Summary of Researches

Chapter 1 Oxidative Degradation of Chlorinated Ethylenes by Potassium Permanganate  Y. Eugene Yan and Franklin W. Schwartz

The oxidative treatment of chlorinated ethylenes in ground water using permanganate was investigated in a series of batch kinetic tests. Five chlorinated ethylenes including tetrachloroethylene (PCE), trichloroethylene (TCE), and three isomers of dichloroethylenes (DCEs) were examined. The degradation process was rapid with pseudo-first-order rate constants ranging from 4.5×10^{-5} to 0.03 s^{-1} at MnO_4^- =1 mM. The rate increased with a decreasing number of chlorine substituents on the ethylene. The higher reactivity of trans-DCE (k_{obs}=30×10^{-3} s^{-1} at MnO_4^- =1 mM) as compared to cis-DCE (k_{obs}=0.9×10^{-3} s^{-1} at MnO_4^- =1 mM) is thought to be caused by a significant steric effect due to the formation of a large cyclic activated complex. TCE oxidation as a second-order reaction was confirmed and the rate constant, k=0.67±0.03 M^{-1} s^{-1}, is independent of pH over the range of 4-8. The activity of both Cl^- and hydrogen ions was monitored over time and suggests essentially complete dechlorination, making the degradation products less harmful than the parent compounds. Competition for MnO_4^- from other organic compounds in ground water or highly contaminated ground water was also evaluated in experiments. A simple and quick approach was demonstrated to estimate permanganate consumption by other organic compounds for field applications and to predict the TCE degradation rate in a system involving multiple contaminants. The modeling results suggest that the effect of autocatalysis by MnO_2 on TCE degradation is significant when the system contains high concentration levels of MnO_4^- and TOC.

Key Words: Permanganate, Trichloroethylene, Oxidation, Kinetics, and Remediation

Chapter 2 Kinetics and Mechanisms for TCE Oxidation by Permanganate  Y. Eugene Yan and Franklin W. Schwartz

The oxidation of trichloroethylene (TCE) by permanganate was studied via a series of kinetic experiments. The goal in product identification and parameterization of the oxidation kinetics was to assess the utility of this reaction as the basis for the in-situ remediation of ground water contaminated by chlorinated ethenes. TCE oxidation mainly involves the formation and decomposition of an organometallic compound (hypomanganate ester) to form carboxylic acids, and eventually, oxidation to the final product, CO_2. The initial and final reactions in the TCE oxidation are subject to rate-limiting steps, which control the destruction rate of TCE and formation rate of the final product. The fast reactions involved in the second step determine the nature of products. Four carboxylic acids, including formic, oxalic, glyoxylic and glycolic acids, and CO_2 were identified and quantified in kinetic measurements. The distribution of products is highly dependent upon experimental conditions, particularly pH. Based on our understanding of various processes involved with TCE oxidation, a kinetic model was developed and the model parameters (seven rate constants) were estimated. The kinetic model proposed in this study successfully simulates observed experimental data.
Chapter 3  
**Phase-Transfer-Catalyst Applied to the Oxidation of Trichloroethylene by Potassium Permanganate**  
*Yongkoo Seol and Franklin W. Schwartz*

The use of potassium permanganate to oxidize chlorinated solvents has been demonstrated as an effective process for treating nonaqueous phase liquids in ground-water systems. This study evaluates the effectiveness of phase-transfer-catalysts (PTCs) in enhancing the degradation rate. PTCs work by transferring permanganate ion into the nonaqueous phase where it initiates oxidative decomposition. We studied the oxidation of trichloroethylene (TCE) by potassium permanganate, conducting kinetic batch experiments in conjunction with three PTCs that varied in terms of their extraction constants and molecular structures. Using the same batch technique, we examined whether PTCs could enhance the aqueous solubility of TCE. Solubilization could also increase oxidation rates in the aqueous phase. Rates of TCE oxidation in solutions containing the PTCs and a blank were estimated separately by measuring chloride concentration and UV/Vis absorbance in the aqueous phase. The enhanced rate of TCE destruction by the PTCs was reflected by an increase in the rate of consumption of permanganate ion and production of chloride ion. There was no tendency for the PTCs, however, to solubilize TCE in the aqueous phase. Therefore, the PTCs increased the rate of TCE decomposition by catalyzing permanganate oxidation in the organic phase. This study suggests that there is significant potential for testing this scheme under field conditions.

**Key Words:** Phase-transfer-catalysts; Potassium permanganate; Oxidation; and Trichloroethylene;

Chapter 4  
**Oxidation of DNAPL Mixtures Using Potassium Permanganate with a Phase-Transfer-Catalyst: Kinetic Results from a Digital Photographic Monitoring Method**  
*Yongkoo Seol, Sangsuk Lee, and Franklin W. Schwartz*

Phase-transfer-catalysts (PTCs) can enhance the oxidation of pure DNAPLs using potassium permanganate by initiating reactions in the organic phase. This study examined the influence of pentyltriphenylphosphonium bromide (PTPP) as a PTC on the rate of permanganate (MnO₄⁻) oxidation of DNAPLs in pure phases and mixtures. Kinetic batch experiments with trichloroethylene (TCE), 1,1,2-trichloroethane (TCA), tetrachloroethylene (PCE), 1,1,2,2-tetrachloroethane (PCA), and their mixtures (1:1, v/v) were performed in test tubes to assess reaction rates with the PTC. The disappearance of MnO₄⁻, which was evidence of the oxidative decomposition of DNAPLs, was quantified by capturing digital images of the tubes. This rapid photographic monitoring approach was validated by comparison with an UV-Vis spectrophotometer method. The comparative rates of MnO₄⁻ consumption were TCE > PCA > PCE > TCA, and the same decreasing order was observed with the PTC. PTPP increased MnO₄⁻ consumption rates especially for TCE and PCA as pure phases. The consumption rates of mixtures without PTPP were lower than those of pure phases. However, due to high extraction capabilities for catalyst-MnO₄⁻ ion pairs, TCA and PCA appeared to increase the MnO₄⁻ consumption.
significantly when they were mixed with TCE or PCE. The increase in consumption rates with PTPP was most remarkable with the mixture of PCE and TCA. The PTCs appear to be promising in their ability to increase oxidation rates of DNAPL mixtures.

**Key Words:** Phase-transfer-catalysts; Potassium permanganate; Oxidation; Digital Image, and Trichloroethylene;

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**Chapter 5** Efficiency Problems Related to Permanganate Oxidation Schemes

*David Li and Franklin W. Schwartz*

This study investigates problems that potentially could impact a permanganate oxidation scheme, such as competitive permanganate utilization in reactions with aquifer materials, MnO$_2$ precipitation around zones of high DNAPL saturation, and permeability-related flow bypassing. A series of batch experiments were conducted to examine whether typical aquifer materials (glacial deposits, alluvium and carbonate-rich sand) reacted with permanganate. The results show a dramatic consumption of the oxidant and a significant change in the concentrations of some chemical species, which may be of environmental concern. 1-D column and 2-D flow tank experiments have been conducted to examine mass removal rates and related flushing efficiencies. The results indicate that mass removal rates are also greatly influenced by the MnO$_2$ precipitation and flow bypassing. It is anticipated that in actual field settings, the issue of flushing efficiency needs to be considered in the design.

**Chapter 6** Simulating the *In Situ* Oxidative Treatment of Chlorinated Ethylenes by Potassium Permanganate

*Hubao Zhang and Franklin W. Schwartz*

Several laboratory and field studies have demonstrated the potential viability of oxidation schemes using MnO$_4^-$ for the in-situ treatment of DNAPL source areas, which are contaminated by chlorinated ethylenes (PCE, TCE and DCE). Chemically, the chlorinated ethylenes are oxidized to CO$_2$, Cl$^-$, and MnO$_2$. The goal of this study was to develop a theoretical framework for the chemical and physical processes involved. To this end, a computer model was developed to simulate the coupled processes of NAPL dissolution, chemical reactions, and solute mass transport in the in-situ chemical oxidization scheme. The model incorporates a kinetic description of reactions between the MnO$_4^-$ and the chlorinated ethylenes and the rate of dissolution of the NAPL. A Strang operator-splitting method, which coupled the different physical and chemical processes and an exponentially-expressed solution of the kinetic equations, led to a significant speed up in the solution process. The products in reactions were calculated based on the stoichiometry of the reaction. We demonstrated the capabilities of this code using already published results of column, test cell, and field experiments. Generally, the simulated results matched well with experimental measurements. The computer model provides a useful tool for assisting the design and the prediction of the oxidization processes under field conditions.