Long-Term Performance Monitoring of Zero-Valent Iron Sites

Laura Cook, PG, LEED GA (Laura.Cook1@Jacobs.com) (Jacobs, Virginia Beach, VA, USA)
Kyle Kirchner (United States Army, Fort Riley, KS USA)
Jovan Popovic (NAVFAC EXWC, Port Hueneme, CA, USA)
Dean Williamson (Jacobs, Gainesville, FL, USA)
Rick Wilkin (USEPA, Ada, OK, USA)
Rick Johnson (OHSU, Portland, OR)

Background/Objectives. Since its initial use for groundwater treatment in 1994, zero-valent iron (ZVI) has been demonstrated to be an aggressive and effective treatment for volatile organic compounds (VOCs) at numerous sites. However, data collection following treatment has been focused primarily on compliance and VOC concentrations. Little focus has been placed on determination of iron longevity and degradation processes following iron treatment such as a shift from beta elimination to reductive dechlorination and secondary reactivity from bivalent iron minerals such as magnetite or iron sulfides. The focus of this study was to determine the long-term performance of iron at sites 5-12 years following treatment and to identify the most prevalent degradation processes at these more mature ZVI treatment sites.

Approach/Activities. A desktop review of nine sites with ZVI treatments completed at least 5 years prior to initiation of this study was conducted to assess long-term performance based on existing data. Two sites were identified for further field study, one soil mixing site and a landfill with a ZVI permeable reactive barrier. ZVI samples were collected from the two field test sites and mineralogy and reactivity were evaluated using x-ray diffraction (XRD), x-ray absorption near edge structure (XANES) spectroscopy, magnetic susceptibility, magnetic separation, energy dispersive line scans, acidification and hydrogen generation and resazurin dye testing. Site groundwater samples were collected and analyzed for site contaminants, total and dissolved metals, total organic carbon (TOC), chloride, fluoride, nitrate, nitrite, sulfide, sulfate, phosphate, alkalinity, hardness, sulfide, ammonia, methane, ethane, ethene, and acetylene. Field measurements including pH, dissolved oxygen (DO), and oxidation/reduction potential (ORP) were also collected. Microbial populations were assessed through Next Generation Sequencing (NGS) and QuantArray-Chlor analysis. Water levels and slug testing were completed to assess impacts of mineralization on hydraulic characteristics of each site.

Results/Lessons Learned. Results indicated ZVI remaining at both sites is weathered with some passivation due to precipitation of coatings (e.g., calcium carbonate) and transformation of ZVI into less reactive minerals. Remaining iron identified was primarily magnetite and goethite. However, despite the passivation, evidence of both primary and secondary reactivity (through iron sulfide minerals) was noted. ORP values as low as -400 millivolts (mV) or lower were observed in some locations, indicating likely presence of reactive ZVI. Resazurin testing indicated higher reduction potential for the treated source area core material relative to background. Notable geochemical changes were observed across the PRB and mixing area including decreases in calcium, magnesium, strontium, and alkalinity and increases in methane, ethane, and ethene. A “clean front” was also observed on the immediate downgradient side of the PRB, indicating continued treatment of VOCs. At the PRB site, halorespiring bacteria were not detected downgradient of the wall. Genes involved in aerobic direct metabolism and cometabolism of VC were also not identified. However, NGS data indicate the presence of sulfur-oxidizing bacteria (*Sulfurimonas*) just downgradient of the wall, but not in other portions of the site, which may be a result of the release of reduced sulfur species in groundwater from the PRB. At the mixing site, concentrations of halorespiring bacteria were one to three orders of magnitude higher within the mixing area and downgradient of the mixing area than they were cross-gradient or upgradient indicating enhancement of biological degradation processes. Genes associated with direct metabolism and/or cometabolism of VC were also present indicating possible aerobic microzones with multiple biological degradation processes occurring at the site. Hydraulic evaluations at both sites indicated precipitation of minerals such as calcium carbonate is not impacting hydraulic conductivity or remedy performance.