

# Laboratory and Modeling Efforts to Refine the use of In Situ Chemical Oxidation for Addressing Residual VOC Plumes on the Savannah River Site

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REFERENCE: *Proceedings of the 2011 Georgia Water Resources Conference*, held April 11–13, 2011 at The University of Georgia.

**Abstract.** In situ chemical oxidation (ISCO) has been widely used in recent years for the remediation of VOC contaminated soil and groundwater. Among several chemical oxidizing agents injected into the subsurface for ISCO, persulfate has often been selected due to the advantage of being less reactive and longer-lived in the subsurface environment. Through this research, the effect of side reactions occurring during the remediation of a VOC plume at the Department of Energy's Savannah River Site (SRS) was evaluated using lab-scale experiments as well as a model simulation. Two SRS soils with different mineral and organic compositions were used to study persulfate adsorption and consumption by the oxidation of soil organic matter. A high degree of reversible persulfate sorption was observed for the SRS materials that contained significant Fe oxides and limited organic matter. The consumption of persulfate caused by the oxidation of organic matter for the surface soil material was significant as well. The details of adsorbed persulfate speciation on the soil and oxidation of persulfate are currently under investigation using the PHREEQC geochemical modeling code.

## INTRODUCTION

Contaminated ground water plumes containing volatile organic compounds (VOC's) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) remain a major remediation challenge at the SRS (Seaman et al. 2007). Although PCE and TCE are not recognized as carcinogens, both human metabolites and natural microbial degradation products such as vinyl chloride (VC) may cause significant health risks (Sims et al. 1991; Russell et al. 1992). In recent years, the subsurface injection of chemical oxidizing agents (known as ISCO) has been successfully used in the remediation of VOC-contaminated groundwater. Highly reactive chemical oxidants such as persulfate, permanganate, Fenton's reagent, and peroxide have been used to degrade chlorinated solvents. Among them, persulfate has the advantage of being less reactive and longer-lived in the environment, providing greater residual effectiveness and the ability to deliver to more isolated aquifer zones within the subsurface environment where residual solvents may persist (Liang et al. 2007; Liang and Bruell 2008; Liang et al. 2008).

SREL conducted an initial site treatability test to evaluate the efficacy of Na-persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) in oxidizing TCE and PCE under the specific geochemical conditions of the field test site on the SRS. In addition to evaluating the reaction kinetics of the proposed oxidizing agent, laboratory tests also evaluated the effect of side reactions such as the adsorption of persulfate and the oxidation of soil organic matter. Persulfate adsorption by the SRS subsurface sediments was significant, presumably due to the presence of iron oxides in the sediment. Thus, the behavior of persulfate was further investigated using geochemical modeling techniques such as PHREEQC. The results of laboratory experiments and geochemical modeling will be used in refining the application of ISCO at the SRS and other VOC contaminated sites.

## MATERIALS AND METHODS

All chemicals used in this study were ACS grade or better. An artificial ground water (AGW) surrogate was used as the background solution. The composition of AGW was determined based on routine sampling of non-impacted water-table wells on the SRS (Strom and Kaback 1992) (mg/L): 1.00  $\text{Ca}^{2+}$ , 0.37  $\text{Mg}^{2+}$ , 0.21  $\text{K}^+$ , 1.40  $\text{Na}^+$ , and 0.73  $\text{SO}_4^{2-}$ . The 10 mM Na-persulfate treatment solution made of AGW was freshly prepared for the proper concentration of persulfate solution. Two soils (SRS A and SRS B) were used for the batch isotherms and column experiments. The characteristics of each soil are summarized in Table 1.

Approximately 5 g of each soil was placed in a pre-weighed Oak Ridge centrifuge tube for the batch experiments. The proper amount of AGW and the Na-persulfate treatment dosing solution were added to bring the total volume to 30 mL. The target persulfate concentration varied from 0.1 mM to 10 mM. The mixed samples were placed on a shaker and equilibrated for 24 hrs. The equilibrated samples were centrifuged for 10 min at 10,000 rpm; then the supernatant was filtered with 0.2  $\mu\text{m}$  pore size nylon syringe filter (VWR, West Chester, PA) prior to persulfate analysis. The pH and weight of each sample were monitored before and after the equilibration. Each treatment series had 3 sets of duplicates with blank control samples.

**Table 1. Water Physical, chemical, and mineralogical properties of SRS soil samples**

Sample	SRS A	SRS B
Sampling location	top	deep
PSD*	gm 100 gm <sup>-1</sup>	gm 100 gm <sup>-1</sup>
Sand (>53 µm)	85.3	68.2
Silt (53-2 µm)	3.1	3.9
Clay (<2 µm)	11.6	28.0
Tex. Classification*	loamy sandy	sandy clay loam
pH <sub>(water)</sub> **	4.63	5.10
EC <sub>(water)</sub> (µS cm <sup>-1</sup> )**	122.7	13.46
pH <sub>(KCl)</sub> ***	4.05	4.18
BET SA (m <sup>2</sup> g <sup>-1</sup> )	1.79	13.8
TOC (g 100g <sup>-1</sup> )	0.76	0.09
CDB Fe (mg gm <sup>-1</sup> )	1.65 ± 0.03	12.5 ± 0.3
CDB Al (mg gm <sup>-1</sup> )	0.76 ± 0.01	1.70 ± 0.03
Clay Mineralogy	K, HIV	K, Goe, (trace HIV)

\*PSD: Particle Size Distribution hydrometer method

\*\*2:1 solution/soil ratio in deionized water

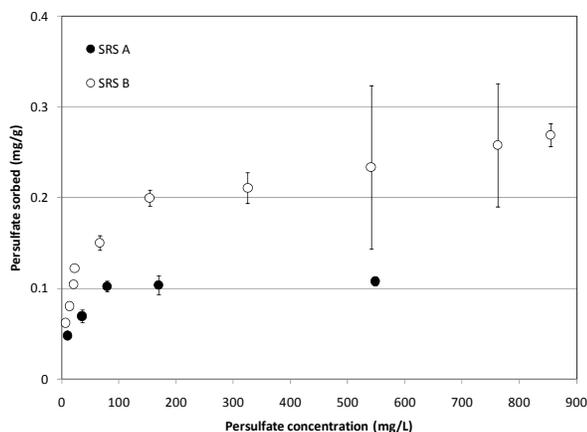
\*\*\*2:1 solution/soil ratio in 1M KCl

Clay mineralogy determined by XRD: K=kaolinite, HIV=hydroxy-interlayered vermiculite, Goe=goethite

Non-reactive acrylic columns (2.5 cm ID and 15 cm long) were packed with each kind of SRS soil for the continuous flow experiments. A 30 µm pore size nylon filter and a known amount of Ottawa sand were placed at the top and bottom end of the columns to improve the flow distribution over the cross section of the column. An AGW solution containing 1 mM of persulfate and tritiated water ( $\approx 200$  pCi mL<sup>-1</sup>) was introduced into the columns at 0.5 mL min<sup>-1</sup> rate under saturated conditions. The columns were saturated with AGW (minus persulfate and tritium) prior to the introduction of persulfate-containing AGW to determine the porosity of each column. A peristaltic pump was used to provide a constant flow from the bottom-to-top of the column, and a pressure transducer was installed at the inlet to monitor pressure build-up and clogging in the column during the experiment. Over the course of the column experiment, pH and electrical conductivity (EC) of the effluent were continuously monitored using a series

of flow-through cells, and the effluent was collected for chemical analysis. After persulfate breakthrough was observed, AGW without persulfate and tritium was leached through each column at the same flow rate (0.5 mL min<sup>-1</sup>) in order to evaluate persulfate desorption behavior and conduct a mass balance analysis to differentiate various sorption processes, i.e., reversible adsorption vs. reactant consumption.

The concentration of persulfate was quantified using a UV-Vis spectrophotometric method (Liang et al. 2008). Tritium concentration in the effluent was determined using liquid scintillation analysis (Agilent, Palo Alto, CA). The mineralogy was determined using XRD (X2 Advanced Diffraction system, Scintag Inc., Cupertino, CA), and BET specific surface area (SAA) was analyzed with surface area analyzer (ASAP2000, Micromeritics Inc., Norcross, GA) after fractionating the clay from the soil (Carter et al. 1986; Whittig and Allardice 1986).



**Figure 1. Batch persulfate isotherm on SRS Soil A and Soil B.**

Citrate-dithionite-bicarbonate (CDB) extraction was used to determine the amorphous Fe and Al in the soil (Mehra and Jackson 1960; Jackson et al. 1986). The extracted metal cations were quantified using ICP-OES (Optima 4300 DV, Perkin Elmer, Waltham, MA) after filtration with a 0.22  $\mu$ m syringe filter, and total organic carbon (TOC) was measured with a dry combustion method (Nelson and Sommers 1982).

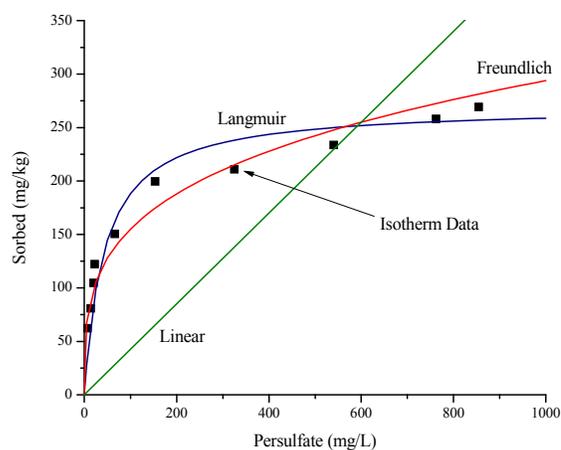
The PHREEQC geochemical code was used to study the adsorption mechanism of persulfate. The model code (version 2.17.5) was downloaded from the USGS PHREEQC web site ([http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled/phreeqc/](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/)). Most of the thermodynamic parameters for simulation were found in the database file prepared at Lawrence Livermore National Laboratory. If specific parameters were not available, optimized values were used through a trial-and-error method based on the comparison to the experimental data.

## RESULTS AND DISCUSSION

The results of the persulfate equilibrium sorption experiments using the SRS soils are shown in Figure 1. More persulfate was adsorbed on Soil B than Soil A, and the persulfate adsorption on Soil B had not fully leveled off, even at the highest concentration applied for the experiment. The observations may be related to the higher surface area and Fe oxide content of SRS soil B (Table 1). The measured BET surface areas of SRS B and SRS A were 13.8 and 1.79  $\text{m}^2/\text{g}$ , respectively. The SRS B soil also had a higher extractable iron concentration than SRS A, 12.5 compared to 1.65 mg Fe/g, respectively. The iron oxide in the soil is known as an important reactive site for surface complexation. Since the pH of the two SRS soils

was acidic, the surface of the SRS soils might have significant positive charge, enhancing the persulfate sorption. However, more detailed speciation on the surface needs to be further examined. Thus, PHREEQC geochemical model was adapted to conduct simulations to identify the specific species and the mechanism of surface complexation.

The sorption isotherm of persulfate for SRS B soil is described using three empirical sorption isotherms in Figure 2, i.e., Freundlich, Langmuir, and Linear partition coefficients. The persulfate sorption isotherm showed non-linear behavior. The comparison demonstrated the ability of the Langmuir isotherm to describe sorption behavior at lower treatment concentration ranges. On the other hand, the Freundlich isotherm was better able to describe persulfate sorption at higher treatment

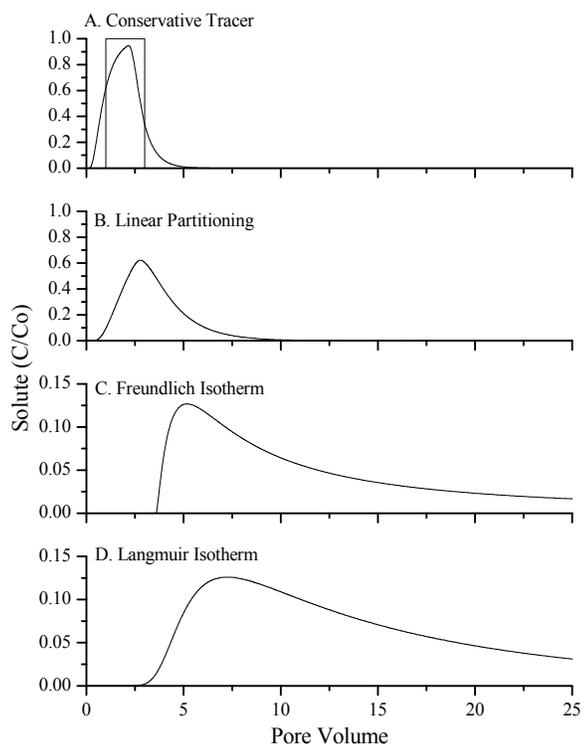


**Figure 2. Persulfate sorption isotherm data for Soil B described using the three most common empirical sorption isotherms: Freundlich, Langmuir, Linear partition coefficients.**

concentration ranges. This result could be simulated with the multiple layer surface complexation model with properly optimized equilibrium constants.

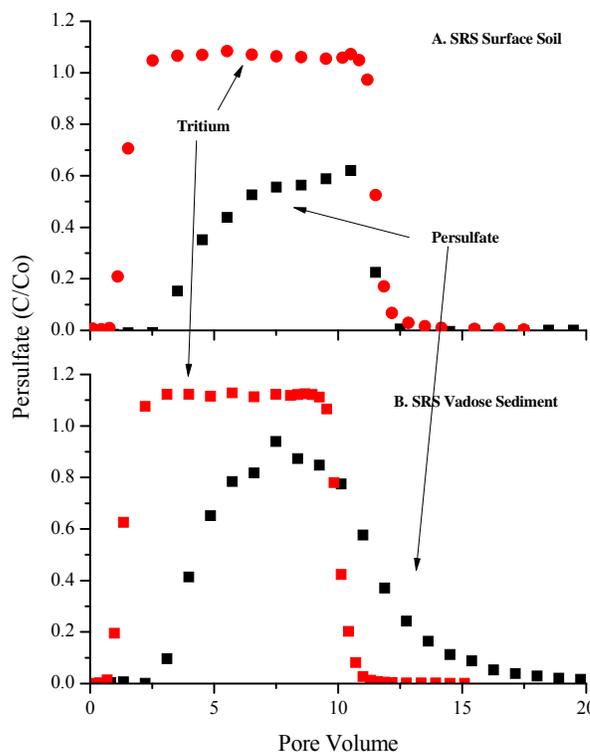
The breakthrough concentrations of persulfate and tritium are often reported in dimensionless terms as a fraction of the inlet treatment concentrations ( $C_0$ ), i.e.,  $C/C_0$ . Figure 3 illustrates the impact of isotherm shape on the transport behavior of a sorbing solute (in the present case, persulfate) when compared to a conservative tracer (i.e., tritium) in a simple one-dimensional transport system (such as the current laboratory column experiments) using a simulation. With the exception of the linear isotherm (i.e.,  $K_d$ ), the isotherm shape will greatly impact the observed persulfate recovery behavior.

The relative concentration profiles of persulfate and tritium from continuous column experiments are presented in Figure 4. The tritium did not react and showed a clear breakthrough during adsorption and desorption in both columns. Compared with tritium, the persulfate profile showed significant effects of adsorption and oxidation. The retardation of persulfate breakthrough during the adsorption was almost identical in both columns. However, the highest concentration of persulfate in the effluent from the Soil A column was approximately only two thirds of that from the Soil B column. The consumption of persulfate may be caused by the oxidation of soil organic matter existing in the soil. The organic



**Figure 3. Simulated relative outlet concentration ( $C_o = 200$  ppm) as a function of time (Pore Volume) for a reactive solute (2 PV pulse) based on sorption isotherm: (A) conservative, no partitioning; (B) Linear partitioning, (C) Freundlich partitioning; and (D) Langmuir partitioning.**

content (in terms of TOC) of Soil A was almost 10 times higher than the Soil B (Table 1). The tailing of persulfate during desorption was evident in the Soil B column, which was believed to be an effect of non-linear adsorption. The greater degree of reversible sorption observed for Soil B is presumably related to the greater amount Fe oxides, as estimated by CDB Fe extraction.



**Figure 4. Laboratory column results illustrating the influence of both persulfate consumption (SRS A) and sorption (SRS B) on persulfate fate and transport in SRS soils and aquifer sediments.**

## SUMMARY AND CONCLUSION

The behavior of persulfate in SRS soils, according to the experimental results, was a combination of adsorption and oxidation. Depending on the soil characteristics, the dominant mechanism might shift from one to another. To apply the persulfate injection effectively in ISCO at the SRS, precise understanding of these reactions is essential. To address this issue more clearly, geochemical modeling will be conducted to account for both reaction scenarios.

## ACKNOWLEDGEMENTS

The project was funded by Cooperative Agreement DE-FC09-96SR18546 between The University of Georgia and the Department of Energy.

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