Chapter 5

EFFICIENCY PROBLEMS RELATED TO PERMANGANATE OXIDATION SCHEMES

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Introduction

Oxidation schemes for the *in situ* destruction of chlorinated solvents, using potassium permanganate, are receiving considerable attention. Potassium permanganate is a powerful oxidant that has been used for long time in wastewater treatment. Batch scale experiments have demonstrated the rapid 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 Laboratory have conducted experiments to investigate permanganate-oxidation schemes in field and laboratory tests. The results suggested that permanganate oxidation is 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 our work are that permanganate oxidation schemes have inherent problems that could severely limit their applicability. As a powerful oxidant, permanganate is not only capable of oxidizing chlorinated ethylenes, but also inorganic compounds in ground water and solid aquifer materials. For example, Drescher and others (1998) reported the significant consumption of permanganate by humic acid in a system consisting of sand, TCE, permanganate and humic acid. With aquifer materials consuming some of the permanganate, the overall efficiency of the cleanup is reduced and costs are increased. Reaction also can release metals (e.g. Cr^{3+}) to the aqueous phase at concentration of regulatory concern. Given the present, relatively limited understanding of the oxidation reactions, there is a need for studies to understand these problems and to improve the efficiency of permanganate delivery.

Another potential problem is that key reaction products, manganese dioxide and carbon dioxide, can cause plugging and flow diversion. There is little research on the impact of these problems on mass removal rate and on possible approaches to inhibit precipitation. This study specifically addresses gaps in knowledge that bear on the realistic use of permanganate-oxidation schemes in DNAPL clean ups. Here, we present preliminary data on the likely metals that can be released due to permanganate-aquifer interaction. We also discuss the results of various column and flow tank experiments that elucidate problems of flooding inefficiencies, and pore plugging related to reaction products.

Materials and Methods

The study involves two types of experiments. We utilize batch studies to investigate the consumption of MnO_4^- by aquifer materials and the release of potentially hazardous metals. Column (1-D) and flow tank studies (2-D) are used to examine the impact of oxidation products on DNAPL removal efficiencies.

Permanganate Consumption and Metal Release.

Batch experiments with natural aquifer materials are used to examine the interaction of potassium permanganate with aquifer material and the extent to which metals are released. Samples were collected from various aquifer materials, such as, alluvium, glacial till, glacial outwash, and carbonate sand. Special efforts were made to collect samples at depth, away from soil horizons.

Samples were placed in aluminum pans to air dry for two to three days. Experiments were conducted at room temperature in 25 mL vials. 15 gram of each sample was mixed with 15 mL of 0.5 g/L potassium permanganate solution. A control was prepared with the same potassium permanganate solution, but without any aquifer material. After the permanganate solution was added to the aquifer solids, the vials were covered with aluminum foil and black cloth, and kept in the dark to avoid photo-induced degradation of potassium permanganate. 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. Permanganate concentrations were measured with a Varian Cary 1 UV–visible spectrophotometer at a wavelength 525 nm.

The study of metals released by the oxidation of aquifer materials followed a similar procedure. The controls in this case were mixtures of 15 mL Milli-Q deionized water and aquifer materials. By comparing the differences between metals released from the control experiments and oxidized materials, the effect of MnO_4^- treatment could be established. After ten days, when the permanganate had mostly been consumed, solutions of both the controls and samples 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 step, a semi-quantitative screening analysis was performed to identify the elements with most dramatic change in concentration. A quantitative analysis was then carried out with specific external standards. 12 elements were quantitatively analyzed. The results were then converted to the pore water concentration, based on the porosity of the media.

1-D Column Experiment.

The 1-D column experiment was conducted using a glass column with Teflon end fittings and packed with medium silica

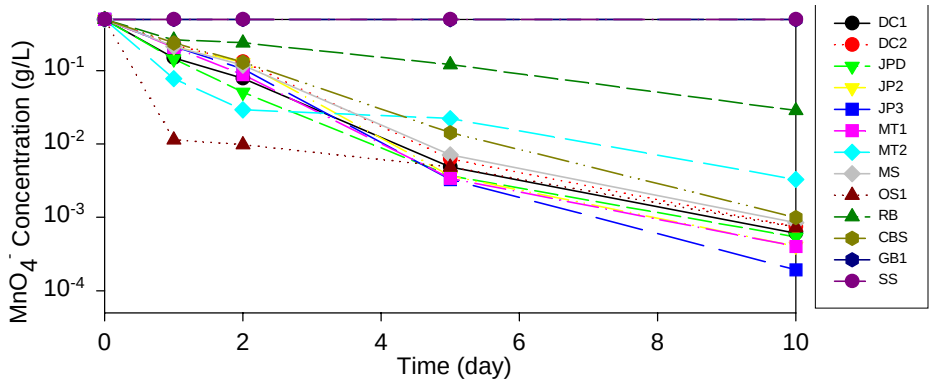

FIGURE 5.1. Utilization of MnO_4^- through oxidation of various aquifer materials.

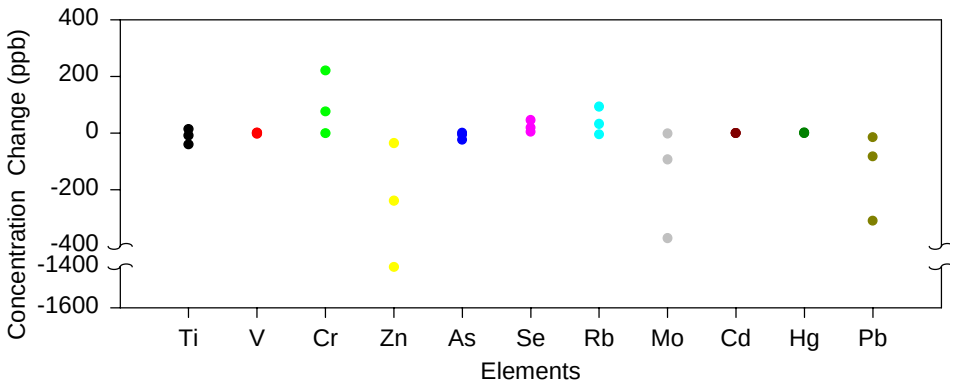

FIGURE 5.2. Average, maximum and minimum concentrations for the elements in pore water after treatment with 0.5 g/L $KMnO_4$ for ten days

sand (US Silica, Ottawa, IL). Details of the experimental set up are summarized in Table 5.1. Once the column was packed, it was positioned upside down. 1 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. MnO_4^- concentration was measured with a UV-visible spectrophotometer as mentioned earlier. TCE was measured with a Fisons Instruments 8060 gas chromatograph equipped with a Ni^{63} electron capture detector and a DB-5 capillary column (J&W Scientific, Rancho Cordova, CA). Cl^- ion concentration was measured with a Buchler Digital Chlorodometer. Samples were taken at 12 hour intervals over a two week period. The experiment was concluded when the effluent TCE concentration fell below 5 µg/L. After the experiment finished, several porous medium samples were taken along the column. The samples were treated with thiosulfate to dissolve the MnO_2. The resulting solution was analyzed by ICP-MS to quantify the distribution of MnO_2 along the column.

2-D Flow Tank Experiments.

A thin, small 2-D glass flow tank with Teflon end fittings was constructed for the experiment (Table 5.1). The flow tank was filled with transparent borosilicate glass beads with a mean grain size of 1 mm. Two PTFE tubes with inside diameter of 1.32 mm were installed in the two ends of the column to

Table 5.1. Experimental design for the 1-D column and 2-D flow tank experiments

Column/tank	Dimension (mm)	Medium	Q (mL/min)	$KMnO_4$ concentration	Porosity
1 – D	605(L)x50 (ID)	Silica sand	1.2	1 g/L	0.385
2 – D	305(L)x50(H)x3 (T)	Glass beads	0.5	0.2 g/L	0.42

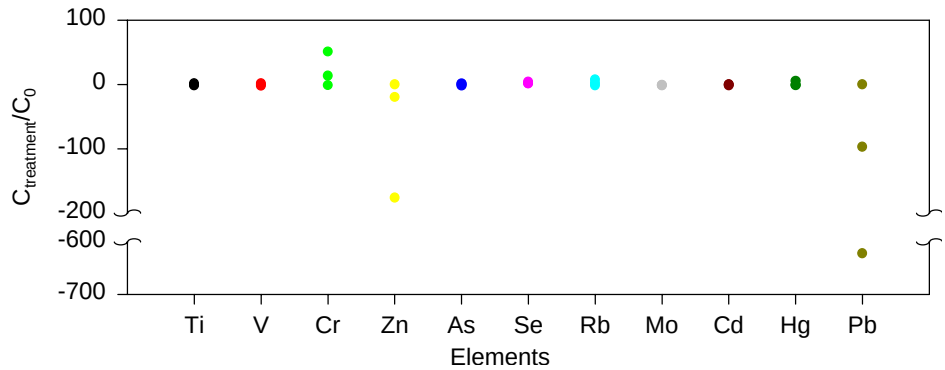

FIGURE 5.3.Average, maximum and minimum ratio of concentrations of elements in pore water before and after treatment with 0.5 g/L $KMnO_4$ for ten days

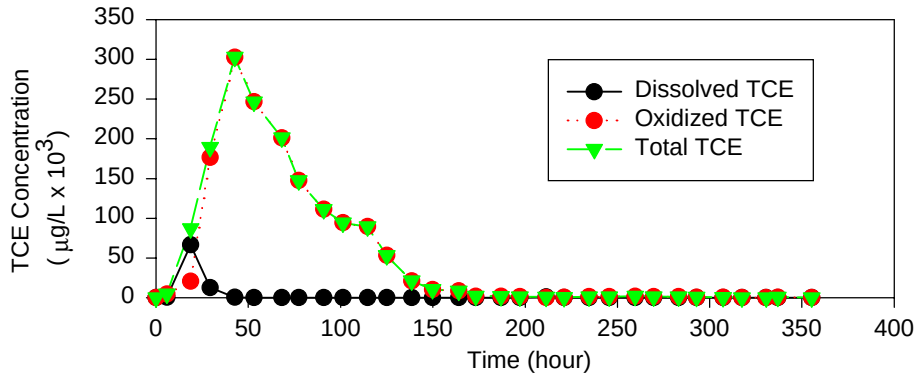

FIGURE 5.4. TCE concentration with time in the effluent of the 1 – D column and calculated removal based on Cl^- stoichiometry.

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.

With both pumps running at the same steady rate, flow was horizontal along the length of the tank. 1 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 $KMnO_4$. Effluent samples were taken three times a day and were analyzed as before. Images of the column were taken with a digital camera to monitor the development of the growing zone of MnO_2 precipitation.

Results

Results of batch experiments to examine the consumption of MnO_4^- by natural materials are plotted in Figure 5.1. After 10 days, the MnO_4^- concentration dropped to near zero for every sample of natural aquifer material, irrespective of the type of sample. There are two exceptions, with virtually no change in the MnO_4^- concentration with time. These two samples are the silica sand and the glass beads, which were used later for the column experiments. The decrease in the MnO_4^- concentration appears follow a first order kinetic rate law. Because permanganate is likely conservative in the aqueous phase, it is unlikely concentration reductions were caused by sorption onto the solids.

The decreasing MnO_4^- concentrations with time implies that the aquifer materials have being oxidized. Results of the ICP-MS analysis of the pore water MnO_4^- treatment (Figures 5.2, 5.3) confirmed this conclusion. In spite of the variability in the types of sample, there are common features among the results. Of the 12 elements that were quantitatively analyzed, chromium, selenium and rubidium generally increased in concentration; and vanadium, zinc, cadmium and lead, decreased. The remaining elements (titanium, arsenic, molybdenum, cesium and mercury) generally showed no significant change. While the pattern of change is relatively consistent, the magnitude of the change is variable. In some

cases, the concentration could change several hundred fold.

The 1-D column experiment confirms the capability of MnO_4^- to oxidize TCE present in the column. Mass balance calculations, based on the measured TCE and chloride concentration in the effluent from the column, indicated the nearly complete removal of the pure TCE in a relatively short time (Figure 5.4). Intergrating 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 when MnO_4^- first fully saturated the column, and decreased with time dramatically. 90% 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 the oxidation reaction had stopped. Flushing continued with Milli-Q water being pumped through the column. Interestingly, TCE concentrations rebounded to about 130 µg/L. Apparently, the Cl^- measurements were not sensitive at the lower level of detection to indicate that small quantities of TCE remained in the column. It is estimated that another couple hundred hours would be needed for the TCE concentration drop to below 5 µg/L.

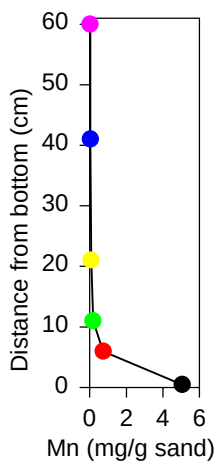

FIGURE 5.5. Distribution of Mn along the column.

The distribution of manganese dioxide precipitation in the column after the experiment is presented in Figure 5.5. The majority of the Mn was presented at or very close to the DNAPL zone. These precipitates tended to plug the column and toward the end of the experiment flushing was increasingly difficult.

The results from the 2-D flow tank experiment (Figure 5.6) were similar to the 1-D experiment, except that removal rates were noticeably smaller. After 313 hours of flushing with MnO_4^-, only 34.9% of the initial TCE was removed from the column. Half of the TCE was removed in the first 25% of the elapsed time. Note that in Figure 5.6 at the end of the experiment TCE concentration rebounded, once the injection of MnO_4^- had stopped.

The visual observation system provided a useful way to monitor the growth of the zone of MnO_2 precipitation. Precipitation started once MnO_4^- came in contact with residual DNAPL. 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.

With time, the precipitation of MnO_2 reduced the permeability. MnO_2 rapidly formed a precipitation rind above the DNAPL pool. Greater injection pressure was required to maintain the flow close to the end of the experiment. The experiment came to a halt when MnO_2 plugged the tank nearly completely and MnO_4^- could no longer be injected. Carefully 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.

Summary and Discussion

In the batch experiments, the gradual disappearance of MnO_4^- and the change in chemistry of the aqueous phase pointed to significant interactions between the porous medium and the MnO_4^-. Given the variability in mineralogy and grain coatings, it is not possible to propose reaction mechanisms. We are now in the processes of elucidating the MnO_4^--solid reactions in more detail. The permanganate likely oxidizes the solid metal oxide. For example, chromium, Cr (III), which often exists as Cr_2O_3 solid, was probably oxidized to Cr (VI), a dissolved species of chromium. Any metals sorbed to organic matters would be added to solution as MnO_4^- oxidizes the organic matter. 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 ability for most natural aquifer materials to consume MnO_4^- reduces concern that the presence of MnO_4^- in solution would emerge as a major problem of contaminant at most sites.

Understanding how the chemical composition of the aqueous phase will change is more complicated because the oxidation of TCE is capable of shifting the equilibra of dissolved-precipitated phase, sorbed-solution phase and complexations by changing pH, E_h and the concentration of Cl^-. For example, selenium tends to much more mobile in the oxic rather than reducing condition (Alloway, 1995) as the E_h goes up with the treatment. Mobilization of several metals (Hg, Cd, Pb) was found to be very sensitive to the concentration of Cl^-. A given element will likely respond to the permanganate treatment differently. Our results suggest caution in the application of oxidation schemes to environmentally sensitive areas and aquifers containing high concentrations of metal oxides at lower

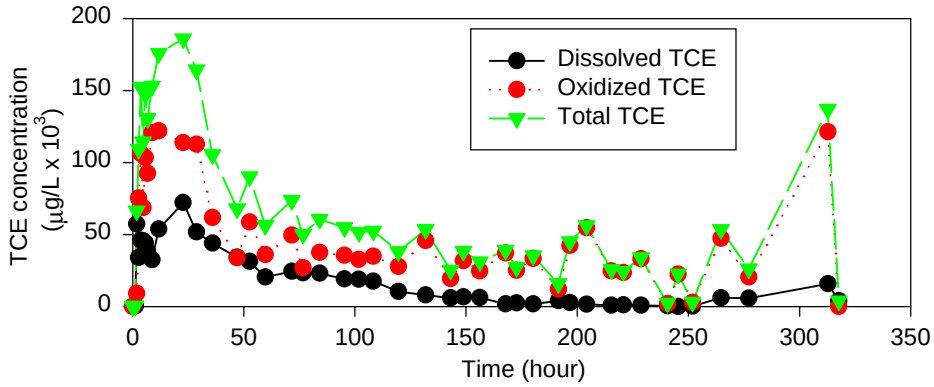

FIGURE 5.6. Effluent TCE concentration change with time in the 2 – D column experiment

oxidation states.

Results from both the 1-D and 2-D experiments indicate that early in the flushing process, the mass removal rate is greatest. As the treatment proceeds, the rate decreases dramatically. Running the experiments to achieve complete DNAPL removal will produces a long tail in the later part of the treatment, which points to inefficiencies in the flushing. This tailing effect has also been noted by researchers studying DNAPL dissolution. Towards the end of their experiments when a large portion of the contaminant was dissolved, small droplets remained in hydraulically stagnant zones in the medium. Preferential flow paths appear to develop even with 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 would tend to bypass these zones and follow a more permeable flow path, causing the DNAPL oxidation process to become diffusion controlled.

These effects are most obvious in the 2-D tank experiment where DNAPL is present in zones of high residual saturation or pools. The pooled DNAPL persisted because the interfacial area is relatively small and MnO_4^- moved around but not through these zones. In zones of residual saturation, DNAPL oxidization was more efficient because MnO_4^- could move through the zones. With the opportunities for MnO_4^- to move around zones of DNAPL saturation in the two dimensional system, there was a much smaller overall destruction of TCE in the 2-D tank as compared to the 1-D column. These results suggest that with 3-D flow conditions, evident at actual contaminated sites, the efficiency of removal would probably be smaller. It appears that MnO_4^- oxidation is more effective in cleaning up residually saturated DNAPLs rather than pool 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.

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