Long-term geochemical behavior of a zerovalent iron permeable reactive barrier for the treatment of hexavalent chromium in groundwater

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Passive, in-situ reactive barriers have proven to be viable, cost-effective systems for the remediation of Cr-contaminated groundwater at some sites. Permeable reactive barriers (PRBs) are installed in the flow-path of groundwater, most typically as vertical treatment walls. Redox-active solids used in PRBs, such as zerovalent iron (ZVI), promote rapid removal of redox-sensitive contaminants, such as Cr, by various mechanisms including adsorption and reductive precipitation. Further development of PRB technology to improve long-term performance, reduce operation and maintenance costs, and to plan post-remediation activities requires a better understanding of the mechanisms responsible for contaminant removal in and around reactive barriers. Long-term trends in groundwater geochemistry and solid-phase characteristics were examined in a full-scale, zerovalent iron, PRB installed in 1996 to treat groundwater contaminated with hexavalent chromium. After 8 years of operation, the PRB remains effective at reducing concentrations of Cr from average values >1500 μg L^{-1} in groundwater hydraulically upgradient of the PRB to values <1 μg L^{-1} in groundwater within and hydraulically downgradient of the PRB. Chromium removal from groundwater occurs at the leading edge of the PRB and also in the aquifer immediately upgradient of the PRB. These regions also witness the greatest amount of secondary mineral formation due to steep geochemical gradients that result from the corrosion of zerovalent iron. X-ray absorption near-edge structure (XANES) spectroscopy indicated that chromium is predominantly in the trivalent oxidation state within and around the PRB, confirming that reductive processes are responsible for Cr sequestration. XANES spectra and microscopy results suggest that Cr is, in part, associated with iron sulfide grains formed as a consequence of microbially-mediated sulfate reduction. Results of this study provide evidence that secondary iron-bearing mineral products may enhance the capacity of zerovalent iron systems to remediate Cr in groundwater.

Presence and impact of micro-organisms in zero-valent iron barriers

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The use of zero-valent iron in reactive barriers has been shown to be very effective for passive, long-term applications of groundwater remediation. Despite significant degradation efficiencies towards a wide range of contaminants, the life span of an Fe^0 barrier is limited due to reduced reactivity and permeability over time. Little is known about the microbial activity and dynamics within and in the vicinity of the Fe^0-barrier matrix, and their beneficial or detrimental effects on the longevity and long-term efficiency of the Fe^0 barriers.

We used PCR-DGGE with general and group specific primersets to examine the evolution of the microbial population in reactive iron barriers, this on water and solid core samples of both lab-scale and pilot-scale zero-valent iron barriers. Four different groups of anaerobic hydrogen consuming bacteria could be detected including sulfate- and metal-reducing bacteria, methanogens, and denitrifying bacteria within and downgradient of the zero-valent iron matrix. More detailed characterization by cloning and sequencing is ongoing.

In addition the geochemical interactions are being studied which includes the observation of aqueous geochemical data as well as the identification of different surface precipitates. Combining the degradation efficiency of the barrier simulation systems with both the microbiological en geochemical data, will learn us more about the impact of the biogeochemical interactions on the performance of zero-valent iron barriers.