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Characterization of controlled-release $KMnO_4$ (CRP) barrier system for groundwater remediation: A pilot-scale flow-tank study

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Abstract

Release and spreading of permanganate (MnO_4^-) in the well-based controlled-release potassium permanganate ($KMnO_4$) barrier system (CRP system) was investigated by conducting column release tests, model simulations, soil oxidant demand (SOD) analyses, and pilot-scale flow-tank experiments. A large flow tank ($L \times W \times D = 8\ m \times 4\ m \times 3\ m$) was constructed. Pilot-scale CRP pellets ($OD \times L = 0.05\ m \times 1.5\ m$; $n = 110$) were manufactured by mixing ~198 kg of $KMnO_4$ powders with paraffin wax and silica sands in cylindrical moulds. The CRP system ($L \times W \times D = 3\ m \times 4\ m \times 1.5\ m$) comprising 110 delivery wells in three discrete barriers was constructed in the flow tank. Natural sands (organic carbon content = 0.18%; SOD = 3.7–11 g MnO_4^- kg^{-1}) were used as porous media. Column release tests and model simulations indicated that the CRP system could continuously release MnO_4^- over several years, with slowly decreasing release rates of 2.5 kg d^{-1} (day one), 109 g d^{-1} (day 100), 58 g d^{-1} (year one), 22 g d^{-1} (year five), and 12 g d^{-1} (year 10). Mean MnO_4^- concentrations within the CRP system ranged from 0.5 to 6 mg l^{-1} during the 42 days of testing period. The continuously releasing MnO_4^- was gradually removed by SOD limiting the length of MnO_4^- zone in the porous media. These data suggested that the CRP system could create persistent and confined oxidation zone in the subsurface. Through development of advanced tools for describing agent transport and facilitating lateral agent spreading, the CRP system could provide new approach for long-term *in situ* treatment of contaminant plumes in groundwater.

Keywords: Groundwater; Remediation; $KMnO_4$; Controlled-release system; Reactive barrier

1. Introduction

In situ chemical oxidation (ISCO) using potassium permanganate ($KMnO_4$) has been investigated as a remedial technology for groundwater since 1990s (e.g., Vella and Veronda, 1992; Schnarr et al., 1998; Yan and Schwartz, 1999, 2000; Zhang and Schwartz, 2000; Siegrist et al., 2001; Lowe et al., 2002; Lee et al., 2003). The technique is considered promising because of the rapid destruction of chlorinated solvents like trichloroethylene (TCE) and dichloroethylene (DCE), relatively cheap cost, and the ease of field implementation. It has been applied for remediation of over 100 sites worldwide (e.g., Siegrist et al., 2001).

Although the ISCO scheme is regarded as a developing technology in an industrial sense, it has not been researched extensively. For example, beyond the active flushing scheme, there have been relatively limited investigations in how the ISCO might be better used. Flushing scheme utilizes wells to inject and extract $KMnO_4$ solution through the contaminant source in the subsurface to clean up contaminated groundwater. Despite many promising results,

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however, efficiency associated with $KMnO_4$ flushing tends to diminish with time due to pore plugging associated with formation of low-permeability reaction products, i.e., MnO_2. Lee et al. (2003) demonstrated from flow-tank experiments that destruction efficiencies greatly diminished with time due to the plugging of porous media by MnO_2. Schroth et al. (2001) reported from column experiments that the formation of MnO_2 and CO_2 gas decreased the relative permeability of the porous medium by 53–90%. In a 2-D flow-tank experiment, Li and Schwartz (2004) found that the dense and non-aqueous phase liquid (DNAPL) mass removal rate by $KMnO_4$ flushing was greatest in the early stages of flushing, but decreased dramatically as the treatment proceeded due to formation of MnO_2 precipitates around zones of higher DNAPL saturation. This localized plugging of aquifer over time was suggested to be sufficient to prevent the efficient delivery of permanganate (MnO_4^-) solution to zones of high TCE or DCE saturation. In field settings, leaving volumes of untreated DNAPL in place contributes to a rebound in aqueous concentrations once flushing is discontinued (e.g., Siegrist et al., 2001). These observations suggested that development of a new approach that can provide both contaminant destruction and plugging/MnO_4^- control would be required.

A well-based ISCO reactive barrier system using controlled-release $KMnO_4$ (CRP) has been recently developed as a new long-term treatment option for aqueous-phase plumes of DNAPLs in aquifers (Lee and Schwartz, 2007a). This CRP system was designed to operate in a semi-passive manner with periodic additions of the CRP pellets into the well-based reactive barriers. As groundwater flows through the wells, MnO_4^- is released to maintain predetermined level of MnO_4^- concentration within the barrier system. Capability of the CRP scheme for releasing MnO_4^- and destroying aqueous-phase TCE plume in porous media has been verified by laboratory-scale column experiments, flow-tank test, and model simulations (Lee and Schwartz, 2007a). In a subsequent study, a generalized numerical model was developed and applied to describe release patterns of agents from controlled-release systems of variable designs (Lee and Schwartz, 2007b). One of next steps in developing the CRP scheme is characterizing MnO_4^- release and spreading in large-scale simulations and experiments. This paper describes release characteristics of pilot-scale CRP and presents results of pilot-scale experiment with a flow tank, showing how the CRP system could create long-term oxidation zone in the subsurface. Results of this study will provide useful information for construction of CRP systems in contaminated aquifers.

2. Materials and methods

2.1. Test-cell construction, CRP manufacture, and column release test

Four pilot-scale flow tanks (tank dimension: $L \times W \times D = 8\text{ m} \times 4\text{ m} \times 3\text{ m}$) were constructed. One of the four tanks was used for this study (Fig. 1, Supplementary material 1). The test cell was filled with 95 tonnes of natural sands, which was packed to an approximate bulk density of 1.47 g cm^{-3}, porosity of 0.45, and depth of 2 m. Input and output chambers on the upstream and downstream ends of the tank helped to control inflow and outflow rates. These chambers were separated from the sand by rigid stainless steel screens to prevent sands from entering the chambers. Tap water (2900 l d^{-1}) was introduced into the inflow chamber to create a uniform flow into the upstream end of the tank. The outflow rate was controlled using water-level control dam installed within the output chamber (Fig. 1, Supplementary material 1).

An extruded form of $KMnO_4$ comprising silica and clays as a means of delaying the dissolution of $KMnO_4$ in water (CAIROX®-CR) is commercially available. Microcapsules of $KMnO_4$ having slow-release properties have also been described in the literature (Kang et al., 2004; Ross et al., 2005). For this study, 110 pilot-scale CRP cylinders ($OD \times L = 5\text{ cm} \times 150\text{ cm}$) were manufactured using the moulding technique (e.g., Lee and Schwartz, 2007a) by dispersing 198 kg $KMnO_4$ granules (CARUS Co. Ltd., USA) in paraffin wax-silica sands matrix (mass of $KMnO_4$ in one CRP = 1.8 kg). Column tests were performed using a plastic column to determine release rates of CRP in flowing water. Subset of the CRP ($OD \times L = 5\text{ cm} \times 20\text{ cm}$) was used for column experiment. Ambient flow rates of 5.76 l h^{-1} were maintained using Ismatec peristaltic pumps (Eijkelkamp Co. Ltd., Netherlands) to regulate perfect sink conditions for CRP release.

2.2. Tracer test

After flushing the sandy media with the tap water for 150 days, a tracer test was conducted to describe solute transport in the flow tank. Bromide tracer solution (40 l, 400 mg l^{-1}) was injected from three upstream delivery wells (C1.0, D1.0, D1.0; see Supplementary material 2 for well locations.) for 1 h. Samples were collected from the monitoring wells downstream of the injection points for one week.

2.3. Sample collection and chemical analyses

Forty two multi-level monitoring wells were emplaced in a rectangular array within the sandy media (see Supplementary material 1). They were constructed with 700 μm stainless steel diffusion stones ($OD \times L = 1.5\text{ cm} \times 10.5\text{ cm}$) attached to the end of polyurethane tubing (ID = 8 mm). Sampling points were set at approximate depths of 1, 1.5, and 2 m below the top of the sandy medium. Approximately 20 ml of water sample was pumped out from each sampling point using a peristaltic pump and prepared for chemical analyses. Bromide concentration was analyzed with ion chromatography (Dionex