

**Project Title: Semi-passive, chemical oxidation schemes for the long-term treatment of contaminants**

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**Research Objective**

This study aims to provide basic research on a new passive remediation concept based on an in-situ chemical oxidation scheme. The first objective is to use laboratory experiments and computer simulations to develop a new semi-passive delivery system for the controlled release of  $\text{KMnO}_4$ . A system is required to facilitate the slow release of  $\text{KMnO}_4$  into flowing ground water in a manner that maximizes the lateral spreading, and minimizes the number of wells. The second objective is to use laboratory experiments to assess whether chemical mixtures or cyclic chemical renovation schemes are capable of providing both contaminant destruction and plugging control. Preliminary experiments have identified compounds capable of delaying precipitation or dissolving precipitates. We have hopes that even in with a passive scheme that plugging can be controlled in the immediate vicinity of wells. The third objective is to evaluate the kinetics of interactions among treatment chemicals and the porous medium in order to optimize design. It is well known that natural, oxidizable compounds in aquifer materials utilize  $\text{KMnO}_4$ . The well design requires knowledge concerning the fate and transport of  $\text{KMnO}_4$ .

**Research Progress and Implications**

As of the first year of this 3-year project, we have performed a series of column and small-scale flow tank experiments to investigate the problems related to the delivery of the permanganate to the subsurface contaminated area. Primary results of this study have been presented in the national conferences and as papers in peer-reviewed publications.

**(1) Permanganate reactive barrier system:**

In order to effectively deliver permanganate solid to a contaminant plume, a permanganate reactive barrier system (PRBS) was studied as a proof-of-concept. The design includes a series of vertical wells to deliver solid  $\text{KMnO}_4$  into the subsurface by diffusion out of the well casing. The

idea is to form a zone of localized reaction through dispersive mixing with dissolved TCE. Thus, as the contaminant plume passes the PRBS, *in situ* oxidation will destroy the contaminant and prevent further spreading. The PRBS involves a series of vertical wells to deliver solid  $\text{KMnO}_4$  to the subsurface, by diffusion out of the well casing. PRBS uses the solubility of  $\text{MnO}_4^-$  in water and dispersion to add appropriate quantities into the flow system. A thin, small 2-D glass flow tank with Teflon end fittings was constructed for the experiments (Figure 1). The flow tank was filled with medium silica sand. A 1 mm (inside diameter) Teflon tube was installed to represent well in the PRBS. The experiment began by flowing de-ionized water through the tank for two days. The inlet pump was then switched to deliver dissolved TCE at a concentration of 25,000  $\mu\text{g/L}$ . 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.



Figure 1. Experiment involving the proof-of-concept of the PRBS.

The proof-of-concept experiment demonstrated that the PRBS could deliver  $\text{MnO}_4^-$  to a dissolved plume at a stable, constant, and controllable rate.

## (2) Slow-release $\text{KMnO}_4$

We manufactured slow-release  $\text{KMnO}_4$  and began testing of properties through batch, column, and flow-tank experiments. Controlled-release and spreading of permanganate was tested using a small-scale flow tank experiment (Figure 2). Figure 3 shows permanganate contours after 93

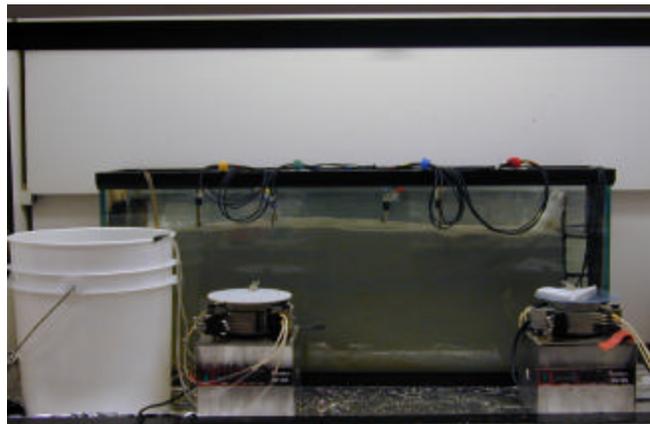


Figure 2. Flow tank experiment for slow-release  $\text{KMnO}_4$  test

days. Permanganate concentrations remained constant throughout the testing period and ranged from  $\sim 900$  ppb nearby the upstream PRBS to  $\sim 100$  ppb in the downstream end of the tank. Flow tank experiment demonstrated that our slow-release  $\text{KMnO}_4$  scheme would be capable of controlling low-concentration DNAPL plumes in a long-term, passive manner.

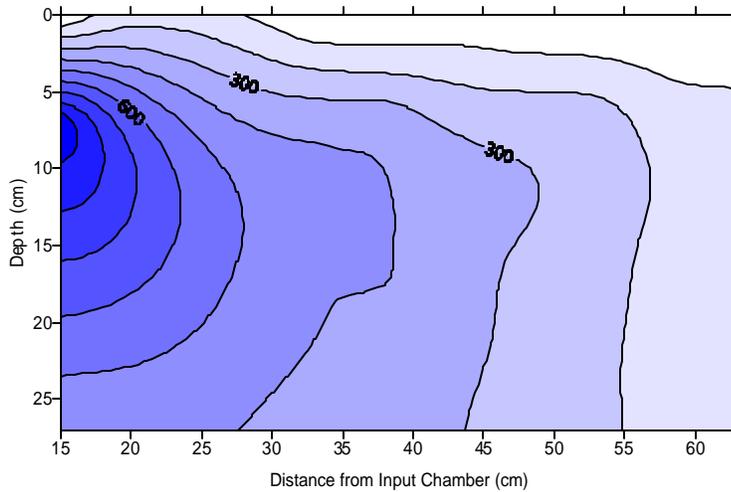


Figure 3. Permanganate contours in the flow tank after 93 days (unit: ppb)

### Planned Activities

During the next year, our study will focus on investigating through both experimental and numerical model approach the factors controlling the release and spreading of the slow-release  $\text{KMnO}_4$  to saturated porous media. A thorough understanding of the dissolution kinetics will help to find the best chemical additions to control or eliminate the precipitate which causes the poor efficiency in the source zone flooding scheme. Our additional tasks will then be to determine the dissolution rate of  $\text{KMnO}_4$  under different conditions of plugging by performing a series batch and flow tank experiments and to further test the PRBS system in a larger, more realistic flow tank experiments. Further, our study group is collaborating with South Korean researchers (Yonsei University and Korean Agricultural and Rural Industrial Corporation) for a field application of our PRBS system at a constructed test cell site in Korea. Funding for the test cell study has not been secured and is being requested through various agencies.

### Information Access

Lee, E.S. and Schwartz, F.W., 2002, Slow-release permanganate from solid  $\text{KMnO}_4$  in TCE contaminated zone, Geological Society of America Annual Meeting, Denver, CO.