

Treatment of AFFF-Impacted Groundwater Using an Electrochemical and Biological Treatment Train Approach

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Background/Objectives. The presence of poly- and perfluoroalkyl substances (PFASs) is a rapidly growing environmental concern. As part of this SERDP-funded research project, both short- and long-term bench-scale studies were performed to assess the effectiveness of boron-doped diamond electrodes for both ex situ and in situ treatment of PFASs under relevant field conditions, and using AFFF-impacted groundwater. Reaction mechanisms were assessed, defluorination pathways were observed, and biological treatment of oxidation byproducts was performed.

Approach/Activities. Electrochemical treatment of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) using a boron-doped diamond (BDD) anode was investigated in a series of bench-scale batch experiments. Experiments focused on assessing the impacts of chloride electrolyte and of hydroxyl radical scavenger *tert*-butyl alcohol (TBA) on both the rates of PFOA and PFOS removal, and the corresponding rates of defluorination. Treatment of PFOA and PFOS in natural groundwater impacted with both fresh and aged AFFF also was assessed, and long-term experiments were performed to assess changes in electrode reactivity over time. Finally, in situ biological treatment of electrochemically generated perchlorate was assessed.

Results/Lessons Learned. Results showed that the presence of chloride and TBA had no measureable effects (within 20%) on the observed rates of PFOA and PFOS removal and defluorination for the range of applied current densities (3 to 50 mA/cm²), and at environmentally relevant concentrations. Treatment rates of PFOA and PFOS in natural groundwater were within a factor of two of those measured in electrolytes at a current density of 15 mA/cm² and environmentally relevant concentrations. These findings are consistent with PFOA and PFOS treatment where rates are controlled by anodic surface reactions, and that the presence of any organic co-contaminants that might serve as hydroxyl radical scavengers would likely not adversely impact treatment of PFOA and PFOS. PFOA removal was greater than that of PFOS, especially at lower current densities.

AFFF-impacted groundwater was evaluated in multiple systems. Removal of PFOS, PFOA, and a large suite of precursor compounds was evaluated as a function of groundwater geochemistry and current density. Results showed that electrochemical treatment oxidized the precursors, followed by removal of the perfluorinated species. Preliminary oxidation pathways were determined. Results also suggest that groundwater geochemistry may have a significant impact on overall treatment effectiveness. Long-term experiments showed no decrease in PFOA or PFOS removal over time. Finally, it was demonstrated that perchlorate produced by oxidation of Cl⁻ during electrochemical treatment could be biologically treated in bioaugmented sand columns, with a 3-log removal observed over a 9-day residence time.