The reactions occurred mainly around the low permeability lenses (Figure 6.8(c)). Eventually, the whole flow tank was flushed. Mn oxide precipitates formed along the high permeability zone (Figure 6.8(d)). Oxidation was evident everywhere in the flow tank except within the low permeability lenses where some Mn oxide solids apparently diffused in (Figure 6.8(e, f)). The flushing with MnO$_4^-$ stopped once severe plugging was evident.
Citric acid was added to remove the Mn oxide after the second cycle of treatment (Figure 6.9). Citric acid entered the flow tank and displaced the MnO$_4^-$ (Figure 6.9(a)). Mn oxide dissolved as the citric acid contacted the precipitates (Figure 6.9(b)). Dissolution of Mn oxide continued as the citric acid front advanced, more rapidly in the zones of high permeability (Figure 6.9(c)). Eventually, all Mn oxide in the tank was removed through dissolution by citric acid. Note that TCE remained in the bottom of the tank in between two low permeability lenses, where flow is stagnant (Figure 6.9(d)).

With the start of the third flushing cycle, MnO$_4^-$ entered the flow tank at the lower right corner of the flow tank (Figure 6.10(a)). MnO$_4^-$ advanced through the flow tank along zones of higher permeability, and diffused into low permeability lenses (Figure 6.10(b)). Figure 6.10(c) showed MnO$_4^-$ reached the right half of the flow tank, except for the low permeability lenses. Once MnO$_4^-$ contacted the TCE pool, TCE was oxidized producing Mn oxide (Figure 6.10(d)). The oxidation reaction continued and produced a more intense zone of precipitation around the DNAPL at the bottom of the tank (Figure 6.10(e)). The MnO$_4^-$ oxidation of the TCE continued in the area surrounding the DNAPL (Figure 6.10(f)). Precipitation of Mn oxide around the DNAPL pool hindered further oxidation of TCE (Figure 6.10(g)).

The third flush by oxalic acid is shown in Figure 6.11. Oxalic acid entered the flow tank (Figure 6.11(a)). The oxalic acid dissolved Mn oxide and a clear dissolution front formed (Figure 6.11(b)). The dissolution front moved forward, faster in zone of high permeability (Figure 6.11(c)). Dissolution of Mn oxide continued, with more than half of the tank cleaned (Figure 6.11(d)). Figure 6.11(e) shows Mn oxide precipitates
removed at most of the flow tank. Again DNAPL becomes visible at the bottom of the
flow tank as the Mn oxide is removed from the entire flow tank (Figure 6.11(f)).

Shortly after the last flush with oxalic acid (Figure 6.12(a)), DNAPL in the tank
dissolved completed into the aqueous phase (Figure 6.12(b)). At this point, a last MnO$_4^-$
flush was performed (Figure 6.12(c, d, e, f, g)). MnO$_4^-$ reacted with the small quantity of
dissolved TCE and formed trace amount of the Mn oxide precipitates inside the flow
tank. After four flushes with MnO$_4^-$ and three organic acid flushes, essentially all the
TCE was removed.

4. Discussion

The batch experiment of the Mn oxide dissolution shows that the rate of
dissolution has greatly increased after adding the organic acid. The dissolution reaction of
citic and oxalic acid appears to be most ligand-promoted dissolution, although proton-
promoted dissolution is happen at a rather small scale, which is indicated by the low
dissolution rate by nitric acid.

The light red color in the solution observed during the experiment with EDTA
lasted for a few minutes after the reaction started. The solution became colorless after the
disappearing of the red color. Of all the manganese ion, Mn(VII) has distinct purple color
and Mn(III) has red color (Stewart, 1965). It is unlikely that permanganate (Mn(VII)) can
exist in this condition, most likely the red color is caused by Mn(III), which indicates a
reductive process is happening. Mn(III) can form color complexes with EDTA as
MnHEDTA$^0$ (red) and MnEDTA$^-$ (yellow). At the pH of the experiment MnHEDTA$^0$
should be the dominant species. The Mn(III)EDTA complexes are fairly stable in the low pH range, with dissociate half-life in the order of ten of minutes (Klewicki and Morgan, 1998). The eventual colorless solution probably indicates the Mn(II) in the solution. So, Mn oxide dissolution with EDTA probably involves proton, and ligand-promoted dissolution as well as reductive dissolution.

The results of the Mn oxide dissolution experiments suggest that the dissolution mechanism involves proton- and ligand-promoted dissolution, as well as reductive dissolution. The reaction with nitric acid provides a case of pure proton-promoted dissolution. The proton-promoted dissolution occurs when H\(^+\) attacks on solid surface, destabilizing the metal-oxygen bond. The proton-promoted dissolution is only important at low pH and dissolution rate is relatively small (Table 6.4). When organic-acid ligands exist, the dissolution process should involves more than one reaction mechanisms. The dissolution reaction enhanced by citric and oxalic acid appears mostly ligand-promoted, although proton-promoted dissolution likely occurs at a much lower rate. The ligand assistant dissolution is obviously more effective, given the particular chemical agent. Citric acid is a dicarboxylic acid while oxalic acid has three carboxyl groups. These chemical groups are capable of forming surface chelates, usually as mononuclear, bidentate or multidentate ligands. These surface complexes can weaken the critical metal-oxygen bonds of the solid and result in the detachment of the metal species (Furrer and Stumm, 1986). The dissolution reaction induced by the citrate and oxalate can be conceptually described in the following equations

\[
\equiv\text{MnO}_2(S) + L^{-1} \Leftrightarrow \equiv\text{MnO}_2(S)\cdot L^{-1}
\]  

(6.31)
\[
\begin{align*}
\equiv \text{MnO}_2(\text{S})\cdot \text{L}^{-1} + \text{H}_2\text{O} => \equiv \text{MnO}_2^{-4}(\text{S}) + \text{MnL}^{3+}_{(\text{aq})} & \quad (6.32) \\
\equiv \text{MnO}_2^{-4}(\text{S}) + 4\text{H}^+ => \equiv \text{MnO}_2(\text{S}) & \quad (6.33)
\end{align*}
\]

where \( \text{L} \) represents the ligands, which can be citrate or oxalate. In this three-step model, the second step would be rate-limiting, while the other two can be considered at equilibrium. The aqueous complexes \( \text{MnL}^{3+}_{(\text{aq})} \) will dissociate in the solution. It is possible that \( \text{Mn(IV)} \) in the dissolved species \( \text{MnL}^{3+}_{(\text{aq})} \) is reduced to \( \text{Mn(II)} \) later. The colorless final solution of the dissolution reaction is an indicator of the possible existence of \( \text{Mn(II)} \) or its complexes.

In nature, citrate, oxalate, and other organic acids are byproducts of the biodegradation of organic matter. Therefore, even without the intentional injection of the dissolution enhancing additions, the naturally available organic acids may increase the solubility of \( \text{Mn oxide} \).

EDTA is a strong chelating agent, which will induce ligand-promoted dissolution; but it can also be an electron donor, which can cause reductive dissolution. Zinder et al. (1986) studied \( \text{Fe(III)} \) oxide dissolution under reducing condition. Both proton- and ligand- promoted dissolution occurred with the addition of the reducing agent ascorbic acid. Obviously, the dissolution promoting ligand can also act as a reducing agent, as is the case of EDTA. My results and others supported this conclusion. Perez-Benito et al. (1996) reported manganese dioxide colloids being reduced by EDTA during dissolution experiment. Klewichi and Morgan (1998) also report reductive dissolution of \( \beta\)-MnOOH.
by EDTA. Reported standard potential for the reduction reaction of similar mineral are shown in equations 6.34, 6.35, and 6.36. These reductive standard potentials indicate the reduction of Mn(IV) can be spontaneous even in the presence of oxygen (air).

\[
\text{Mn}^{3+}_{\text{(aq)}} + e^- = \text{Mn}^{2+}_{\text{(aq)}} \quad 1.51 \text{ V (E}^0\text{)} \quad \text{(Arndt, 1975)} \quad (6.34)
\]

\[
\frac{1}{2} \delta\text{-MnO}_2(s) + 2H^+ + e^- = \delta\text{Mn}^{2+} + H_2O \quad 1.29 \text{ V (E}^0\text{)} \quad \text{(Stone and Morgan, 1984b)}
\]

\[
\text{MnO}_2(s) + 4H^+ + 2e^- = \text{Mn}^{2+} + 2H_2O \quad 1.208 - 1.244 \text{ V (E}^0\text{)} \quad \text{(Arndt, 1975)} \quad (6.36)
\]

My analysis of the mineral structure and chemical composition (Chapter 4) discussed the possibility that both Mn(IV) and Mn(III) could exist in the Mn oxide. Insausti et al. (1995) studied the oxidation of L-Phenylalanine by KMnO\textsubscript{4} and pointed out, during the oxidation process, Mn(VII) can be reduced stepwise to Mn(VI), Mn(IV), Mn(III) and Mn(II). While Mn (VI), and Mn(II) are least stable and exist only momentarily as intermediate product, the final product of Mn oxide may have combination of Mn(IV) and Mn(III). One possibility is that the red color that I observed in the EDTA enhanced dissolution is caused by the release of the Mn(III) already inside the solid. My conclusion is that this is probably not the case. There are two reasons. First, the reaction is reducing. As the standard potential in equation 6.34, 6.35 and 6.36 indicates, reaction of Mn(IV) produces Mn (II). Second, the rate of dissolution with oxalic acid is about one fourth of the rate with EDTA (Table 6.4). If the Mn(III) was
solely produced by the release from the solid mineral, the Mn(III) concentration in the solution would be one fourth of that from EDTA reaction for the oxalic acid, which should be observable.

The dissolution of Mn oxide by EDTA can be conceptually described by the following model.

\[ \text{MnO}_2(S) + \text{HEDTA}^{-2} \rightleftharpoons \text{MnO}_2(S) - \text{HEDTA}^{-2} \] (6.37)

\[ \text{MnO}_2(S) - \text{HEDTA}^{-2} \rightleftharpoons \text{Mn(III)O}_2(S) - \text{HEDTA}^{-1} \] (6.38)

\[ \text{Mn(III)O}_2(S) - \text{HEDTA}^{-1} + \text{H}_2\text{O} \rightarrow \text{MnO}_2^{-4} (S) + \text{Mn}^{3+}_{(aq)} + \text{HEDTA}^{-1} \] (6.39)

\[ \text{MnO}_2^{-4} (S) + 4\text{H}^+ \rightarrow \text{MnO}_2(S) \] (6.40)

where HEDTA\(^{-1}\) and HEDTA\(^{-2}\) are general representations of EDTA species in the solution at low pH. The equation 6.38 is the electron transfer step for the reduction of Mn(IV) to Mn(III). Step three is the detachment process and is expected to be slow and rate limiting. The Mn\(^{3+}\) species is short lived and further reduced to Mn(II) in the solution. Because EDTA is a strong chelating agent and a reductant, Mn oxide dissolution proceeds fairly rapidly with both ligand-promoted and reductive dissolution, and possibly proton-promoted dissolution as well.

The pH of the dissolution reaction have been kept stable by adding a minor amount of HNO\(_3\), indicating the pH of the solution is increasing. A separate runs of each
experiment at the same condition, but without the pH control end up with the pH at 5 to 6 during the 25 hours time course, with the exception of experiment with nitric acid. Since the experiments were run under an open system, CO₂ in the air may buffer the system, but probably not to the extent that has been observed. Proton must be consumed during the dissolution reaction.

My 2-D flow tank experiments demonstrated that porous medium heterogeneity is a factor that influences the performance of a MnO₄⁻ flush. Under heterogeneous conditions, the flushing efficiency is lower and the plugging of Mn oxide precipitation is formed in the high-permeability pathways. Heterogeneity adds complexity to the system, and difficulty in chemical flushing. Zones of low permeability are slow to respond to the flushing and to the Mn oxide removal. DNAPL removal efficiency is markedly lower under heterogeneous media, as compared with earlier results for homogeneous media (Li and Schwartz, 2002). In an experiment of 1-D column filled with a homogeneous medium and contaminated by residual TCE, 96.9% of TCE was removed by the end of experiment. In a similar 2-D flow tank experiment with a homogenous medium, which was contaminated with both residual and pooled DNAPL, 34.9 % of TCE was removed from the tank. The experiment was concluded because the precipitates plugged the medium (Li and Schwartz, 2002). By comparison, with the heterogeneous condition, less than 5% of TCE was removed from the tank after the first round of MnO₄⁻ flushing. The precipitates build up quickly in the low permeability lenses, while in the high permeability zones the precipitates travel for a longer distance and spread over a broader area. This process intensifies the heterogeneity in hydraulic conductivity and makes remediation more difficult. The results from this study support the earlier conclusion that
oxidation by MnO$_4^-$ works better in remediation of residual rather than pooled DNAPL (Li and Schwartz, 2000).

The dissolution rate of Mn oxide can be greatly enhanced by adding acids capable of forming organic ligands, like citrate and oxalate. I have demonstrated the enhanced dissolution reaction in both batch and flow tank experiments. The removal of precipitates from the flow tank by the organic acid is efficient with both the organic ligands tested.

The flow tank experiments show that the rate of removal of Mn oxide is fast. The dissolution of the Mn oxide in the flow tank might be accomplished in part by the remobilized of the colloidal particles that have been attached on the sand surfaces. Liang et al. (2000) have provided two hypotheses to explain ferrihydrite colloid mobilization by citrate. One idea is that ligands sorb on colloids that were on the surface of the silica sand and reversed the charge of the colloid. The resulting repulsive force then creates the detachment. The other one is that the attack of ligand breaks the bond between silica sand and the Fe oxide. While both dissolution and colloid detachment might be functioning in the Mn oxide removal flow tank experiment, no definitive conclusions are possible at this time.

5. Conclusions

Enhanced dissolution with organic acids offers a viable solution to the problem of plugging created by the precipitation of Mn oxide. Chemical additives are available that are capable of dissolving the Mn oxide. Of the four chemical additives tested, EDTA provides the highest dissolution rate, and nitric acid provides the lowest. Both oxalate and
citrate promote Mn oxide dissolution at relatively rapid rates. The rates of the enhanced dissolution are capable of removing the Mn oxide precipitates in the tank experiments.

Likely, multiple reaction mechanisms are involved in the dissolution enhancement reaction. EDTA produces both ligand-promoted and reductive dissolution. The dissolution with oxalate and citrate are mostly ligand-promoted, with a less significant proton-promoted dissolution at low pH. Nitric acid, which was used for comparison with the organic acids, can only cause proton-promoted dissolution. The reductive dissolution appears to have the highest efficiency, while ligand-promoted dissolution following closely. Proton-promoted dissolution is slow and probably not sufficient for the treatment of plugging. With minimal toxicity and high dissolution rate, citric acid is the best choice for applications at real sites.
<table>
<thead>
<tr>
<th>Acid</th>
<th>Organic acid concentration (Mm)</th>
<th>Mn oxide concentration (g/L)</th>
<th>Ionic strength (NaNO$_3$) (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citric</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Oxalic</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>EDTA</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>Nitric</td>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6.1. Experimental conditions for the determination of rates of Mn oxide dissolution with various organic acids.

<table>
<thead>
<tr>
<th>Citric acid concentration (Mm)</th>
<th>Mn oxide concentration (g/L)</th>
<th>Ionic strength (NaNO$_3$) (M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>0.05</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
<tr>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6.2. Experimental conditions for the determination of rates of Mn oxide dissolution with citric acid at various concentrations.
Table 6.3. Experimental conditions for the 2-D heterogeneous flow tank experiment.

<table>
<thead>
<tr>
<th>Dimension (mm)</th>
<th>TCE (g) (DNAPL)</th>
<th>[KMnO₄] (mg/L)</th>
<th>Organic acid (g/L)</th>
<th>Q (mL/min)</th>
<th>Heterogeneous media (porosity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>305x50x3 (L)x(H)x(T)</td>
<td>2 (blue dyed)</td>
<td>200</td>
<td>2</td>
<td>0.5</td>
<td>Silica sand (0.385) with fine glass bead lens (0.31)</td>
</tr>
</tbody>
</table>

Table 6.4. Initial rate of dissolution of Mn oxide with various acids at pH = 2.

<table>
<thead>
<tr>
<th>Acids</th>
<th>Citric</th>
<th>EDTA</th>
<th>Oxalic</th>
<th>Nitric</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (mM/m²/h)</td>
<td>0.126</td>
<td>5.176</td>
<td>1.350</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

Table 6.5. Initial rate of dissolution of Mn oxide with citric acid at various concentrations, pH = 2.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>0</th>
<th>0.05 mM</th>
<th>0.1 mM</th>
<th>0.2 mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>R (mM/m²/h)</td>
<td>0.0025</td>
<td>0.0209</td>
<td>0.126</td>
<td>0.254</td>
</tr>
</tbody>
</table>
Figure 6.1. Experiment setup for the 2–D flow tank.
Figure 6.2. Aqueous manganese concentration change with time during manganese oxide dissolution in various acids at pH 2.

Figure 6.3. Aqueous manganese concentration change with time during manganese oxide dissolution in different citric acid concentration at pH 2. At the early time the dissolution rate increases with the concentration of citric acid. Later, all the solid added dissolved and the aqueous manganese concentration reached limitation.
a. Time: 0. Start pumping.

b. Time: 10 minutes

c. Time: 15 minutes

d. Time: 25 minutes

e. Time: 45 minutes

Figure 6.4. Results of the tracer test showing how the heterogeneous character of the porous medium impacted transport. The medium consists of lenses of fine grain glass beads embedded in the coarser grained sand background. (Continued)
Figure 6.4: continued

f. Time: 1 hour and 25 minutes

![Image of sample at 1 hour and 25 minutes]


g. Time: 1 hour and 55 minutes

![Image of sample at 1 hour and 55 minutes]


h. Time: 2 hours and 10 minutes

![Image of sample at 2 hours and 10 minutes]


i. Time: 2 hours and 30 minutes

![Image of sample at 2 hours and 30 minutes]


j. Time: 2 hours and 50 minutes

![Image of sample at 2 hours and 50 minutes]


k. Time: 3 hours and 10 minutes

![Image of sample at 3 hours and 10 minutes]
Figure 6.5. Chemical measurement at the effluent from the 2-D tank experiment.
a. Before adding TCE.

b. Time: 0. One day after initial injection of TCE, right before started pumping.

c. Time: 0.5 hour

d. Time: 1 hour

Figure 6.6. Visualizations illustrating MnO$_4^-$ transport, TCE removal, and formation of a Mn oxide reaction zone. This is the first flushing with MnO$_4^-$. The blue color is TCE added as DNAPL. The pink color indicates MnO$_4^-$ moving through the tank. The brown color is Mn oxide precipitates formed as the reaction product. Notice DNAPL moved from the original position under the pumping stress and Mn oxide precipitation. (Continued)
Figure 6.6 continued

e. Time: 2.25 hours

f. Time: 4.75 hours

g. Time: 8.75 hours
Figure 6.7. These visualizations show the results of the first flushing with organic acid oxalic acid. At the inlet corner (right) white zone indicates oxalic acid entering the tank and dissolved Mn oxide precipitates. Precipitates in the low permeable fine grain lens dissolved slowly and later. (Continued)
Figure 6.7 continued

e. Time: 13.53 hours

f. Time: 16.53 hours

g. Time: 21.78 hours

h. Time: 27.28 hours

(Continued)
Figure 6.7 continued

i. Time: 32.78 hours

j. Time: 40.28 hours

k. Time: 48.28 hours

l. Time: 75.78 hours

(Continued)
Figure 6.7 continued

m. Time: 78.28 hours

n. Time: 80.78 hours

o. Time: 150.78 hours
Figure 6.8. These visualizations show the second flush the DNAPL with MnO$_4^-$, MnO$_4^-$ entering the flow tank, moves rapidly in zones of high permeability, bypassing low permeability lenses. Mn oxide precipitates form around the DNAPL and some precipitates are captured in the low permeability lens. (Continued)
Figure 6.8 continued

e. Time: 218.75 hours

f. Time: 221.75 hours
a. Time: 238.75 hours

b. Time: 245.75 hours

c. Time: 267.75 hours

d. Time: 288.75 hours

Figure 6.9. These visualizations show the second flush with citric acid. Dissolution of the Mn oxide precipitates is most rapid in zone of high permeability. After precipitates in the tank were removed, DNAPL remains in the bottom of the tank in between two low permeability lenses, where flow is somewhat stagnant.
Figure 6.10. These visualizations show the third flush with MnO₄⁻. MnO₄⁻ contacts pooled, and oxidation produces brown colored Mn oxides. Oxidation reactions continue and eventually hinder further oxidation of TCE by MnO₄⁻. (Continued)
Figure 6.10 continued

e. Time: 339.75 hours

f. Time: 342.75 hours

g. Time: 359.25 hours
a. Time: 389.75 hours

b. Time: 431.75 hours

c. Time: 454.75 hours

d. Time: 537.75 hours

Figure 6.11. The third flush with organic acid (oxalic acid) removes Mn oxide precipitates. These visualizations show a moving dissolution front, and Mn oxide precipitates being dissolved from the tank. The DNAPL pool is noticeably smaller at the bottom of the tank. (Continued)
Figure 6.11 continued

e. Time: 596.75 hours

f. Time: 630.25 hours
a. Time: 631.75 hours

b. Time: 633.75 hours

c. Time: 638 hours

d. Time: 640 hours

Figure 6.12. With fourth MnO$_4^-$ flush the DNAPL in the tank is dissolved completely.  

(Continued)
Figure 6.12 continued

e. Time: 642 hours

f. Time: 643 hours
CHAPTER 7

A SEMI-PASSIVE, OXIDANT-BASED REACTIVE BARRIER SYSTEM FOR
THE CONTROL OF DISSOLVED CONTAMINANT PLUMES

1. Introduction

Organic solvents are found at many sites of subsurface contamination. They usually occur in source areas as dense non-aqueous phase liquid (DNAPL), along with a plume down gradient. Often, site remediation must address both these types of contamination. A variety of *in situ* passive and semi-passive approaches are being developed to control the spread of contaminants in ground water. Zero-valent metal barriers have shown particular promise as a technology for controlling the spread of chlorinated solvents (Gillham and O'Hannesin, 1994). The relatively short degradation half lives for many dissolved chloroethylenes makes them amenable to localized geochemical treatment. Although other reactive metals have been tested in these applications, work on alternative destruction schemes, like MnO$_4^-$ has not been extensive.
Oxidation of chlorinated ethylenes by MnO$_4^-$ has been developed primarily as a remediation method for source-zone DNAPL cleanups. The efficiency and effectiveness of this technology for DNAPL removal has been discussed earlier (Li and Schwartz, 2000, and 2002). In general, MnO$_4^-$ can oxidize chlorinated ethylenes to CO$_2$, while MnO$_4^-$ is reduced to Mn oxide, which precipitates as a solid. To date, there has been limited work in applying MnO$_4^-$ for the treatment of dissolved organic contaminants in plumes. The most important issue in this respect is how to deliver the chemical to the target area in an efficient and economical fashion. Two difficulties in MnO$_4^-$ delivery are its high solubility and strong tendency to react with other materials, including the porous medium. The high solubility makes it difficult to use solid KMnO$_4$ in a conventional reactive barrier wall. Its strong reactivity requires that the delivery be on target before it reacts during transport.

To address these problems, a permanganate reactive barrier system (PRBS) was designed (Figure 7.1). The design involves a series of vertical wells to deliver solid KMnO$_4$ to the subsurface, by diffusion out of the well casing. PRBS uses the solubility of MnO$_4^-$ in water and dispersion to mix appropriate quantities into the flow system. The idea is to form a zone of localized reaction through dispersive mixing with dissolved TCE (Figure 7.1). Thus, as the contaminant plume passes the PRBS, in situ oxidation will destroy the contaminant and prevent further spreading. This semi-passive reactive barrier system is similar to concept proposed by Devlin and Barker (1999), in which a permeable injection zone was used to deliver potassium acetate to stimulate bioremediation.
The objective of this study is to use 2-D flow tank experiment to investigate the feasibility of the PRBS. Digital visualization techniques provide the detailed monitoring necessary to establish how the system is likely to perform.

2. Methods

Experiment setup

A thin, small 2-D glass flow tank with Teflon end fittings was constructed for the experiment (Table 7.1). The flow tank was filled with medium silica sand (US Silica, Ottawa, IL). A 1 mm (inside diameter) Teflon tube was installed in the flow tank to represent an inlet well in the PRBS. On one side of the Teflon tubing wall, micro holes 1 mm in diameter were drilled to release \( \text{MnO}_4^- \) into the porous medium. The \( \text{MnO}_4^- \) was released as small volumes of water entered the tube to slowly dissolve the solid \( \text{KMnO}_4 \) particles inside the tube. Two PTFE tubes with inside diameter of 1.32 mm were installed in the two ends of the column to function as recharge and discharge wells. Both tubes had ends open at a depth of 0.5 cm from the bottom of column. Once the flow tank was packed, it was saturated with Milli-Q water. A Spectroflow 400 solvent delivery system (Kratos Analytic, NJ) was used to maintain inflow to the tank, the Ismatec pump removed fluid at the outlet (Figure 7.2). With both pumps running at the same steady rate, flow was horizontal along the length of the tank.

An ambient horizontal flow was established using pumps on the inlet and the outlet to the tank. The experiment began by flowing de-ionized water through the tank for two days, at that time, the inlet pump was switched to deliver dissolved TCE at a
concentration of 25,000 μg/L. This unusually large concentration was used in part to facilitate the visual monitoring of the experiment. At the outlet, effluent samples were collected at regular time intervals. The narrow tank permitted back lighting and visual monitoring of the Mn oxide, which formed an observable brown precipitate.

Visualization

During the PRBS experiment, digital photography was used to monitor the flooding and plugging with Mn oxide. With either the glass beads or the silica sand, the flow tank is semi-transparent with light from the back of the tank. The formation of the reaction product was monitored with time using images from a Nikon 950 digital camera. The visual monitoring was carried out inside a dark room to avoid interference from ambient light. After the experiment was completed, the images were downloaded to a PC, and were processed with Photoshop to correct the slight size differences among the images during the extended experiment. Effluent from the column and flow tank was collected periodically for chemical analysis to monitor TCE degradation. Concentrations of TCE, Cl⁻, and MnO₄⁻ were monitored during the entire experimental period. I utilized the Cl⁻ concentration to estimate the quantity of TCE that was oxidized, and the overall efficiency of the cleanup scheme.

Chemical analysis

TCE concentration was measured with a Fisons Instruments 8060 gas chromatograph equipped with a Ni⁶³ electron capture detector and a DB-5 capillary column (JandW Scientific, Rancho Cordova, CA). Pentane was used for liquid-liquid
extract of TCE. CI ion concentration was measured with a Buchler Digital Chlorodometer. Permanganate concentrations were measured with a Varian Cary 1 UV–visible spectrophotometer at a wavelength 525 nm. The samples of Mn oxide were dissolved and analyzed by a Perkin-Elmer Sciex ELAN 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

3. Results

Figure 7.3 shows how the concentration of MnO$_4^-$ changed with time at the outlet of the flow tank during the test of PRBS. The concentration of MnO$_4^-$ remained at 0.5 g/L, after a decrease at early time, which was caused by solid KMnO$_4$ particles dropping out of the tubing during and following the initial loading. This is a problem related to the scale of the setup, which can be eliminated with a bigger, more realistic design. The results indicate that the system is capable of delivering the permanganate at a relative constant rate to the plume. At the outlet, the TCE concentration was below 20 ìg/L most of the time (Figure 7.4), which is a three to four order of magnitude decrease as compared with the inflow concentration. The measured chloride concentration at the outlet (Figure 7.5) also indicates the breakdown of TCE with time.

Digital images of the experiment are presented in Figure 7.6. After the initial setup, MnO$_4^-$ started to diffuse out of the PRBS (Figure 7.6(a)). Unexpectedly a small chuck of solid MnO$_4^-$ fell from the tubing causing a large load of MnO$_4^-$ introduced into the system (Figure 7.6(b)), and a high MnO$_4^-$ concentration at outlet, which corresponds with the early high concentration from Figure 7.3. Also noticeable in Figure 7.6(b) is
variable-density flow due to the high concentration of MnO$_4^-$.

In effect, MnO$_4^-$ sinks to the bottom of the flow tank because this solution is denser than the ambient water. Clearly, when MnO$_4^-$ concentration is high, and density differences between the KMnO$_4$ solute and background are large, the MnO$_4^-$ concentration distribution in the vertical direction will be affected by density-driven flow. Density effects need to be taken into consideration in any design. However, these flows can be helpful in mixing the treatment chemical with the contaminated water. After the initial high concentration, MnO$_4^-$ addition into the system stabilized. Visual observation (Figure 7.6(c)) shows a fairly uniform distribution of the MnO$_4^-$ across the depth of the flow tank, indicating mixing by dispersion as expected. Once TCE passing through PRBS, it reacts to breakdown TCE and produces MnO$_2$. The digital images (Figure 7.6 (d, e)) show the progressive accumulation of MnO$_2$ on the downstream side of the PRBS. Although the concentration of the TCE used in these experiment is very high, the Mn oxides are precipitated across a broad zone in the porous media. Therefore, during the whole course of the experiment, there is no noticeable change in the permeability as reflected by the pumping pressure monitoring. However, as revealed from an earlier study, Mn oxide precipitates will lower the permeability of the porous media by plugging. This plugging may have reduced the hydraulic conductivity and led to lower MnO$_4^-$ concentrations observed in the latter part of the experiment.
4. Discussion and summary

The proof-of-concept experiment demonstrated how the PRBS could deliver \( \text{MnO}_4^- \) to a dissolved plume at a stable, constant, and controllable rate. The design works well in reducing the concentration of TCE in a small contaminant plume. The experiment also shows that density-driven flow and clogging due to Mn oxide precipitates are factors to be considered in the design. This idea of PRBS could be developed as a long-term reactive barrier for the remediation of chlorinated solvents in plumes. Once installed, the long-term management cost would probably be low compared with other alternatives, and maintenance should be limited to sporadic recharging with permanganate.

Mn oxide precipitates may cause plugging of the pore space and reduce the permeability in the downstream of the PRBS. However, my earlier studies indicated that the Mn oxide precipitates formed during the permanganate reaction with chlorinated ethylene can be quickly removed through ligand-enhanced dissolution using chemical additives. By installing of wells to deliver the chemical additives to the zones of greatest plugging would likely solve problems related to Mn oxide precipitates and related permeability changes.

Based on the preliminary results, there are several problems that need to be addressed by future research. The 2-D flow tank experiment did not provide information about the horizontal spreading of \( \text{MnO}_4^- \) solutions. Three-dimensional experiments in flow tanks need to be conducted to provide this information. It is also necessary to find out the optimized combination of density flow effect and dispersion that are required to create the appropriate mixing of the \( \text{MnO}_4^- \) plume to match the flux of contaminants.
through the treatment zone. Another problem for future work is to determine the minimum sufficient concentration of MnO$_4^-$ that must be released into the system to destroy the contaminant, based on the stoichiometric relationship of the reaction and the sediment consumption capacity.

The test of a permanganate reactive barrier system in this study has shown positive results. With its potential benefit of cost and time efficiency, PRBS can be developed as a field technology for the remediation of the contaminant plume.
<table>
<thead>
<tr>
<th>Experiment</th>
<th>Dimension (mm)</th>
<th>Medium</th>
<th>Q (mL/min)</th>
<th>KMnO₄</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRBS</td>
<td>305(L)x50(H)x3 (T)</td>
<td>Silica sand</td>
<td>0.05</td>
<td>Solid</td>
<td>0.385</td>
</tr>
</tbody>
</table>

Table 7.1. Experimental design for the 1-D column and 2-D flow tank experiments
Figure 7.1. Design of the permanganate reactive barrier system (PRBS) (map view)
Figure 7.2. Experiment setup for the testing of PRBS in a 2-D flow tank.
Figure 7.3. KMnO$_4$ concentration at the outlet, downstream of the PRBS

Figure 7.4. TCE concentration at both inlet and outlet of the flow tank containing the PRBS
Figure 7.5. Oxidized TCE concentration at outlet, downstream of the PRBS.
(a) Time: 1 hour after the start of pumping Milli-Q water. MnO$_4^-$ is diffusing from the tube.

(b) Time: 4 hours after the start of pumping Milli-Q water. The dissolved MnO$_4^-$ created downward density-driven flow that helps to facilitate mixing.

(c) Time: 3 days after the start of pumping TCE solution. Considerable MnO$_2$(s) is noticeable downstream of the PRBS.

(d) Time: two weeks after the start of pumping TCE solution.

(e) Time: four weeks after the start of pumping TCE solution. MnO$_2$(s) continue to accumulate.

Figure 7.6. Experiment involving the proof-of-concept of the PRBS. Early images capture the diffusion and the sinking of the KMnO$_4$ solution in (e.g., b). MnO$_2$ precipitates downstream and accumulates through the experiment. (e.g., d, e).
CHAPTER 8

CONCLUSIONS

Through a series of laboratory experiments, I examined problems that could
potential impact the success of ISCO schemes involving MnO$_4^-$ such as MnO$_4^-$/porous
media interactions, and reduction in oxidation flushing efficiency by reaction products. In
an effort to solve these problems, I looked into issues of mineral structure, chemical
composition and chemical properties of the Mn oxide formed during the oxidation,
inhibition of colloidal Mn oxide formation, and dissolution of the solid Mn oxide.
Finally, I proposed a reactive barrier system based on MnO$_4^-$ (PRBS) that is developed
and tested for the remediation of contaminant plume. The results from these experiments
indicate that ISCO is a promising remediation technology. This study provides a basic
scientific foundation for ISCO to be applied in the remediation of contaminated sites.
This study should help to solve problems that may be encountered during the remedial
actions. The following are the main findings of this study.
Interactions between MnO$_4^-$ and sediments

The consumption of MnO$_4^-$ is significant for most sediments tested. This process will lower the delivery efficiency of MnO$_4^-$ in remedial schemes. However, the ability for most natural sediments to consume MnO$_4^-$ reduces concern that MnO$_4^-$ itself would emerge as a major problem of contaminant at most of the site.

MnO$_4^-$ likely oxidizes solid metal oxides and mobilizes metals during the treatment. Metals that increased in concentrations include Cr, Se, and Hg, which are of environmental and health concerns. Clearly, MnO$_4^-$ is a powerful oxidant that is capable of oxidizing solids and organic contaminants indiscriminately. The heavy metal loading is of regulatory concern, although it is not clear how mobile these constituents might be. Because the MnO$_4^-$ change in redox condition is limited to the zone where MnO$_4^-$ contacts the sediments, the mobilization of the metal species should be a localized, short-term problem.

Influence of flushing efficiency by the oxidation products

The column and flow tank experiments continue to indicate that the oxidation of chlorinated ethylenes by MnO$_4^-$ is a useful remediation technology. The kinetics of the oxidation reaction are generally fast and capable of reducing the mass of DNAPL, especially early in the treatment. However, MnO$_2$ precipitates and CO$_2$ gas bubbles present significant delivery problems. The rapid buildup of these reaction products in zones with high DNAPL saturation leads to pore plugging, which lowers the permeability, and causes flow bypassing. The flushing efficiency will be reduced without
controlling this problem. It is anticipated that in actual field settings, the issue of flushing efficiency needs to be considered in the design.

Mineralogy of Mn oxide formed in the oxidation

The solid reaction product from the oxidation of chlorinated ethylene by permanganate is identified as semi-amorphous potassium-rich birnessite, which has a layered mineral structure with an interlayer spacing of 7.3 Å. Its chemical formula was determined as $K_{0.854}Mn_{1.786}O_4 \cdot 1.55H_2O$. It has a relatively small specific surface area at 23.55 $m^2/g$.

Once formed in the subsurface, birnessite could participate in the various reactions with existing organic and inorganic matter, making it relatively unstable in natural settings. These reactions may be slow as compared with the $MnO_4^{-}$ oxidation reaction, but in the long term, or over geological time, it may add dissolved Mn into the ground water at levels above regulatory standards.

Inhibition of colloid Mn oxide formation with phosphate

The study indicates that phosphate ion can slowdown the formation of colloidal Mn oxide from the permanganate oxidation. Phosphate ion can delay of the formation of Mn oxide colloids by forming a soluble Mn(IV)-phosphate species. The rate of the colloid formation decreases with the concentration of phosphate ion in the range of our experiment. However, the phosphate delay effect is limited by rapid reaction rate of the $MnO_4^{-}$ oxidation, increased ionic strength, and low pzc of the Mn oxide. It is not likely
phosphate can be applied to the ISCO schemes at real sites to control the problem of precipitation.

Enhanced dissolution of the Mn oxide

Enhanced dissolution with organic acids offers a viable solution to the problem of plugging created by the precipitation of Mn oxide. Chemical additives are available that are capable of dissolving the Mn oxide. Of the four chemical additives tested, EDTA provides the highest dissolution rate, and nitric acid provides the lowest. Both oxalate and citrate promote Mn oxide dissolution at relatively rapid rates. The rates of the enhanced dissolution are capable of removing the Mn oxide precipitates in the tank experiments.

Likely, multiple reaction mechanisms are involved in the dissolution enhancement reaction. EDTA produces both ligand-promoted and reductive dissolution. The dissolution with oxalate and citrate are mostly ligand-promoted, with a less significant proton-promoted dissolution at low pH. Nitric acid, which was used for comparison with the organic acids, can only cause proton-promoted dissolution. The reductive dissolution appears to have the highest efficiency, while ligand-promoted dissolution following closely. Proton-promoted dissolution is slow and probably not sufficient for the treatment of plugging. With minimal toxicity and high dissolution rate, citric acid is the best choice for applications at real sites.
Development of permanganate reactive barrier system

The test of a permanganate reactive barrier system in this study has shown positive results. With its potential benefit of cost and time efficiency, PRBS can be developed as a field technology for the remediation of the contaminant plume.

Mn oxide precipitates may cause plugging of the pore space and reduce the permeability in the downstream of the PRBS. The Mn oxide precipitates can be quickly removed through ligand-enhanced dissolution using chemical additives. In future research, three-dimensional experiments in flow tanks need to be conducted to provide information on horizontal spreading of MnO$_4^-$ solutions. It is also necessary to find out the optimized combination of density flow effect and dispersion that are required to create the appropriate mixing of the MnO$_4^-$ plume to match the flux of contaminants through the treatment zone. Another problem for future work is to determine the minimum sufficient concentration of MnO$_4^-$ that must be released into the system to destroy the contaminant, based on the stoichiometric relationship of the reaction and the sediment consumption capacity.
REFERENCES


