

Geochemical Investigation of Three Permeable Reactive Barriers to Assess Impact of Precipitation on Performance and Longevity

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Abstract: A geochemical assessment was conducted at three permeable reactive barrier sites to evaluate performance and longevity issues. The assessment was carried out at former NAS Moffett Field (California), Dover AFB (Delaware), and former Lowry AFB (Colorado). These sites were selected because they differ in barrier design, contaminant types, hydrology, and geochemistry, and therefore represent a number of factors that could have bearing on long-term performance. Analysis of groundwater and iron cores were the primary means used to evaluate the potential for precipitate formation, which could affect both the surface reactivity of the iron as well as the hydraulic conductivity of the reactive cell. In addition, geochemical modeling with *PHREEQC* and *Geochemist's Workbench* was used to simulate iron reactivity in each of the three groundwater types and assist in understanding precipitation sequences. The study focused on behavior of native inorganic constituents of the groundwaters, such as dissolved oxygen, calcium, magnesium, alkalinity, and sulfate, as potentially able to influence precipitation within the reactive cells. In addition, long-term accelerated column tests are currently underway using two different iron-groundwater systems which model the Moffett Field and Lowry barriers. Results of the column tests will assist in understanding precipitation kinetics and physicochemical characteristics.

Measurement of groundwater species in PRBs reveals that concentrations of inorganic ions diminish rapidly inside the reactive cell. In particular, concentrations of bicarbonate, calcium, magnesium, sulfate, nitrate, and silica tend to be significantly lower in the reactive cell than in the upgradient aquifer. For example, at the Moffett Field PRB, alkalinity values are generally about 215 to 330 mg/L upgradient of the reactive cell and fall below 100 mg/L in well clusters inside the reactive cell. Calcium concentrations are approximately 160 mg/L in the aquifer and typically less than 10 in the reactive cell. Changes in magnesium are less pronounced but are also apparent. The magnesium concentration in the aquifer is about 50 to 73 mg/L and decreases below 40 mg/L in the first foot of the reactive cell, then decreases to approximately 1 mg/L at greater distances. Nitrate levels are about 1 to 3 mg/L in the aquifer and below detection (0.05 mg/L) in the reactive cell. Sulfate ranges from about 250 to 360 mg/L in the aquifer and pea gravel and decreases to less than 100 mg/L in most reactive cell wells.

The changes in inorganic constituents noted above suggest that inorganic compounds are precipitating within the reactive cell due to changes in pH and Eh (redox potential). Reductions in the concentrations of calcium and bicarbonate are believed to be caused by precipitation of aragonite or calcite (CaCO₃). Sulfate concentrations are not sufficiently high to cause precipitation of minerals, such as gypsum (CaSO₄·2H₂O). It is more likely that reducing conditions lead to conversion of sulfate to sulfide or bisulfide, which form precipitates with iron. Whether reduction of sulfate occurs biotically or abiotically is presently unknown.

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Figure 1 shows geochemical modeling results for an incremental reaction of zero-valent iron with Moffett Field groundwater. In the top portion of the figure, pH increases rapidly, then becomes stabilized at approximately 11.2; Eh decreases concomitantly. In the lower portion of the figure, concentrations of inorganic species change in response to mineral precipitation reactions that occur as a result of changes in pH and Eh. The areas marked *equilibrium* indicate the maximum extent of reaction. It is unlikely that true equilibrium is attained in the iron-water system, as evidence given below will support.

Coring locations at all three sites were chosen to provide specimens throughout the PRBs. Cores were collected from the reactive cells for examination of signs of the corrosion and precipitation, which are predicted by the groundwater analysis and geochemical modeling. Vertical cores were taken from top to bottom of the iron. Angled corings were taken to expose greater surface area and to cut across the interface of the iron and pea gravel.

X-ray diffraction (XRD) analysis of iron samples retrieved from the Moffett Field PRB (Battelle, 1998) indicates that the corrosion coatings are composed primarily of magnetite (Fe_3O_4) and of hematite ($\alpha\text{-Fe}_2\text{O}_3$). Small amounts of aragonite and marcasite (FeS_2) were also detected by XRD. In addition, various forms of amorphous iron hydroxide compounds were identified by Raman spectroscopy. No carbonates were observed in the unused iron, which suggests that precipitation occurred inside the barrier. Amorphous silicate was detected on iron surfaces by infrared spectroscopy and x-ray photoelectron spectroscopy. The silicate material was not found in the unused iron, indicating that silica was absorbed from the groundwater. This is consistent with losses of dissolved silica (silicic acid) in the groundwater within the reactive cells.

These observations differ from predicted mineral precipitation reactions, based on geochemical modeling of the Moffett Field PRB. Figure 2 shows geochemical modeling results for non-ferrous minerals (top portion) and ferrous minerals (lower portion). In the simulation, siderite (FeCO_3) and marcasite (FeS_2) are the initial phases to precipitate. As the reaction between iron and groundwater progresses, marcasite becomes unstable with respect to mackinawite (FeS). Also, siderite becomes

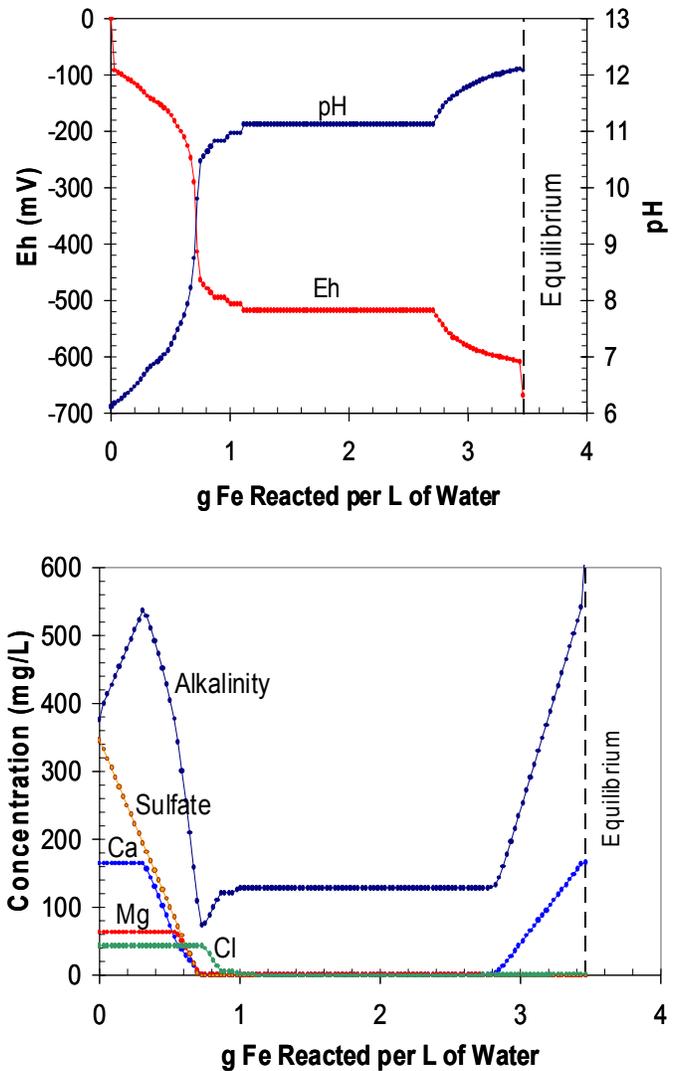


Figure 1. Geochemical modeling results of aqueous species; incremental reaction of zero-valent iron with Moffett Field groundwater.

unstable and “green rust” begins to form. Ferric hydroxide [Fe(OH)₃] becomes the predominant iron-bearing compound to precipitate as the reaction progresses. Non-ferrous minerals are predicted to precipitate in the order of: aragonite (or calcite), magnesite (MgCO₃) and brucite [Mg(OH)₂], although magnesite is stable for only a brief interval along the reaction pathway.

Analysis of core samples did not reveal siderite, green rust, magnesite, or brucite. This discrepancy could mean either that these phases did not form in the barrier due to unfavorable kinetics, or that the material had precipitated but did not remain in the pore spaces of the reactive cell. One explanation is that colloidal-size particles may be carried by advection through the barrier or settle within it.

Based on examination of the iron cores from Moffett Field, an insufficient amount of solids have precipitated to have had a significant effect on the porosity and permeability. A second coring event at the Moffett Field PRB was conducted in May 2001. Results of this coring event are pending. Although the hydraulic efficiency of the barrier may be maintained over the long term, it is not clear how or when its reactivity will be affected to the extent that the degradation rate of chlorinated VOCs in the groundwater is significantly reduced. Based on these findings it is difficult to make a quantitative assessment of the life expectancy of the iron in the PRBs. Long-term accelerated column tests are currently underway and will assist in determining how long the desired reactivity and hydraulics of the PRB may be expected to last.

Reference

Battelle (1998) “Performance Evaluation of a Pilot-Scale Permeable Reactive Barrier at Former Naval Air Station Moffett Field, Mountain View, California.” Prepared for Naval Facilities Engineering Service Center (NFESC), 1100 23rd Avenue, Port Hueneme, CA 93043. November 20.

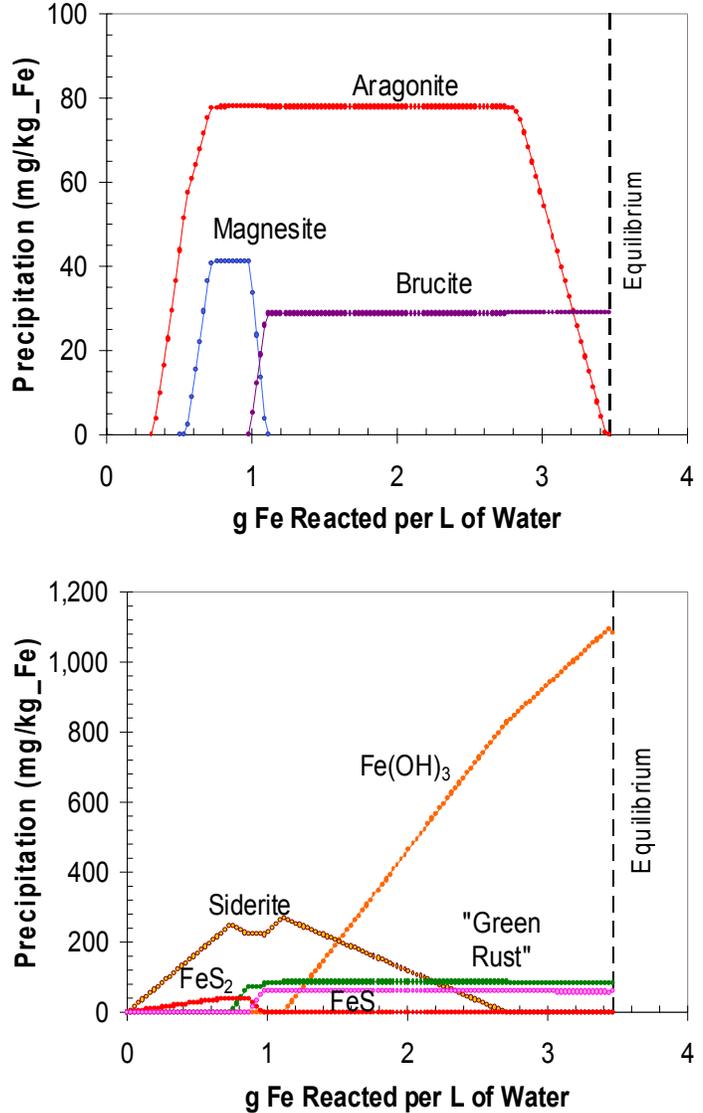


Figure 2. Geochemical modeling results of mineral precipitation; incremental reaction of zero-valent iron with Moffett Field groundwater.