

**COMBINATION OF SURFACTANT SOLUBILIZATION WITH  
PERMANGANATE OXIDATION OF GROUDNWATER  
REMEDATION**

**Zhaohui Li**

2005

Combination of Surfactant Solubilization with Permanganate Oxidation for  
Groundwater Remediation

Project Completion Report

By

Zhaohui Li, Associate Professor

Department of Geosciences

University of Wisconsin – Parkside

Kenosha, WI 53141

September 30, 2005

*This project was supported, in part, by General Purpose Revenue funds of the State of Wisconsin to the University of Wisconsin System for the performance of research on groundwater quality and quantity. Selection of projects was conducted on a competitive basis through a joint solicitation from the University and the Wisconsin Departments of Natural Resources; Agriculture, Trade and Consumer Protection; Commerce; and advice of the Wisconsin Groundwater Research Advisory Council and with the concurrence of the Wisconsin Groundwater Coordinating Council.*

## Table of Contents

Project Summary	.....	4
Introduction	.....	6
Procedures and Methods	.....	6
Results and Discussion	.....	7
Conclusions and Recommendations	.....	13
References	.....	15
Appendix	.....	16

## List of Figures and Tables

Table 1 .....	9
Table 2 .....	10
Table 3 .....	11
Table 4 .....	14
Fig. 1 .....	8
Fig. 2 .....	9
Fig. 3 .....	10
Fig. 4 .....	11
Fig. 5 .....	12
Fig. 6 .....	12
Fig. 7 .....	13
Fig. 8 .....	14
Fig. 9 .....	14
Fig. 10 .....	15

## Project Summary

- Title:** Combination of Surfactant Solubilization with Permanganate Oxidation for Groundwater Remediation
- Project ID:** WR03R009
- Investigators:** Dr. Zhaohui Li, Associate Professor of Geology, Department of Geosciences, University of Wisconsin – Parkside
- Period of Contract:** 07/01/2003 – 06/30/2005
- Background/Need:** At some heavy industrial sites and DOE nuclear weapon manufacture and test sites, free phase chlorinated solvents in soils and aquifers impose potential threat to groundwater. Pump-and-treat, a common practice to remove subsurface contaminants proved inefficient to remove these solvents, due to their lower water solubility and higher density. Although the contaminant extraction efficiency increased dramatically in the presence of surfactant, the extracted water will need further onsite decontamination. Oxidation of chlorinated solvent by permanganate is an emerging technology. However, the reaction occurs only in dissolved phase. Thus, a test for combination of surfactant solubilization with permanganate oxidation was proposed.
- Objectives:** The central goal of this research is to test the feasibility of using surfactant to significantly increase the solubility of chlorinated solvents while using permanganate to degrade solubilized chlorinated solvents. The objectives are to investigate the effects of types of surfactants, concentration of surfactants and of permanganate on oxidation of different types of chlorinated solvents.
- Methods:** The tests were conducted in batch, column as well as 3-dimensional tank scales. Batch tests were focused on effects of types of surfactants, concentrations of surfactants and permanganate on reduction kinetics of chlorinated solvents. The best surfactant with an optimal concentration was tested in one-dimensional column studies to investigate the efficiency of present surfactant on TCE reduction by permanganate at different volumes of free phase TCE. Finally, a 3-dimensional tank test was performed to verify the column test results. Aqueous concentrations of chlorinated contaminants, permanganate, and product chloride were monitored with time to determine the reaction rate and rate constants as well as the TCE removal efficiency.
- Results and Discussion:** Batch results showed that chloride production, an indication of TCE degradation, followed a pseudo-first-order reaction kinetics with respect to  $\text{KMnO}_4$  in the presence of free phase TCE. A higher chloride production rate was seen when anionic surfactant, particularly sodium dodecyl sulfate (SDS), was present. When the surfactant concentration was less than its critical micelle concentration (CMC), the TCE reduction rate constant  $k_{obs}$  increased by a factor of three while the TCE half-life  $t_{1/2}$  decreased by three folds. With the surfactant concentration greater than the CMC, further increase in  $k_{obs}$  and decrease in  $t_{1/2}$  was seen. The reaction rates also increased when ninate 411 and Calfax, both anionic surfactants, were present in the system at concentrations of 0.1, 0.3 and 1.0%.

Contrast to the much greater enhancement for TCE oxidation, no significant increase in PCE oxidation by  $\text{KMnO}_4$  in the presence of SDS was found.

Column experiments on fine beach sand lasted for only 6 hours. A higher effluent chloride (about 20%) and TCE (about 100%) concentration was found from the columns eluted with 1% SDS, indicating enhanced solubilization and oxidation of TCE. However, hydraulic conductivity of the sand decreased significantly caused by precipitates of  $\text{MnO}_2$ , making it essentially impermeable after 6 hours. Column experiments on well sorted coarse Ottawa sand showed increase in effluent TCE concentration during earlier stage of flushing. TCE concentration decreased much faster in the presence of SDS. For example, after 1 mL of TCE was placed in the columns, the effluent TCE concentration for the columns fed with SDS and permanganate was below 5 mg/L after 1740 to 1870 minutes. While for columns fed with permanganate only, it took 2200 and 4400 minutes before the effluent concentration reached 5 mg/L or below. For the columns fed with SDS and permanganate, The highest effluent TCE concentration was about 1700 mg/L when SDS was present contrast to less than 300 mg/L when SDS was absent, indicating enhanced solubilization. In addition,  $\text{MnO}_4$  breakthrough occurred after 21-25 hour injection when SDS was present. Without SDS,  $\text{MnO}_4$  breakthrough occurred 45-70 hours later. The earlier  $\text{MnO}_4$  breakthrough indicates exhaustion of dissolved TCE during the flushing stage. Chloride analysis revealed a slightly high chloride concentration in the earlier stage of the column experiment and chloride concentration decreased quickly once permanganate is seen in the effluent. Mass balance of TCE eluted plus chloride generated showed that only 25-50 % of the input TCE was either eluted or degraded, the rest may be entrapped within the sand, possibly due to the formation of  $\text{MnO}_2$  zone, or being transformed into other intermediates which were not monitored.

The 3-dimensional tank test further confirmed the results from column study, i.e. with the presence of surfactant SDS a higher amount of TCE was removed within given time. Furthermore, visualization showed that a  $\text{MnO}_2$  precipitation front was formed much quickly when 1% SDS was present.

**Conclusions/  
Implications/  
Recommendations:**

The research shows that anionic surfactants, such as SDS, are able to increase the chloride production in batch test. In column tests, the removal of TCE in the presence of SDS is faster, particularly when the volume of free phase TCE was large. Although no clogging was found when coarse Ottawa sand was used in the column study, the decrease in hydraulic conductivity when fine beach sand was used imposes a limitation to the method.

**Related  
Publications:**

Li, Z. (2004). Surfactant-Enhanced Oxidation of Trichloroethylene by Permanganate – Proof of Concept, *Chemosphere* **54**, 419-423.

**Key Words:**

Permanganate, Perchloroethylene, Trichloroethylene, Surfactant.

**Funding:**

Funding was provided by the State of Wisconsin Groundwater Research Program through the University of Wisconsin Water Resources Institute.

## Introduction

Remediation of dense non-aqueous phase liquids (DNAPLs) presents a great challenge to modern remediation science and technology. A common practice for removal of DNAPL contamination from groundwater is by “pump-and-treat”, i.e., clean water is injected into the ground from the up-gradient of the contaminant plume and withdrawn from the down-gradient of the plume. As the water moves across the plume, the free phase contaminants dissolve in water and are pumped out with water. Then, the contaminated water is subject to onsite decontamination before the water can be reused. The major problem associated with “pump-and-treat” is the low aqueous solubility of the contaminants, thus, more “pump-and-treat” cycles are needed before the free phase DNAPLs can be completely removed. In addition, tailing of contaminant concentration persists for a longer time. To overcome the low solubility of DNAPLs in water, surfactants have been used to increase the solubility of the contaminants and decrease the interfacial tension between water and the organic free phase. The addition of surfactants to the “pump-and-treat” system greatly enhanced the remediation performance, resulted in significantly shortened operation time and cost. However, due to the addition of surfactants, the water withdrawn from the “pump-and-treat” operation contains high concentrations of contaminants, thus, onsite treatment of the contaminated water becomes inevitable, which would dramatically increase the treatment cost.

*In situ* chemical oxidation with permanganate is a promising alternative for the remediation of aquifers contaminated with DNAPLs, such as perchloroethylene (PCE) and trichloroethylene (TCE) (Schnarr et al., 1998; Hood et al., 2000). In-situ oxidation is accomplished when an aqueous solution of  $\text{KMnO}_4$  is injected or flushed through the source area. The basic stoichiometry for the oxidation of PCE is (Yan and Schwartz, 2000):



where  $\gamma$  and  $\eta$  are stoichiometric coefficients and CA are various carboxylic acids. Oxidation of chlorinated compounds to CA's occurs at pH's above 3. Carbon dioxide is formed instead at lower pHs (Huang et al., 2000). It has been shown that the observed TCE degradation rate in the presence of 1mM permanganate was extremely fast with a half-life of 17.8 min (Schwartz and Zhang, 2000). The degradation of PCE and TCE by permanganate occurred in dissolved phase and followed first order reaction with respect to their initial concentration (Yan and Schwartz, 2000). In addition, the degradation products and intermediates are environmental innocuous with  $\text{CO}_2$  as the ultimate degradation products (Yan and Schwartz, 2000). Thus, it is logical to combine the superior solubilization and mobilization power of surfactants with fast contaminant degradation rate of permanganate during “pump-and-treat” operation to synchronize contaminant solubilization and degradation in a single step, i.e. to achieve simultaneous “pump-while-treat” for DNAPL remediation, instead of common “pump-then-treat” as most “pump-and-treat” systems do.

## Procedures and Methods

### Chemicals

The PCE, TCE and potassium permanganate used were from Fisher Scientific (Pittsburgh, PA). The surfactants used were anionic sodium dodecyl sulfate (SDS) from Sigma (St. Louis, MO),  $\text{C}_{10}$  linear sodium diphenyl oxide disulfonate (Calfax 10L-45) from Pilot Chemical Company (Santa Fe Spring, CA), isopropyl amine branched dodecylbenzene sulfonate (Ninate 411) from Stapan (Northfield, IL), and nonionic octylphenol ethylene oxide condensate (Triton X-100) from LabChem Inc. (Pittsburgh, PA) and nonyl phenol ethoxylate (Witconol NP-120) from Akzo Nobel (Chicago, IL). SDS has a formula weight of 288.4 and critical micelle concentration (CMC) of 8.2 mM (Rosen, 1989). Others were industrial grade having varying amount of surfactants of different chain-length. All the surfactants were used as is without further purification.

### *Batch PCE and TCE degradation kinetics*

All experiments were performed in three to five replicates in a continuous stir batch reactor (CSBR), composed of a 200 mL beaker, a magnetic stir, a chloride electrode and a pH electrode inserted into the reaction solution. To each CSBR, 98, 99, or 99.5 mL of water or surfactant solution was mixed with 2 mL of ionic strength adjustor (ISA) made of 5 M of NaNO<sub>3</sub> (from Thermo Orion, MA), resulting in an ionic strength of 0.1 M. The addition of ISA is for chloride electrode measurement, which has a detection limit of 0.05 mM. As Huang et al. (2002) pointed out the rate constants were independent of the ionic strength when it was < 0.2 M. After the mV reading on the electrode became stabilized, 1 mL of free phase PCE or TCE was added to the system. As the mV reading stabilized again, 2.0, 1.0, or 0.5 mL of 150 mM KMnO<sub>4</sub> solution (corresponding to KMnO<sub>4</sub> concentration of 3, 1.5, and 0.75 mM) was added to the system and the changes in mV readings were recorded at different time intervals and then converted to Cl<sup>-</sup> concentrations. The effects of surfactant concentrations on TCE degradation rate were evaluated at the initial SDS concentrations of 3.5, 10.5 and 35 mM, corresponding to 0.42, 1.3, and 4.2 times the CMC and at the initial Calfax concentrations of 0.1, 0.2 and 1.0%.

Control samples were run under the same condition except that no KMnO<sub>4</sub> was added. It was found that in the present of SDS and TCE, no chloride was formed without addition of KMnO<sub>4</sub>. Also, no chloride was detected when only SDS and KMnO<sub>4</sub> were present in the system. A stable purple color was achieved over time when an anionic or a nonionic surfactant solution was in contact with KMnO<sub>4</sub> as revealed by monitoring the change in absorbance at 525 nm with time using a UV-Vis spectrophotometer.

The solution pH was monitored but not controlled. After the addition of KMnO<sub>4</sub>, the pH dropped to 3, and then slowly reduced to 2 as the reaction proceeded. At this low pH, the oxidation pathway goes directly to the formation of CO<sub>2</sub> and Cl<sup>-</sup> (Huang et al., 2002).

### *Column study*

Glass columns (2" in diameter by 12" in length) from Acer Glass (Vineland, NJ) were packed with fine beach sand or coarse Ottawa sand. Fixed volumes of TCE (0.1, 0.3, 1.0, and 3.0 mL) was placed 7 cm above the influent port using a 15 cm long stainless steel needle. The permanganate or surfactant/permanganate solution was fed into the column using a four-head peristaltic pump at a constant flow rate of 20 mL/hour. The effluent concentrations of TCE and chloride were measured with time until the TCE concentration was below 5 mg/L. The TCE mass balance was determined by the input and output TCE and chloride concentrations.

### *Three-dimensional tank study*

The dimension of the tank was 27 cm wide, 8 cm deep, and 20 cm high, Two 3 kg portions of Ottawa sand was packed into each tank with 100 g of STx-1 smectite packed as impermeable layer on top of each portion. Two injection wells and two extraction wells were emplaced in the upper sand portion at a depth of 6 cm below the surface. Due to the presence of smectite layers on the upper and lower boundary, the upper portion behaves like a confined aquifer. After the tank was saturated, 1 mL of TCE was placed 5 cm below the surface in the center of the tank, and then permanganate flushing initiated.

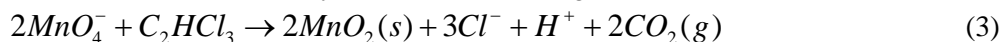
### *Chemical analysis*

PCE and TCE concentrations were determined using an Alltech HPLC equipped with a 4.6- by 150-mm Regis ODS column and a UV-Vis detector at 195 nm. The mobile phase was 70% acetonitrile/30% water. At a flow rate of 2.0 mL/min, the retention times for PCE and TCE were 3.1 and 2.1 min, respectively. The detection limit was 0.05 mg/L for both chemicals. All calibration curves using four to six standards had linear regression coefficients greater than 0.99. Chloride analysis for column experiment was performed using an HPLC system with a Shimadzu 9-A autoinjector, a Hamilton PRP-X100 column, and an Alltech electric conductivity detector. The mobile phase was 2 mM potassium phthalate with pH 6 adjusted by NaOH. At a flow rate of 2 mL/min, the retention time was 2.6 min.



## Results and Discussion

The reaction between TCE and permanganate is a complex reaction involving several steps (Yan and Schwartz, 2000) and the overall reaction may be written as (Huang et al., 1999; Hood et al., 2000):



In pH 3–10 range the  $\text{Cl}^-$  production rate was nearly equal to the PCE degradation rate (Huang et al., 2002). Also, the amount of  $\text{Cl}^-$  produced could be quantitatively correlated to the consumption of  $\text{MnO}_4^-$  (Schnarr et al., 1998, Seol and Schwartz, 2001). TCE degradation was pseudo-first-ordered with respect to  $[\text{TCE}]$  and  $[\text{MnO}_4^-]$ , and an overall second order reaction (Yan and Schwartz, 1999, 2000; Huang et al., 1999; Hood et al., 2000). If the TCE dissolution rate is faster than its combined degradation and volatilization rates, the TCE solution concentration could be assumed constant. Since TCE has an aqueous solubility of 1100 mg/L or 8.4 mM, in the presence of free phase, TCE was in excess and  $\text{MnO}_4^-$  was the limiting reagent. The overall second order reaction can be approximated as a pseudo-first-order reaction

$$\frac{1}{3} \frac{d[\text{Cl}^-]}{dt} = -\frac{1}{2} \frac{d[\text{MnO}_4^-]}{dt} = k_{obs} [\text{MnO}_4^-] \quad (4)$$

where the square brackets donate concentrations and  $k_{obs}$  is the observed pseudo-first-order rate constant.

The amounts of chloride generated due to the reaction of TCE with 1.5 mM  $\text{KMnO}_4$  in the absence and presence of different types of surfactants can be seen in Figure 1a. The rate of chloride production is faster in the presence of SDS compared to the case when other surfactants were present. The amounts of chloride produced, in the presence of different initial permanganate concentrations but absence of surfactants, are plotted in Figure 1b. All data for the three sets of experiments followed a slightly curvy straight-line relationship between chloride produced and reaction time. A similar relationship was found when TCE was in excess and initial  $\text{KMnO}_4$  was 2.5 mM (Seol and Schwartz, 2001). Also noticed from Figure 1b is that the chloride production rate increased as initial permanganate concentrations increased.

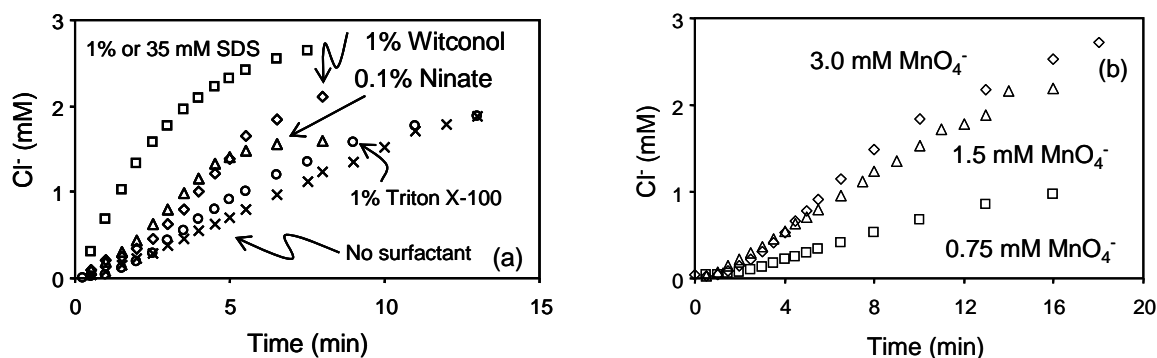


Figure 1. Chloride production as affected by types of surfactants (a) and initial permanganate concentrations when surfactant was absent in the system (b). Each symbol is an average of triplicates.

Due to the presence of free phase TCE, if the chloride production follows a first order reaction with respect to  $\text{MnO}_4^-$  as indicated by Eq. (4), a plot of  $\ln([\text{MnO}_4^-]_t/[\text{MnO}_4^-]_0)$  against time ( $t$ ) will follow a straight-line relation with the slope indicating the  $k_{obs}$ . The  $[\text{MnO}_4^-]_t$  at each time was calculated based on the stoichiometry of the chemical reaction (Eq. (3)). The  $k_{obs}$  values together with their  $r^2$  values are listed in Table 1 when SDS was used as the solubilizing surfactant. It can be seen from Table 1 that, as the initial permanganate concentrations increased from 0.75 mM, to 1.5 mM, and 3.0 mM, the  $k_{obs}$  values increased from 0.08 to 0.13, and then to 0.19  $\text{min}^{-1}$ , reflecting that a higher initial  $\text{MnO}_4^-$  concentration results in a higher TCE consumption and chloride production. The half-life ( $t_{1/2}$ ) of  $\text{MnO}_4^-$  varied from 4

to 9 min when no surfactants were present. The  $k_{obs}$  and  $t_{1/2}$  were  $0.04 \text{ min}^{-1}$  and 18 min when TCE concentration was 2-10 mg/L and  $\text{MnO}_4^-$  concentration was in 10-fold excess (Yan and Schwartz, 1999), or  $0.08 \text{ min}^{-1}$  and 8 min when TCE and  $\text{MnO}_4^-$  concentrations were 25 mg/L and 1.58 mM, respectively (Huang et al., 1999). Contrast to these published results, the  $k_{obs}$  values from this study are larger and  $t_{1/2}$  values are smaller due to a significantly higher initial TCE concentration (in the presence of free phase TCE). The  $k_{obs}$  and  $t_{1/2}$  values are similar to the results of  $0.12\text{--}0.16 \text{ min}^{-1}$  when free phase TCE was present (Seol and Schwartz, 2001).

Table 1. Pseudo-first-order rate constants  $k_{obs}$  and half-life  $t_{1/2}$  for  $\text{MnO}_4^-$  consumption in the presence of SDS.

Initial $\text{MnO}_4^-$ Conc. (mM)	Initial SDS Conc. (mM)	$k$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min)	$r^2$
0.75	0	0.08 (0.07-0.09)	9 (8-10)	0.99
1.5	0	0.13 (0.12-0.15)	5 (4-6)	0.99
3	0	0.19 (0.15-0.22)	4 (3-5)	0.98
0.75	3.5	0.46 (0.44-0.49)	1.5 (1.4-1.6)	0.99
1.5	3.5	0.43 (0.39-0.48)	1.6 (1.4-1.8)	0.98
3	3.5	0.42 (0.40-0.43)	1.7 (1.6-1.8)	0.99
1.5	10.5	0.55 (0.50-0.61)	1.3 (1.1-1.4)	0.99
0.75	35	0.58 (0.55-0.62)	1.2 (1.1-1.3)	0.99
1.5	35	0.58 (0.54-0.62)	1.2 (1.1-1.3)	0.99
3	35	0.56(0.54-0.58)	1.3 (1.2-1.4)	0.99

Numbers in parentheses indicate 95% confidence interval.

The amounts of chloride produced were also proportional to the initial  $\text{MnO}_4^-$  concentration when SDS was present in the system (Figure 2a and 2b). At any given reaction time, a higher amount of chloride was produced with a higher initial  $\text{MnO}_4^-$  concentration. The  $k_{obs}$  values fall into a narrow range ( $0.44\pm 0.02 \text{ min}^{-1}$ ) when the input SDS concentration was less than its CMC, regardless of the initial  $\text{MnO}_4^-$  concentrations. When initial SDS concentration was greater than the CMC, a similar result was obtained, i.e. a higher initial  $\text{MnO}_4^-$  concentration resulted in a larger amount of chloride produced in a given time period (Figure 2b). The rate constant of  $\text{MnO}_4^-$  consumption was  $0.57\pm 0.01 \text{ min}^{-1}$  (Table 1), a 30% increase ( $t$ -test indicates that the difference is significant) compared to the case when the initial SDS concentration was less than the CMC (Figure 2a vs. 2b). The  $t_{1/2}$  was reduced to 1.5-1.7 min when the SDS concentration was less than its CMC compared to the case when SDS was absent and was further reduced to 1.2-1.3 min when the SDS concentration was greater than its CMC (Table 1).

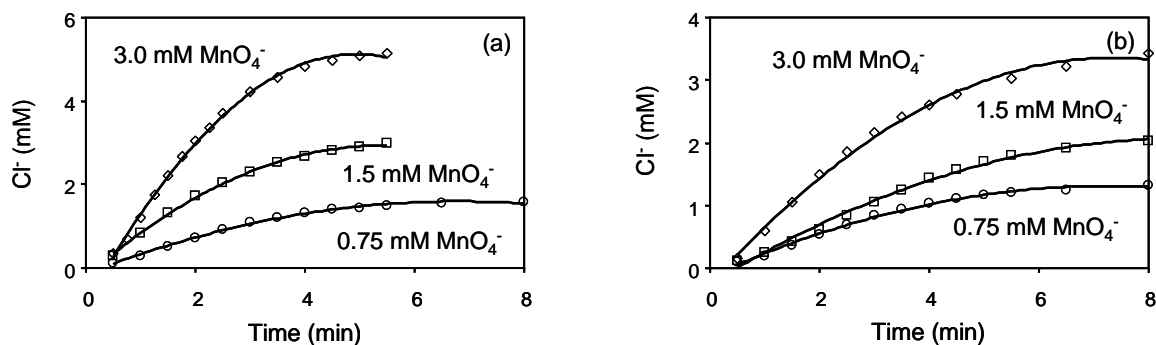


Figure 2. Chloride production with time as a function of initial permanganate concentrations, when SDS concentrations were 3.5 mM (a) and 35 mM (b). Each symbol is an average of triplicates. Lines are second polynomial fit to the observed data.

The amounts of chloride generated in the presence of a fixed initial  $\text{MnO}_4^-$  concentration (1.5 mM) and varying SDS concentrations are plotted in Figure 3a. It can be seen that as surfactant concentration increased, the experimental data became more and more nonlinear and the rate constant increased correspondingly (Table 1). The results from Figure 2 indicated that in the presence of a surfactant the initial  $\text{MnO}_4^-$  concentration had minimal influence on  $\text{MnO}_4^-$  consumption rate constant. A greater increase in chloride production rate was achieved due to the fact that TCE is in excess. On the other hand, as the initial SDS concentrations increased, both the chloride production rate and the  $\text{MnO}_4^-$  consumption rate constant increased. Similar to the results using SDS, the  $k_{obs}$  systematically increased and  $t_{1/2}$  values decreased as the input Niniate concentration increased from 0.0% to 1.0% (Figure 3b). The  $k_{obs}$  increase by a factor of 4 and  $t_{1/2}$  decreased by a factor of 8 in the presence of 1% Niniate (Table 2). In the presence of a phase transfer catalyst, the  $k_{obs}$  value was found to be 0.12–0.16  $\text{min}^{-1}$  (Seol et al., 2001). Compared to the phase transfer catalyst, both SDS and Niniate increased the  $k_{obs}$  significantly, which could be interpreted as an increase in initial TCE concentration due to enhanced solubilization by the surfactants and/or a catalytic effect in the presence of anionic surfactants.

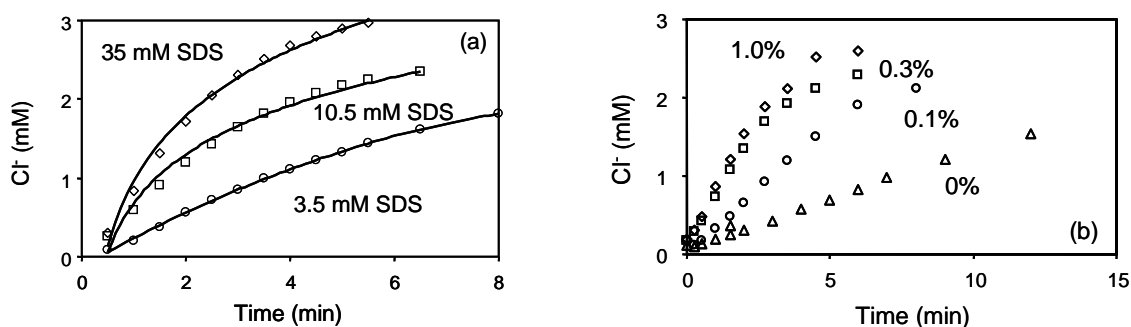


Figure 3. Chloride production due to TCE degradation as a function of initial SDS (a) and niniate (b) concentrations when permanganate concentration was 1.5 mM. Each symbol is an average of triplicates. Lines are second polynomial fit to the observed data for TCE degradation.

Table 2. Pseudo-first-order rate constants  $k_{obs}$  and half-life  $t_{1/2}$  for  $\text{MnO}_4^-$  consumption in the presence of Niniate 411.

Initial $\text{MnO}_4^-$ Conc. (mM)	Initial Niniate Conc. (%)	$k$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min)	$r^2$
1.5	0	0.08 (0.07-0.09)	9 (8-10)	0.99
1.5	0.1	0.19 (0.17-0.21)	3.6 (3.3-4.1)	0.98
1.5	0.3	0.30 (0.23-0.37)	2.3 (1.9-3.0)	0.92
1.5	1.0	0.32 (0.26-0.38)	1.2 (1.8-2.7)	0.96

Numbers in parentheses indicate 95% confidence interval.

In the presence of fixed amount of permanganate, the production of chloride increased as the input Calfax concentration increased (Figure 4). Moreover, a higher permanganate concentration resulted in a higher amount of chloride production (Figure 4a and b). Similar to the results using SDS and Niniate, the  $k_{obs}$  systematically increased and  $t_{1/2}$  values decreased as the input Calfax concentration increased or as the permanganate concentration increased (Table 3). These results show that anionic surfactant had a better enhancement in TCE oxidation.

Column experiments were conducted in fine beach sand and in coarse Ottawa sand. When the fine beach sand was used, the porosity was 0.21-0.24 and the pore volume (PV) was 62-68 mL. At a flow rate of 20 mL/hour a significantly higher TCE concentration was seen after 3 hours, corresponding to 1 PV. A higher effluent chloride (about 20%) and TCE (about 100%) concentration was found from the

columns eluted with 1% SDS, indicating enhanced solubilization and oxidation of TCE. However, hydraulic conductivity of the sand decreased significantly caused by precipitates of  $\text{MnO}_2$ . The system quickly rendered its hydraulic conductivity and was completely clogged after 6 hours of flushing, corresponding to 2 PVs. Reduction of hydraulic conductivity as high as 80% was seen even for oxidizing a small quantity of TCE (Li and Schwartz, 2004).

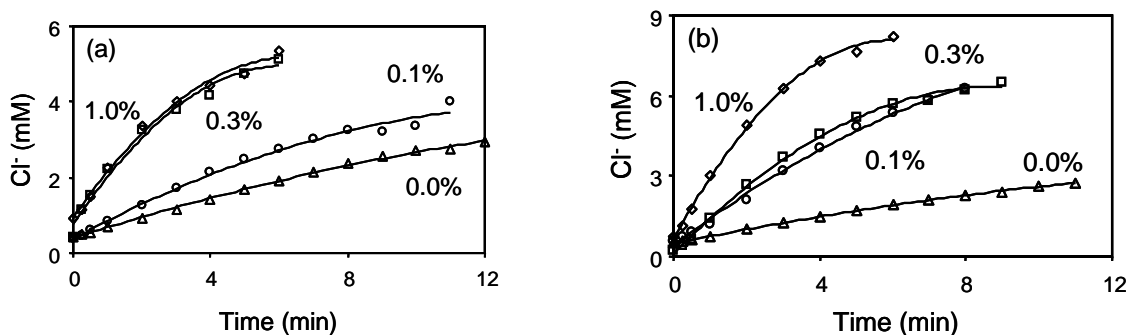


Figure 4. Chloride production with time as a function of initial Calfax concentrations when permanganate concentrations were 1.5 (a) and 3.5 mM (b). Each symbol is an average of four replicates. Lines are second polynomial fit to the observed data.

Table 3. Pseudo-first-order rate constants  $k_{obs}$  and half-life  $t_{1/2}$  for  $\text{MnO}_4^-$  consumption in the presence of Calfax.

Initial $\text{MnO}_4^-$ Conc. (mM)	Initial Calfax Conc. (%)	$k$ ( $\text{min}^{-1}$ )	$t_{1/2}$ (min)	$r^2$
1.5	0	0.15 (0.13-0.17)	4.6 (4.1-5.3)	0.97
3	0	0.15 (0.14-0.17)	4.6 (4.1-5.0)	0.97
0.75	0.1	0.25 (0.18-0.31)	2.8 (2.2-3.9)	0.91
1.5	0.1	0.22 (0.19-0.25)	3.2 (2.8-3.6)	0.95
3	0.1	0.52 (0.47-0.58)	1.3 (1.2-1.5)	0.98
0.75	0.3	0.28 (0.18-0.39)	2.5 (1.8-3.9)	0.88
1.5	0.3	0.51 (0.36-0.65)	1.4 (1.1-1.9)	0.91
3	0.3	0.50 (0.40-0.59)	1.4 (1.2-1.7)	0.93
0.75	1.0	0.30 (0.20-0.41)	2.3 (1.7-3.5)	0.89
1.5	1.0	0.53 (0.38-0.68)	1.3 (1.0-1.8)	0.91
3	1.0	0.90 (0.67-1.13)	0.8 (0.6-1.0)	0.93

Numbers in parentheses indicate 95% confidence interval.

The porosity of the coarse Ottawa sand was 0.17-0.20 and the PV was 52-60 mL. Four sets of experiments were conducted. The difference among the experiments was the volume of free phase TCE. They were 0.1, 0.3, 1.0 and 3.0 mL, corresponding to 1.1, 3.3, 11 and 33 mmol. The accumulated amount of TCE eluted can be seen in Figure 5. In the presence of 1% SDS + 0.1% permanganate the amount of accumulated TCE eluted is either larger than that from permanganate only, or broke out earlier. The effluent TCE concentration against flushing time is plotted in Figure 6. Again, a much higher initial TCE concentration is seen with columns flushed with 1% SDS + 0.1% permanganate. When the volume of free phase TCE used was 0.1 mL, the effluent concentrations never reached its solubility even when SDS was present. However, the peak effluent concentration was 3 times higher when 1% SDS was present (Figure 6a). As the input TCE volume increased to 0.3 mL, the peak effluent TCE concentration exceeded its water solubility and was 4 to 8 times higher when 1% SDS was present. These results showed enhanced solubilization in the presence of 1% SDS (figure 6b-d). In addition, the TCE concentration reached 5

mg/L or lower much sooner when surfactant was present (Figure 6). If the ratio of the time to reach this concentration when surfactant was absent to that when surfactant was present was used as an indication of flushing efficiency, the efficiency was 0.9, 1.7, 1.6-2.4, and 1.9-2.5 for the conditions with initial TCE volume of 0.1, 0.3, 1.0 and 3.0 mL, respectively.

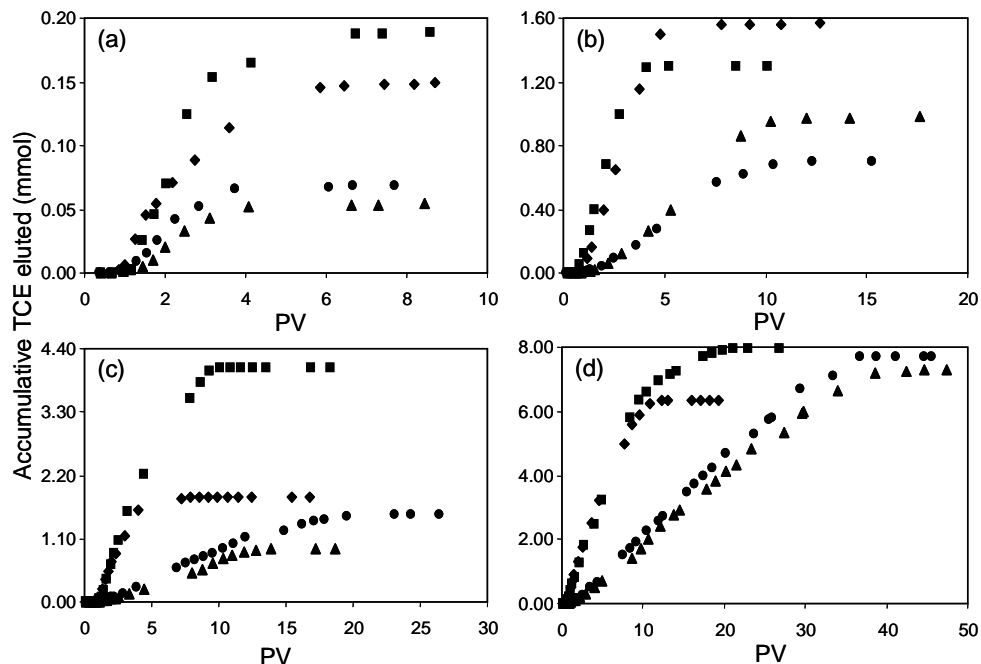


Figure 5. Accumulative TCE eluted from column flushed with 0.1% KMnO<sub>4</sub> (▲, ●) and with 0.1% KMnO<sub>4</sub> + 1% SDS (■, ◆). The initial volumes of TCE employed were 0.1 (a), 0.3 (b), 1.0 (c), and 3.0 (d) mL.

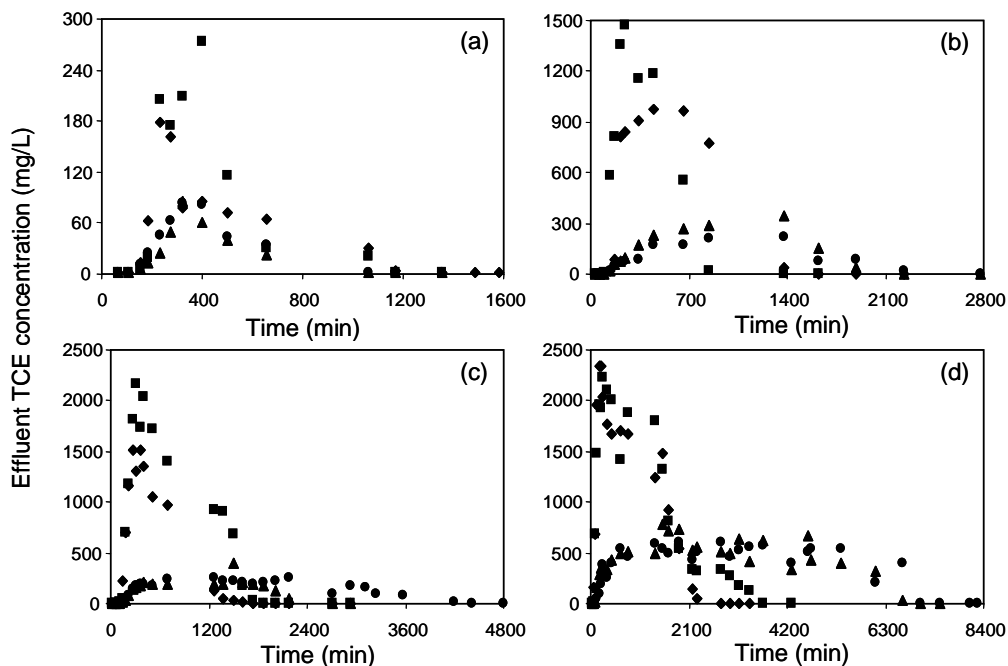


Figure 6. Effluent TCE concentrations from column flushed with 0.1% KMnO<sub>4</sub> (▲, ●) and with 0.1% KMnO<sub>4</sub> + 1% SDS (■, ◆). The initial volumes of TCE employed were 0.1 (a), 0.3 (b), 1.0 (c), and 3.0 (d) mL.

Compared to effluent TCE concentrations, the effluent chloride concentration with time showed a slightly different trend (Figure 7). Chloride analysis revealed a slightly high chloride concentration in the earlier stage of the column experiment and chloride concentration decreased quickly once permanganate is seen in the effluent.

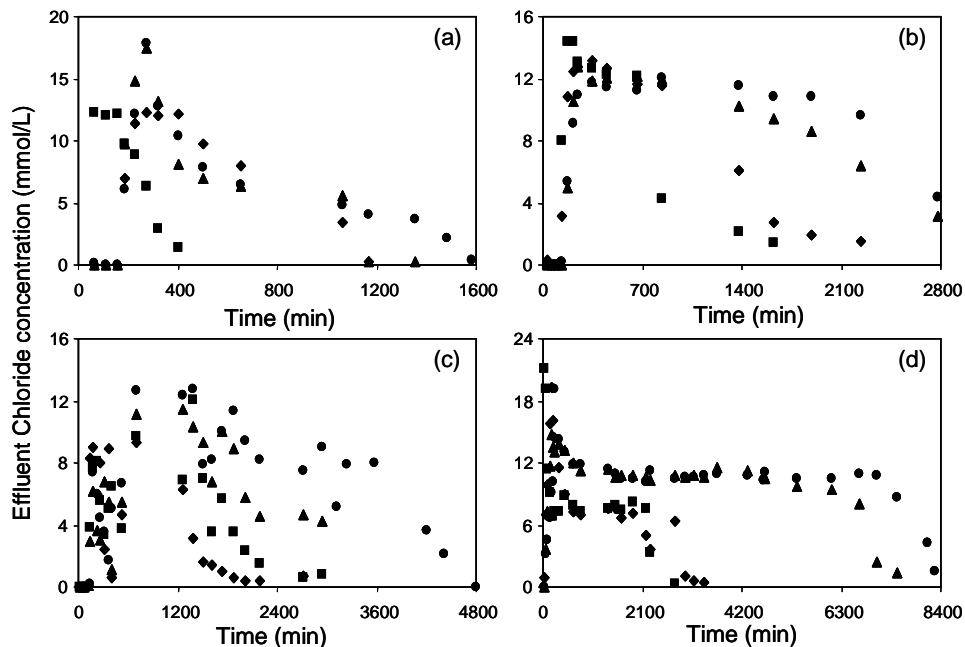


Figure 7. Effluent chloride concentrations from column flushed with 0.1% KMnO<sub>4</sub> (▲, ●) and with 0.1% KMnO<sub>4</sub> + 1% SDS (■, ◆). The initial volumes of TCE emplaced were 0.1 (a), 0.3 (b), 1.0 (c), and 3.0 (d) mL.

The enhancement of surfactant solubilization on TCE oxidation can also be seen through visualization of the permanganate transport through the TCE-emplaced columns. Figure 8 shows that, after 23 hours of flushing, permanganate front migrated to a longer distance away from the source zone, which is placed about 7 cm up from the bottom of the sand pack, when surfactant was present in the permanganate flushing solution. The lower portion of Figure 8 shows the change in color of effluents after 23 hours of flushing. The flasks containing effluent from columns flushed with 1% SDS + 0.1% MnO<sub>4</sub><sup>-</sup> revealed a slightly opaque and brownish color, which is caused by micellar solubilization as the TCE solution concentration was as high as 1800 mg/L, far exceeding 1100 mg/L, the solubility of TCE in water. With an initial TCE volume of 3 mL, the effluent TCE concentration was already at 1480 and 1950 mg/L after 140 minutes of flushing when surfactant was used, in contrast to 55 and 160 mg/L when surfactant was absent (Figure 6). After 2 days of flushing, breakthrough of permanganate is seen in columns flushed with surfactant (Figure 9). In contrast, the permanganate front when surfactant was absent was still limited to the vicinity of the TCE pool area. The effluent became complete purple when surfactant was present, while the solution was still colorless in the absence of surfactant (Figure 9). The TCE concentration from the columns when surfactant was used was below 5 mg/L and the chloride concentration was below 1 mM in 2.5 days. In contrast, in the absence of surfactant after 3 days of flushing, the TCE concentration was still at 140 and 340 mg/L and the chloride concentration was at 11 mM, indicating significant oxidation of TCE is still occurring. Assuming that all analytical data were accurate, using Eq. (3) as the stoichiometric reaction for TCE oxidized and accumulated amount of TCE in the effluent, the percentage of TCE removal from the column owing to combination of flushing and oxidation can be estimated. The results are listed in Table 4. Although, the percentage of TCE removal

with and without presence of SDS was statistically similar, the time required to reach a final effluent TCE concentration less than 5 mg/L was significantly shorter in the presence of SDS for all four sets of column experiments (Table 4). The short injection time also means reduction in permanganate material cost.

Table 4. Total TCE removed, permanganate used and time used to reach an effluent TCE concentration of 5 mg/L in the presence and absence of SDS.

Initial free phase TCE placed	0.1 mL	0.3 mL	1.0 mL	3.0 mL
TCE removed without SDS (%)	69, 87	102, 104	29, 45	46, 50
TCE removed with SDS (%)	86, 92	69, 88	25, 50	26, 34
Permanganate used to reach < 5mg/L effluent TCE concentration without SDS (mmol)	1.1, 1.1	2.3, 2.9	2.3, 4.4	7.4, 7.4
Permanganate used to reach < 5mg/L effluent TCE concentration with SDS (mmol)	1.2, 1.2	1.7, 1.4	1.8, 2.0	2.9, 3.9
Time needed to reach < 5mg/L effluent TCE concentration without SDS (hour)	18, 18	37, 46	36, 70	117, 117
Time needed to reach < 5mg/L effluent TCE concentration with SDS (hour)	20, 20	27, 23	29, 31	47, 62

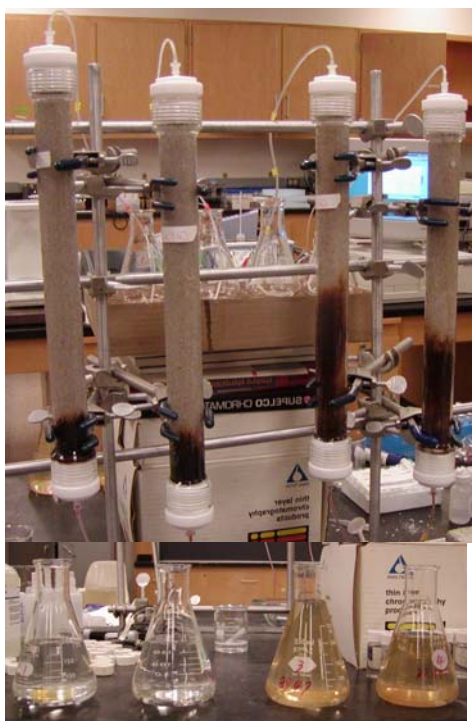


Figure 8. Columns after 23 hours of flushing with 1% SDS + 0.1%  $\text{MnO}_4^-$  (right two) and with 0.1%  $\text{MnO}_4^-$  (left two) (upper photo) and the effluent from these columns after being flushed for 23 hours.

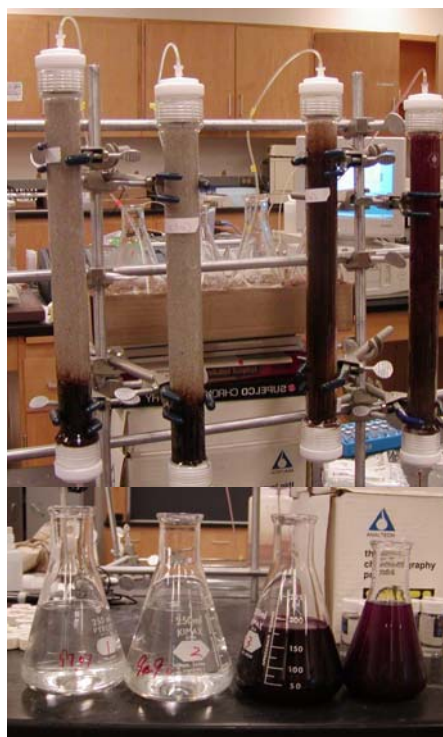


Figure 9. Columns after 47 hours of flushing with 1% SDS + 0.1%  $\text{MnO}_4^-$  (right two) and with 0.1%  $\text{MnO}_4^-$  (left two) (upper photo) and the effluent from these columns after being flushed for 72 hours.

Three-dimensional tank study showed a consistent trend as seen in column study, i.e. with the presence of surfactant SDS a higher amount of TCE was removed within given time. Furthermore, visualization showed that a  $\text{MnO}_2$  precipitation front was formed much quickly when 1% SDS was present (Figure 10).

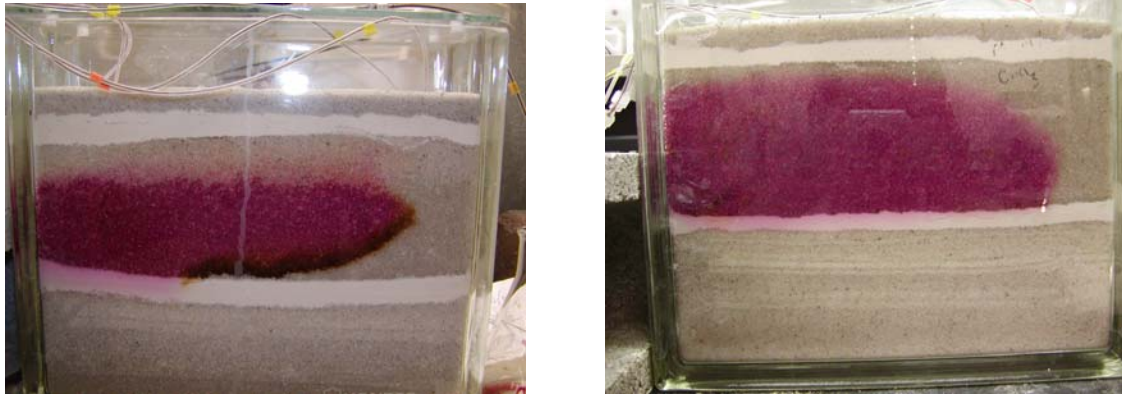


Figure 10. Reaction of Permanganate and TCE in the presence (left) and absence (right) of 1% SDS in 3-d tank study. The injection wells were on the left and extraction wells on the right. 1 mL of TCE was placed in 5 cm below the upper smectite layer in the center.

### Conclusions and Recommendations

Degradation of TCE can be enhanced in the presence of anionic surfactants. The observed pseudo first order rate constant increased as much as 3 to 5 times in the presence of SDS at a concentration above its CMC. This increased rate constant would shorten the reaction time if fixed amount of TCE is present in the system. In addition, less amount of permanganate will be needed. The batch results were verified by column experiment in terms of permanganate consumption as well as time required to reach an effluent TCE concentration less than 5 mg/L. Based on the column results, as much as 50% of pumping time and permanganate could be saved in the presence of 1% SDS. However, the reduction of hydraulic conductivity due to production of manganese dioxide is still an important issue. Thus further studies in restoring original hydraulic conductivity during the surfactant/permanganate flushing will be needed before the approach can be used in pilot or field scale test. In addition, further studies on mechanism of influence of present surfactant on TCE oxidation are also necessary. Nevertheless, the results of this project provided extended data for remediating groundwater and soil contaminated with free phase chlorinated solvents using permanganate as the oxidant.

### References

- Hood, E.D., Thomson, N.R., Grossi, D., Farquhar, G.J. 2000. *Chemosphere* 40:1383.
- Huang K.C., Hoag, G.E., Chheda, P., Woody, B.A., Dobbs, G.M., 1999. *Environ. Engineer. Sci.* 16:265.
- Huang, K-C., Chheda, P. Hoag, G. E., Woody, B. A., Dobbs, G. M. 2000. In Proceeding from the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA.
- Huang K.C., Hoag, G.E., Chheda, P., Woody, B.A., Dobbs, G.M., 2002. *Chemosphere* 46:815.
- Lee E.S., Seol, Y., Fang, Y.C., Schwartz, F.W. 2003. *Environ. Sci. Technol.* 37:2540.
- Li, X.D., Schwartz, F.W. 2004. *Geophysical Research Letters* 31, no.6 p. L06504 1-5.
- Rosen, M. J. 1989. *Surfactants and Interfacial Phenomena*, 2<sup>nd</sup> ed., John Wiley & Sons, New York, 431p.
- Schnarr, M., Truax, C., Farquhar, G., Hood, E., Gonullu, T., Stickney, B., 1998. *J. Contam. Hydrol.* 29:205.
- Schwartz, F.W., Zhang, H. 2000. *Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes*, Final Report to US DOE. 137p.
- Seol, Y. Schwartz, F.W., Lee, S., 2001. *Ground Water Monitoring and Remediation* 21:124.
- Yan, Y.E., Schwartz, F.W., 1999. *J. Contam. Hydrol.* 37:343.
- Yan, Y.E., Schwartz, F.W., 2000. *Environ. Sci. Technol.* 34:2535.



## Appendix A:

- Journal Publications:** Li, Z. (2004). Surfactant-Enhanced Oxidation of Trichloroethylene by Permanganate – Proof of Concept, *Chemosphere* **54**, 419-423.
- Conference Presentation:** Li, Z. Surfactant Enhanced Oxidative Dechlorination of Chlorinated Solvents by Permanganate – Proof of Concepts. ARWA Wisconsin section meeting, February 2003.
- Li, Z. Surfactant Enhanced Oxidative Dechlorination of Chlorinated Solvents by Permanganate – Proof of Concepts. GSA annual Meeting, Seattle, WA, November 2003.
- Other Presentation:** Li, Z. Surfactant Enhanced Oxidative Dechlorination of Chlorinated Solvents by Permanganate – Proof of Concepts. Carus Chemicals, Peru, IL, July 2004.