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IN SITU CHEMICAL OXIDATION OF CONTAMINATED GROUND WATER: PERMANGANATE REACTIVE BARRIER SYSTEM FOR THE LONG-TERM TREATMENT OF CONTAMINANTS

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In situ chemical oxidation of chlorinated solvents with permanganate has proven to be effective in destroying these compounds in the aqueous phase. Due to its high solubility and strong reactivity with aquifer materials, permanganate has to be delivered right on the targeted contaminant at a controllable rate. A semi-passive, well-based permanganate reactive barrier system (PRBS) was designed in order for the long-term treatment of dissolved contaminant in the ground water. Results from laboratory experiments indicate the PRBS could to deliver permanganate at a stable, constant and controllable rate. In this paper, different field designs of the PRBS are discussed and tested with numerical simulations.

DESIGN OF THE PERMANGANATE REACTIVE BARRIER SYSTEM

The design of PRBS includes a series of vertical wells to deliver solid potassium permanganate into the subsurface, through diffusion out of the well casing. A mechanism has been developed to control the release rate of permanganate from the well into the ambient ground water. The idea is to form a zone of localized reaction through dispersive mixing with dissolved contaminant. Thus, as the contaminant plume passes the PRBS, *in situ* oxidation will destroy the contaminant and prevent further spreading.

Various types of PRBS were proposed here. Interception type can be used to cut-off the contaminant plume. Source flooding type, with higher permanganate release concentration, can be used in DNAPL source area to enhance the reduction of

contaminant at source zone. One or more PRBSs can be applied to the same site, which is one tier, two tier or multiple tier type. Due to the effect of density-driven flow, different types of PRBS were designed at certain vertical location for better targeted delivery, which includes hanging, centered and bottom release type. A combination of designs of PRBS may be applied to a particular remediation site based on site specific geological, hydrological and contaminant information.

CONSUMPTION OF MnO_4^- BY AQUIFER MATERIALS

Batch studies were utilized to investigate the consumption of MnO_4^- by sediments. Twenty-three samples were collected from various media, such as, alluvium, glacial till, glacial outwash and carbonate sand. Fifteen grams of each sediment sample was mixed with 15 mL of 2.5 g/L $KMnO_4$ solution. A control was prepared with the same $KMnO_4$ solution, but without the sediment. 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. MnO_4^- concentrations were measured with a Varian Cary 1 UV–visible spectrophotometer at a wavelength of 525 nm.

Results of batch experiments to examine the consumption of MnO_4^- by natural materials are plotted in Figure 1. After 10 days, for more than half of samples of natural sediment, irrespective of type, MnO_4^- concentrations dropped to near zero, with more than 99% of MnO_4^- consumed. The decrease in the MnO_4^- concentration appears following a first order kinetic rate law for most of the samples (Figure 1). Because MnO_4^- is likely conservative in the aqueous phase, it is unlikely concentration reductions were caused by sorption onto the solids.

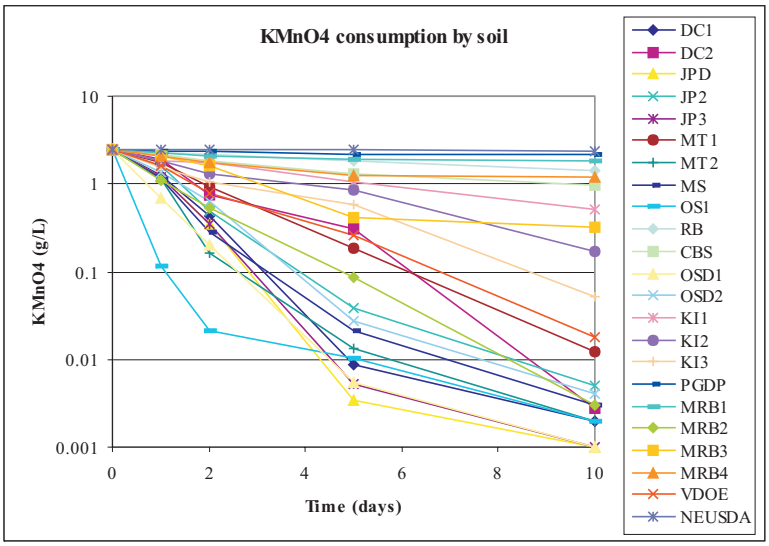

Figure 1. Utilization of MnO_4^- through oxidation of various sediments. The initial MnO_4^- concentration is 2.5 g/L.

NUMERICAL SIMULATION OF THE DESIGN PRBS

Numerical simulation was conducted to elucidate the parameters that will influence the field implementation of a PRBS. SUTRA, a three-dimensional model for saturated-unsaturated, variable-density ground-water flow with solute or energy transport developed by USGS was used for the modeling. We investigated issues such as permanganate consumption by aquifer materials, variable density flow effect, as well as lateral spreading under different geological settings. Permanganate consumption rates determined from the batch experiment were used in the model. Our simulation has shown that density-driven flow can sink the permanganate plume (Figure 2) and deviate from a perfect match with the contaminant plume. In this case, a maximum target concentration for permanganate should be determined through modeling to avoid such deviation. It may require a multiple tier type of PRBS in order for a complete destruction of the dissolved contaminant.

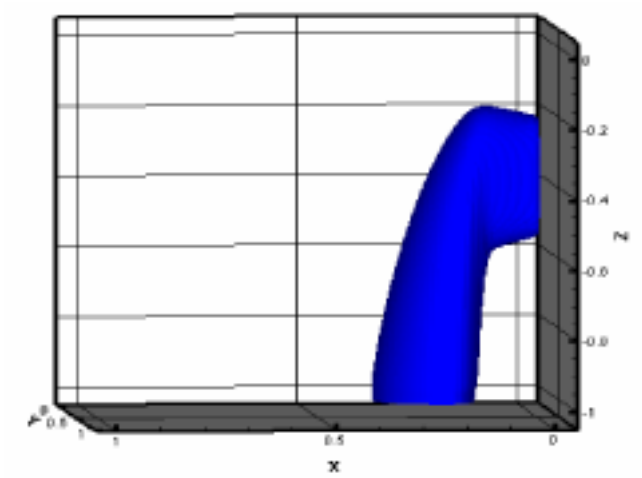

Figure 2. Distribution of permanganate driven by density flow may alter the path of the PRBS plume as shown in this numerical simulation.

Results from this study continue to point to the promise of *in situ* chemical oxidation scheme. PRBS provides a potential treatment of the contaminated ground water at relatively low management cost as compared with other alternatives