SUSTAINED-RELEASE PERMANGANATE (REMOX® SR ISCO REAGENT) AND PERSULFATE FOR PASSIVE TREATMENT OF CHLORINATED SOLVENTS AND EMERGING CONTAMINANTS

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ABSTRACT

A sustainable, simple, and low O&M approach has been developed using innovative oxidation chemistries in concert with innovative slow-release deployment strategies to achieve passive, cost-effective treatment of large chlorinated solvent and emerging contaminant plumes. This novel remedial technology involves oxidants in the form of sustained-release permanganate and sustained-release persulfate. Paraffin wax is used as the environmentally benign and biodegradable matrix material for encapsulating solid potassium permanganate ($KMnO_4$) or sodium persulfate (NaS_2O_8) particles. Sustained-release (SR) oxidants contain ~80% permanganate or unactivated persulfate and can be formed as cylinders for direct push applications, inserted into holders for emplacement in permanent or temporary wells. The material may also be chipped/cubed for hydro-fracturing into low permeability media for treating back diffusion of organic contaminants. This presentation will provide the results of a variety of experimental and modeling efforts as well as preliminary results from RemOx® SR ISCO Reagent pilot-scale field studies.

Keywords: Permanganate, Persulfate, Passive, Chlorinated Solvents, Chemical Oxidation

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1. INTRODUCTION

Reactive materials in barrier and zone configurations have proven very effective at transforming or destroying organic contaminants *in situ*. Controlled-release techniques have been utilized extensively in diverse fields such as pharmaceutical and agricultural applications. Sustained-release of an oxidant during *in situ* chemical oxidation (ISCO) is an emerging concept that is extremely relevant to the field of environmental remediation. ISCO using the oxidants permanganate, persulfate, and catalyzed hydrogen peroxide has shown great promise for remediation of many recalcitrant organic contaminants of concern (COC). Because the oxidants are highly soluble the presence of a protective barrier that slows down and controls oxidant release could enhance the efficiency of ISCO and allow for long-term passive treatment of organic contaminants in reactive barriers and zones (Figure 1).

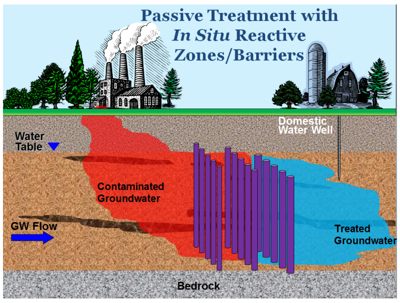


Figure 1: Conceptual Model of Sustained-Release Oxidant Reactive Barriers/Zones

To this end, sustained-release (SR) permanganate and persulfate has been developed. Paraffin wax is used as the environmentally benign and biodegradable matrix material for encapsulating the solid potassium permanganate ($KMnO_4$) or sodium persulfate ($Na_2S_2O_8$). The paraffin matrix protects the oxidant particles from instant dissolution and potentially undesirable nonproductive reactions. The oxidants are released from the cylinders through the processes of dissolution and diffusion. The SR oxidants contain ~80% permanganate or unactivated persulfate and can be formed as cylinders for direct push technology (DPT) application, emplaced in holders and installed in existing wells, or manufactured as spherical bee-bees for hydro-fracturing into low permeability media (Figure 2).

Figure 2: Sustained-Release Permanganate Cylinders (left), Sustained-Release Persulfate Cylinders (middle), and Sustained-Release Bee-Bees

The SR permanganate or persulfate cylinders are manufactured in two sizes: 1) 1.35 inch diameter and 18 inches long and 2) 2.5 inch diameter and 18 inches long. These particular dimensions were chosen so that the cylinders would easily fit into traditional DPT tooling. The SR bee-bees are in the experimental and manufacturing development stage and range in size from 5-8 mm.

2. OBJECTIVES

A variety of experiments were conducted to: 1) characterize oxidant release from a variety of SR cylinder sizes and small cubes, 2) determine contaminant removal efficiencies, and 3) develop a model to characterize the release of oxidants from SR cylinders. One-dimensional (1-D) column and two-dimensional (2-D) tank experiments were conducted to evaluate permanganate or unactivated persulfate release behavior using deionized (DI) water (Figure 2). For the 1-D column and 2-D tank studies a variety of cylinders with different diameters were emplaced into the sand pack and DI water was used as the influent. The purpose of these experiments was to determine if data obtained from small laboratory created mini-cylinders would provide data that could be scaled-up and applied to SR cylinders that would be used in the field and support the development of an SR Design Tool. In addition, 1-D column experiments were conducted with SR permanganate cubes with dissolved trichloroethene (TCE) as the influent to evaluate TCE removal efficiency (Figure 3).

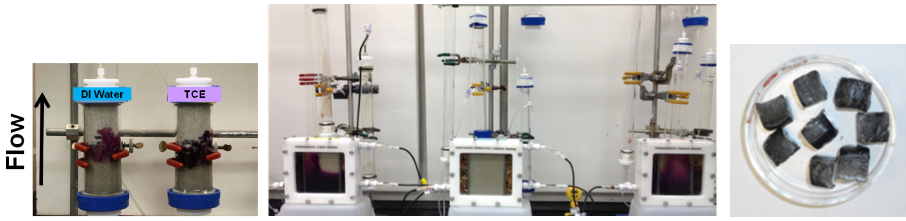
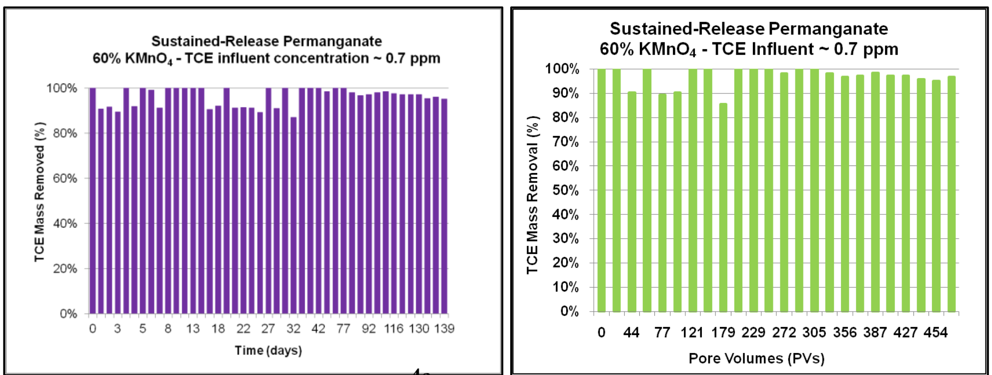


Figure 3: 1-D Columns (left), 2-D Tanks (middle), and SR Permanganate Cubes (right)

For the 1-D column studies, the influent TCE concentrations were 0.7 mg/L. The flow rates for the column and tank studies was approximately7 mL/min. Column and tank effluent samples were collected and analyzed for TCE and oxidant throughout the duration of the experiments.

3. RESULTS

The results of 1-D SR permanganate column studies with dissolved TCE as the influent resulted in TCE removal efficiencies ranging from 87%-100% over 170 days of operation (Figures 4a and 4b).



4a 4b

Figures 4a and 4b: 1-D Column with SR Permanganate Cubes, TCE Influent (left) – Removal Efficiencies as a Function of Time or Pore Volumes (right)

To further evaluate SR permanganate performance the temporal $KMnO_4$ release rates (Flux, J) and concentration ratio (C_r) were determined. The flux was calculated using equation 1

$$J = (Cn+1V-CnV)/(tn+1 - tn)] \qquad (1)$$

where C_{n+1} = concentration of permanganate in solution at time t_{n+1}, C_n = concentration of permanganate in solution at time t_n, V = the volume of the solution, and $t_{n+1} - t_n$ = elapsed time between sampling time points. The concentration ratio was calculated using equation 2

$$C_r = CV/M \qquad (2)$$

where C = the permanganate concentration measured in the effluent, V = the solution volume, and M = the initial mass of permanganate in the SRP (Ross et al., 2005). The figures below illustrate the observed and projected permanganate flux from SR permanganate cubed material (Figure 5).

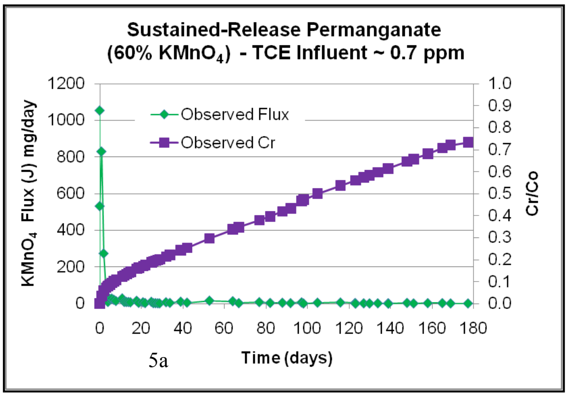


Figure 5: Observed and Projected Flux (*J*, mg/day and C_r) from Cubed SR Permanganate with Dissolved TCE influent

There is an initial high flux of permanganate (e.g., ~1100 mg/day) when flow is first started to the column as the exposed permanganate particles on the outside of the chipped material are dissolved in the TCE influent (Figure 5). The results of 2-D tank experiments with water as the influent indicate that paraffin wax effectively protected solid potassium permanganate and sodium persulfate particles from rapid dissolution (Figure 6).

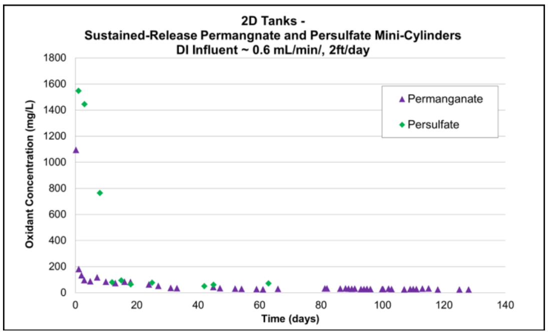


Figure 6: 2-D Tank Studies with SR permanganate or SR Persulfate Mini-Cylinders and DI Water Influent: Measured Data

SR permanganate release is generally characterized by a relatively fast initial rate followed by a significantly slower rate in the later phases (> 300 days). The measured and modeled permanganate concentrations from SR permanganate mini-cylinders fit the modeled data (Figure 7).

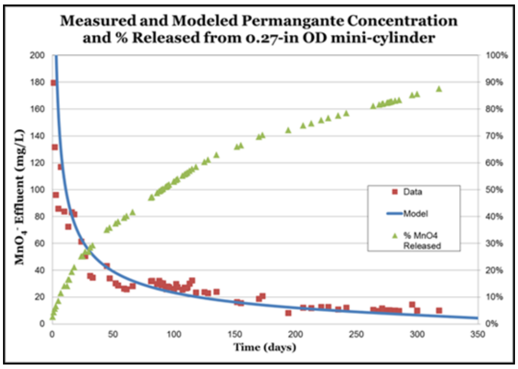


Figure 7: 2-D Tank with SR Permanganate Mini-Cylinder and DI Water Influent : Measured and Modeled Data

In addition to characterizing oxidant release and understanding contaminant degradation using the SR oxidants it is important to be able to model the release of the oxidants in support of the development of a SR Design Tool. The SR Design Tool will be a user friendly spreadsheet tool for pracitioners to use in order to design their site and understand cylinder spacing, cylinder longevity, oxidant transport as a function of time and space as well as other important parameters. The graph below illustrates that the measured permanganate release data obtained in a variety of experiments fits the simulated permanganate concentrations and that as expected there is a relationship with cylinder diameter (Figure 8).

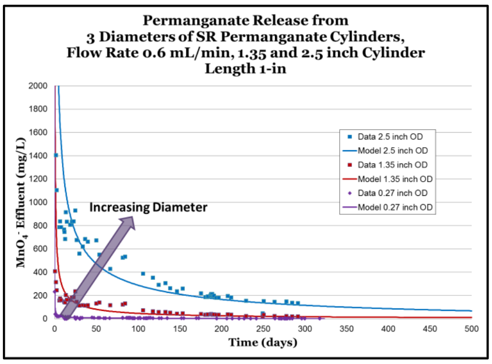


Figure 8: Permanganate release as a Function of SR Permanganate Cylinder Diameter: Measured and Modeled Data

Figure 8 establishes that as the cylinder diameter increases the permanganate concentrations that are released increase due the increased surface area.

3. CONCLUSIONS

These results support that a reactive SR oxidant barrier could serve as a long-term passive treatment for chlorinated solvents. There are a number of potential options for implementing SR oxidants including direct push or in-well applications for source or barrier treatment that will last years. The SR oxidant technology could allow for passive *in situ* treatment without above ground equipment/infrastructure with the added benefit of project monies being spent on the remedial treatment vs. man power or injection well installation. SR permanganate cylinders have been emplaced at over 10 sites to date, including one site in Brazil.

4. REFERENCES

Ross, C., Murdoch, L. C., Freedman, D. L., and Siegrist, R. L. (2005). "Characteristics of potassium permanganate encapsulated in polymer." *J. Env. Eng.*, 131(8), 1203-1211.