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Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes

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Research Objective

The goals of this study are: (1) to elucidate the basic mechanisms by which potassium permanganate oxidizes common chlorinated solvents, various constituents in aqueous solution, and porous-medium solids, and (2) to assess the potential for chemical oxidation by potassium permanganate to serve as a remedial scheme involving either source zone flooding or reactive barriers. The combined theoretical and experimental study is designed to contribute fundamental knowledge about reaction pathways, reaction rates, specific intermediates formed, and controls on reaction processes. The specific objectives of this study are: (1) to describe through batch experiments the kinetics and mechanisms by which potassium permanganate oxidizes dissolved tetrachloroethene (PCE), trichloroethene (TCE), and dichloroethene (DCE), (2) to examine using column studies the nature and kinetics of reactions between potassium permanganate, residual DNAPLs (PCE, TCE, and DCE) and porous medium solids, (3) to represent the process understanding in flow and transport models that demonstrate the potential applicability of the approach, and (4) to apply the resulting computer code in the development of appropriate field tests for assessing the approach.

Research Progress and Implications

Approaching the end of Year 2 of this 3-Year project, we can report significant progress in meeting the objectives of the study. Through a series of batch experiments, it has been shown that permanganate oxidation is effective in degrading various chlorinated ethylenes in aqueous solution. The disappearance of chlorinated ethylenes can be simply characterized by a pseudo-first-order model. Degradation half-lives for TCE, cis-1,2-DCE, trans-1,2-DCE and 1,1-DCE reacting with 1mM MnO_4^- range from about 24 s to 18 min. Degradation of PCE is much slower with a half-life of about 257 min. Overall, the degradation rate is inversely proportional to the number of chlorines present as substituents on ethylenes. These rates of degradation are impressive given the fact that the experiments were run with MnO_4^- concentrations only a factor of 10 or so greater than that of the particular chlorinated ethylene. It would be feasible in practice to increase rates of reaction by increasing MnO_4^- concentrations.

Our experiments also showed how the efficiency of degradation is reduced due to competition from other organic compounds. Contaminated ground water was synthesized as a mixture of ground water and landfill leachate. Three experiments were run with a fixed TCE concentration of 2 mg/L, a concentration of other organic compounds of 101 mg/L (TOC) and concentrations of MnO_4^- of 20, 80 and 120 mg/L. As expected, the competition for MnO_4^- led to a reduction in the reaction rate, as compared to experiments with TCE in Milli-Q water. However, with the largest MnO_4^- concentration, the competition appeared to be offset by other processes that effectively increased the degradation rate of TCE. Our preliminary assessment is that colloidal MnO_2 was catalyzing reactions between MnO4- and TCE. We will explore this aspect of the study in the coming year.

Early in the study, we confirmed previous work that indicated TCE degraded completely to CO_2 in a series of three steps. However, little was known about the overall reaction pathways and intermediates that formed. Preliminary indications were that TCE reacted with MnO_4^- to produce a cyclic complex, then carboxylic acids, and finally CO_2, along with Cl- and MnO_2. Of particular interest in our work were steps two and three. We undertook kinetic experiments with radiolabeled TCE (i.e., 1,2-^{14}C) to understand these reactions.

In the initial step, an organometallic compound (cyclic hypomanganate ester) is formed via the insertion of a p bond in the carbon-carbon in the carbon-carbon double bond into the metal-oxo bond of permanganate. This initial reaction is a rate-limiting step in the overall set of reactions and is not pH dependent. In the second step, the decomposition of the cyclic ester (Mn-V) proceeds via different reaction pathways to form various carboxylic acids. The particular acids that form depend upon the experimental conditions. At low pHs, formic acid is the dominant compound. At high pHs, glyoxylic and oxalic acids dominate. Kinetically, step 2 is a very rapid process with decomposition rates approximately 100 times higher than the formation rate.

All carboxylic acids formed in the second reaction step will be eventually oxidized to the final product, CO_2. Thus, the third step completes the overall degradation reaction. In the pH range 4-8, permanganate ion mainly reacts with the anionic species of the carboxylic acids, which is good agreement with our kinetic model. Thus, pH conditions affect the accumulation rate of CO_2. We developed an overall kinetic model that describes the loss and gain of compounds through the sequence of reactions.

The results of these experiments have important implications as far as the development of permanganate oxidation schemes as a remedial technology. Rapid and complete dechlorination is possible in reacting various chlorinated ethylenes with MnO_4^-. The reaction scheme does not yield the same intermediates, as is the case with reductive dechlorination. The main intermediates are four carboxylic acids including: formic, oxalic, glyoxylic and glycolic acids. Under conditions where permanganate is not present in excess and some of these acids end up in solution, they should be relatively mobile.

In general, the laboratory studies continue to support the continued development of permanganate oxidation schemes for the treatment of solvent spills. Issues, however, remain to be addressed. Foremost among them is the extent to which plugging by MnO2 may interfere with flushing schemes. Our work to date on dissolved compounds has an obvious extension to problems of pure phase liquids, which is how the solvents occur at many sites. The most important problems to consider in this respect are the rate limiting steps in the dissolution of free products and the effect of phase saturation on relative permeability and displacement efficiencies.

The fate and transport modeling for this study are being undertaken in Albuquerque, NM by Dr. Zhang of Duke Engineering Services. Dr. Zhang has developed a 3-D flow and transport code. The three-dimensional model simulates ground water flow and reactive transport of dissolved TCE, permanganate (MnO_4^-), end products (CO_2, MnO_2 and Cl^-), and various intermediate products (COOH, $[COOH]_2$, and others) away from a residually saturated TCE NAPL source. The flow and transport equations were formulated and solved using a control-volume finite-element method. Accordingly, mass balance can be calculated for each node and each species in the simulation domain. By formulating the kinetic-reaction processes as a single equation, it easier to couple the kinetic reactions and mass transport equations. The dissolution of NAPL was also treated kinetically using a mass transfer coefficient model. The reactive-transport equations for each species were coupled using a sequential iteration procedure in which the reaction rate term is calculated using concentrations at the previous time step and at the previous iteration of the current time step. Two different schemes, Strang operator splitting and Newton-Raphson, are being examined to compare their iteration efficiencies and memory requirements. Illustrative simulation trials have been conducted with the code to support on oral presentation at AGU. The rate constants used in the simulations were determined through our batch experiments. Preliminary simulation results show that significant quantities of TCE can be oxidized in a relative short period of time within short transport distance in the two cases. The model correctly predicts the formation of intermediate products at early times, as the oxidization process proceeds.

We are now in the process of comparing our simulation results with column experiments in which permanganate flooding is being used to remove TCE. Additional experimental data will become available from our own laboratory studies, later this year. Overall, there are two papers in press and one nearly ready for submittal, which is concerned with the reaction pathways. In the next few months, the first work related to the model studies should be submitted.

Planned Activities

In the coming year, we will undertake detailed column studies to better understand DNAPL dissolution processes. These experiments will be undertaken with thin rectangular columns to facilitate optical monitoring as well as conventional monitoring. Of particular interest is the relative efficiency of flushing and the factors that control the flushing and the extent to which solid products may lead to plugging. We will examine multiphase effects in a qualitative sense. Initially, experiments will be undertaken with glass beads. Later, we will move to geological materials that have oxidizable components capable of competing with chlorinated etheylenes for oxidation.

During the coming year, we will also begin to examine the possibilities for surface reactions and the possibilities for catalyzing oxidation reactions. We are presently working on the experimental design for this work.

Work is nearly complete on the validation of the code with experimental results from the literature. The next step with the modeling is a sensitivity analysis with the flow and transport model. The objective is to generalize the experimental results and to expand the understanding of reaction and transport mechanisms. This analysis will vary key parameters individually to study their effects on the redox processes.

Although this study is mainly oriented toward the characterization of various types of reaction pathways and geochemical processes, we expect that the approach would see eventual applications to site remediation. The modeling approach will be utilized in the study to provide testing schemes that would provide the next step forward in testing permanganate oxidation under field conditions. The eventual implementation could involve both reactive barrier systems (e.g., funnel and gate systems) or flooding for mass removal. Thus, we would develop appropriate tests for both types of potential applications.