Carbon and Sulfur Accumulation and Iron Mineral Transformations in Permeable Reactive Barriers Containing Zero-Valent Iron

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Abstract: Permeable reactive barrier technology is an in-situ approach for remediating groundwater contamination that combines subsurface fluid flow management with passive chemical treatment. Factors such as the buildup of mineral precipitates, buildup of microbial biomass (bio-fouling), and changes in subsurface transport combine to govern long-term performance of in situ Permeable Reactive Barriers. A detailed understanding of these factors is critical to understanding how long these passive systems will remain effective and what methods may be employed to improve their performance and extend their lifetime.

Authigenic precipitates that form within PRBs impact remedial performance by decreasing iron reactivity and permeability. Ultimately these impacts will decrease reaction efficiency and may result in the rerouting of subsurface flow paths. Reactive barriers containing zero-valent iron alter ambient groundwater chemistry by increasing pH and decreasing the oxidation-reduction potential. Depending on the composition and oxidation state of ambient groundwater, these conditions may favor the precipitation of mixed iron oxyhydroxides, Ca-Fe carbonates, magnetite, or mixed valence Fe(II)/Fe(III) ternary compounds (such as green rusts). In sulfate-rich groundwater, reducing conditions promote microbial sulfate reduction, the precipitation of iron monosulfides, and subsequent transformation to pyrite. The presence of a large reservoir of iron and substrate availability (H_2) favor the activity of iron-reducing, sulfate-reducing, and methanogenic bacteria. Enhanced biologic activity may beneficially influence zero-valent iron reductive dehalogenation reactions through favorable impacts to the iron surface or through direct microbial transformations of the target compounds. However, this enhancement may come at the expense of faster corrosion leading to faster precipitate buildup and potential biofouling of the permeable treatment zone. The results of long-term monitoring studies (groundwater chemistry and soil/iron characterization) are presented here from PRBs at the U. S. Coast Guard Base (Elizabeth City, NC) and the Denver Federal Center (Lakewood, CO), each with contrasting groundwater compositions. At both sites, barrier installations have been in place for over 4 years. We present a comparison of groundwater equilibrium modeling with the results of mineralogical characterization using microscopy, XRD, stable sulfur isotope ratios, and extraction studies.

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The Elizabeth City (NC) (continuous wall) and the Denver Federal Center (CO) (funnel-and-gate) systems use zero-valent iron filings (Peerless) to intercept and remediate groundwater contaminated with chlorinated hydrocarbons and hexavalent chromium at Elizabeth City (e.g., McMahon et al., 1999; Puls et al., 1999). Mineral precipitates were identified with a variety of techniques (XRD, SEM, XPS, chemical extraction, reflected-light microscopy). The observed mineral phases are in general agreement with those expected to form based on thermodynamic reaction path modeling. Zero-valent iron at both sites is a long-term sink for C, S, Ca, Si, and Mg. Iron is largely conserved although multiple reaction pathways and mineral precipitation processes involving iron are important and discussed here. Solid phase characterization studies indicate an average rate of inorganic carbon and sulfur accumulation to be ~0.1 and ~0.05 kg/m^2y at Elizabeth City where upgradient waters contain up to 400 mg/L total dissolved solids (TDS). At the Denver Federal Center site, upgradient groundwater contains up to 1100 mg/L TDS and rates of IC and S accumulation are as high as ~2 and ~0.8 kg/m^2y, respectively. At both sites, consistent patterns of spatially heterogeneous mineral precipitation and microbial activity are observed. Mineral precipitates and microbial biomass accumulate the fastest near the upgradient aquifer-Fe^0 interface. Estimates are presented of the rate of pore space infilling in the upgradient aquifer-Fe^0 interface based on the accumulation of IC and sulfur (porosity loss) and calculated Fe^0 dissolution (porosity gain).
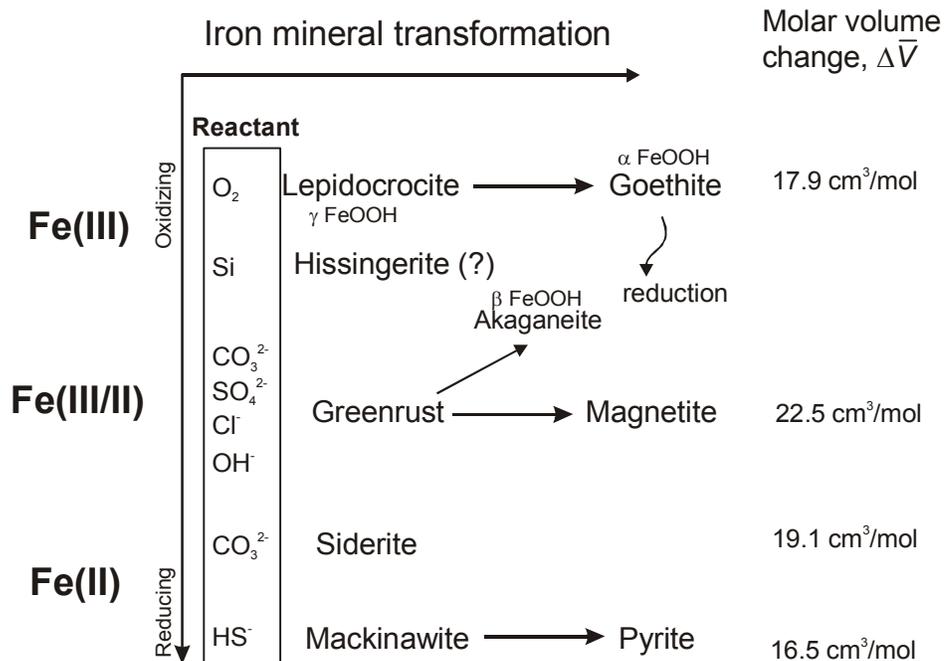

Figure 1. Iron mineral transformations in Fe^0 PRBs. Molar volume changes calculated assuming that iron is conserved through the transformation reaction of interest, e.g., $3Fe^0 + H_2O = Fe_3O_4 + 4H_2$.

Several transformation pathways of iron minerals in Fe^0 PRBs are important to evaluations of long-term performance by affecting the surface properties and reactivity

of the iron particles and by reducing available porosity (see Figure 1). Oxidized, reduced, and mixed-valence iron phases form and undergo transformation in Fe^0 systems. Oxidized phases (lepidocrocite, goethite) apparently are the result of reactions with dissolved oxygen. Elevated DO concentrations (>2 mg/L) in water entering reactive zones can lead to rapid corrosion and clogging of Fe^0 due to ferric oxyhydroxide precipitation at the upgradient interface (Liang et al., 2000). Akaganéite (β-FeOOH) has been identified from x-ray diffraction analyses at the PRB from Y-12 plant site (Phillips et al., 2000). Akaganéite is rare in nature; its formation is thought to be restricted to Fe- and Cl-rich hydrothermal brines or as a result of iron corrosion in Cl-rich fluids. Akaganéite also forms as an alteration product of green-rust compounds (Schwertmann and Taylor, 1989) and therefore may be related to inadequate sample preservation and the oxidation of green rust compounds rather than incipient precipitation as an iron corrosion product in Fe^0 systems.

Mixed iron valance state minerals include magnetite and green rust compounds. Green rust compounds are corrosion products that are expected to form under more reducing conditions than do iron oxyhydroxides. Their precipitation is favored at high pH and transformation of these compounds to magnetite is expected based on thermodynamic calculations (Bonin et al., 2000). Iron carbonate and monosulfides are the most important reduced iron forms and are likely to persist as long as reducing, alkaline conditions persist. Although iron monosulfides are unstable relative pyrite, the kinetics of the transformation to pyrite decreases with increasing pH (Wilkin and Barnes, 1996) so that iron monosulfides may be the long-term solid phase sulfide in Fe^0 PRBs. Similarly substantial iron carbonate dissolution is not expected so long as alkaline conditions persist.

References Cited
Bonin, P. M. L.; Odziemkowski, E. J., Reardon, E. J.; Gillham, R. W. *J. Sol. Chem.* **2000**, *29*, 1061-1074.
Liang, L.; Korte, N.; Gu, B.; Puls, R.; Reeter, C. *Adv. Environ. Res.* **2000**, *4*, 273-286.
McMahon, P. B.; Dennehy, K. F.; Sandstrom, M. W. *Ground Water* **1999**, *37*, 396-404.
Phillips, D. H.; Gu, B.; Watson, D. B.; Roh, Y.; Liang, L.; Lee, S. Y. *Environ. Sci. Technol.* **2000**, *34*, 4169-4176.
Puls, R. W.; Blowes, D. W.; Gillham, R. W. *J. Haz. Mat.* **1999**, *68*, 109-124.
Schwertmann, U.; Taylor, R. M. Minerals in Soil Environments, eds. J.B. Dixon and S. B. Weed, Soil Science Society of America Book Series, No. 1, 1989, Ch. 8, pp. 379-438.
Wilkin, R. T.; Barnes, H. L. *Geochim. Cosmochim. Acta* **1996**, *60*, 4167-4179.