

In-Situ Chemical Oxidation to Address Residual VOC Plumes on the Savannah River Site

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Abstract. Groundwater plumes containing volatile organic contaminants (VOCs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) remain a major groundwater remediation challenge at various industrial and governmental facilities, including the Department of Energy's Savannah River Site (SRS) located near Aiken, SC. In an effort to address such challenges, the Savannah River Ecology Laboratory (SREL) working in collaboration with Savannah River Nuclear Solutions, LLC-Area Completion Projects (SRNS-ACP) and Redox Tech, Inc. conducted a field-scale technology demonstration to evaluate the utility of in situ chemical oxidation (ISCO) to address residual VOC contamination on the SRS. The chemical oxidant persulfate ($S_2O_8^{2-}$) was chosen because of its limited hazard and extended persistence in the groundwater environment, an advantage in systems where effective contact between the oxidant and target compounds may be kinetically limited.

Prior to designing the field demonstration, a series of laboratory batch experiments were conducted to evaluate the efficacy of various ISCO treatment scenarios under geochemical conditions representative of the SRS. The batch studies evaluated the effectiveness of persulfate and permanganate as oxidants in the presence and absence of various activating agents, including a strong base (i.e., NaOH), Fe(II), common Fe minerals, and Fe-oxide rich SRS sediments. Results indicated that base-activated persulfate was effective in destroying VOCs within two weeks both in the presence and absence of Fe-oxide rich SRS sediments.

The ISCO demonstration site was located in an area of the SRS with an extensive VOC plume with TCE concentrations ranging from 10 to 40 mg L⁻¹. The test site consisted of an injection well (IW) and three observation wells (OW1-OW3), with monitoring wells OW1 and OW2 screened at two depths within the contaminated aquifer. The persulfate reactant was injected intermittently over a ten day period as 10 oxidant batches (≈ 230 g Na₂S₂O₈ L⁻¹) totaling 4,800 gallons (18,168 L). After injection, the observation wells were sampled periodically with the pH, electrical conductivity (EC) and oxidation reduction potential (ORP) determined in the field, and samples were collected for VOC, persulfate, chloride (Cl⁻), sulfate (SO₄²⁻), and metals analyses. The current discussion will focus on the results from OW1 located closest (15 ft) to

IW, the only observation well clearly impacted by persulfate injection. Quantifiable concentrations of persulfate were detected in OW1 approximately two weeks after injection, peaking at ≈ 150 mg L⁻¹ and then slowly decreasing over the 295 days of monitoring. Injectate breakthrough in OW1 was also evident in the EC and Na⁺ concentrations, with ORP increasing initially and then becoming more variable with continued monitoring. TCE and PCE concentrations in OW1 were much lower than observed in OW2 and OW3 throughout the duration of the study. Although some dilution is inherent in the *in situ* chemical treatment of aqueous phase contaminants, elevated concentrations of Cl⁻ and SO₄²⁻ observed in OW1 are indicative of VOC destruction resulting from chemical oxidation.

Subsequent laboratory experiments confirmed the somewhat limited mobility of persulfate in the SRS subsurface environment due to sorption in Fe-oxide rich materials, a factor that can in part account for low persulfate recoveries in the current study. However, some degree of reversible sorption combined with oxidant persistence can facilitate the remediation of aqueous-phase VOCs through the formation of a chemically reactive treatment zone. Furthermore, batch results confirmed the continued effectiveness of persulfate in degrading VOCs in the absence of an activating agent at the relatively low persulfate concentrations (≤ 192 mg L⁻¹) observed in OW1.

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