

Consilience among disciplines on the (bio)geochemistry of zero-valent metals

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Contaminant remediation with zero-valent iron, corrosion of ferruginous metals, and biogeochemistry of iron oxides are three fields with many fundamental processes in common. Despite this, traditional disciplinary boundaries have limited the amount of consilience among these fields.

The most fundamental process that links these three fields is transfer of charge across layers of oxide (Scherer et al. 1998). While some evidence suggest this process is influenced by the presence of zero-valent metal, other evidence suggests charge transfer in the oxide can be treated seperately from the effects of the metal.

Other issues that link all three fields include the fate and effects of sulfate and hydrogen; the coupling of dissolution and precipitation processes; the kinetics of autoreduction of oxides by metal; and the role of extracellular electron shuttle compounds. Recent evidence from various fields will be synthesized to address some of these issues.

Reference

Scherer, M. M.; Balko, B. A.; Tratnyek, P. G. (1998) In: Mineral-Water Interfacial Reactions: Kinetics and Mechanisms; Sparks, D. L.; Grundl, T. J., Eds.; American Chemical Society: Washington, DC; ACS Symp. Ser. 715; pp. 301-322.

The reactivity and surface chemistry of granular iron in various geochemical settings

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Reactivity as a Function of Geochemical Setting

The reactivity of Master Builders granular iron, used in the construction of permeable reactive barriers, is affected by the anion chemistry of the water in which it resides. Well mixed batch tests with immobilized iron were performed in which the reduction of 4-chloronitrobenzene (4CINB) was used to gauge iron reactivity. The experiments were repeated with 8 mM ionic strength solutions (pH 10) of SO_4^{2-} , Cl^- , ClO_4^- , NO_3^- , HCO_3^- , given in the order of decreasing observed 4CINB reactivity. In addition, 4CINB was varied from 20 μM to 400 μM and the kinetics modeled with a Langmuir-Hinshelwood (LH) type equation. The fitted LH parameters, indicated that the reaction rates varied as a function of changes in affinity of 4CINB for the surface (HCO_3^-), and changes in sorption capacity and/or the rate constant for a surface reaction (NO_3^- , SO_4^{2-}).

Raman Analysis

Samples of iron were exposed to each of the solutions tested for 96 hours, under anaerobic conditions. The solutions were pH adjusted to match the other experiments, and the solutions were renewed every 24 hours. After exposure, the iron was recovered and selected grains were each examined in 12-15 spots using Raman spectroscopy. Magnetite was present at almost every spot examined, but hematite was also very common (40-90% occurrence). Green rust was identified in iron from every anion solution, but with only 15-30% occurrence. $\alpha\text{-FeOOH}$ and carbon from the steel were also identified, but not in association with every anion. There was no obvious correlation between detectable surface species and observed reactivities, despite these differences in surface compositions. However, the data did suggest that magnetite was the dominant oxide present and that its dominance seemed to increase with the exposure time of the iron to solution.

References

Devlin, J.F., Allin, K.O. (in press) *Environ. Sci. Technol*

Mineralogy of ferrous corrosion products formed in natural seawater

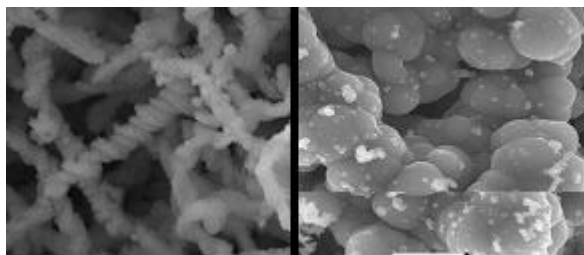
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Carbon steel 1020 coupons were exposed to natural Key West, FL seawater over a one-year period in both stagnant and alternate immersion conditions with varying concentrations of dissolved oxygen (DO) in both the seawater and the atmosphere. A two-tiered oxide layer of lepidocrocite/goethite formed during exposure to stagnant oxygenated seawater (~7 ppm DO). The inner layer was extremely tenacious and resistant to acid cleaning. Under hypoxic conditions (~0.2 ppm DO), dissolved oxygen was completely consumed in the first week by bacterial respiration and corrosion reactions. Numbers of sulfate-reducing bacteria increased and dissolved sulfide could be measured in the bulk seawater. The corrosion product was initially a non-tenacious sulfur-rich corrosion product, mackinawite, with enmeshed bacteria. As more sulfide was produced the mackinawite was transformed to pyrrhotite. Energy dispersive spectroscopy confirmed an increase in sulfide concentration within the corrosion products. Encrusted bacteria were observed using an environmental scanning electron microscope (ESEM) in all cases and corrosion morphology varied with sample orientation and DO concentration.

In alternate immersion, all exposure conditions produced a two-tiered corrosion layer. The outer extremely fragile layer was reddish orange and x-ray diffraction (XRD) indicated halite, lepidocrocite and goethite. The inner layer was black, tenacious and XRD indicated maghemite. Bacteria were associated with all corrosion products.



Chemistry of metallic iron nanoparticles

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Our work with metallic iron nanoparticles has focused on a search for evidence of nanometer-scale size effects on the rate at which they react and on their fundamental chemistry. Iron nanoparticles, synthesized by borohydride reduction (Fe^{BH}) or by thermal reduction of oxide particles under a hydrogen atmosphere (Fe^{H_2}), and micron-sized iron particles, synthesized electrolytically (Fe^{EL}), were characterized by a variety of spectroscopic, microscopic, and electrochemical techniques, and then reacted with either benzoquinone (BQ) or carbon tetrachloride (CT). Surface-area normalized reaction rates showed little difference among the three types of Fe, although Fe^{H_2} had a slightly slower rate than the other two forms in reactions with BQ.

To assess the fundamental chemistry of the three forms of Fe, we measured the branching ratio for the reductive dechlorination of CT. This reaction branches between a pathway that yields chloroform (CF) as its primary product and one or more pathways that yield other, as yet unidentified, products. The results depended in part on initial CT concentration. At low initial CT concentration (4 μM), the yield of CF (Y_{CF}) was typically < 0.4 for the Fe^{H_2} form and > 0.4 for Fe^{BH} and Fe^{EL} forms suggesting that the non-CF pathway was favored when the Fe^{H_2} form was used. At higher CT concentrations (0.9-2.4 mM), however, differences among the forms of Fe were smaller with Y_{CF} values of about 0.46 observed for the Fe^{H_2} form and 0.50 for the Fe^{BH} form.

To help identify the factors that control the branching ratio, we have initiated a series of experiments using electron paramagnetic resonance (EPR) spectroscopy to nondestructively probe the reactivity of Fe^{H_2} and Fe^{BH} particles over time. Aging of the particles (i.e., oxidation by H_2O), and the possible role of nonpolar solvents such as CT in this process, are the primary foci of these experiments.

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 $>1500 \mu\text{g L}^{-1}$ in groundwater hydraulically upgradient of the PRB to values $<1 \mu\text{g L}^{-1}$ 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 and geochemical data, will learn us more about the impact of the biogeochemical interactions on the performance of zero-valent iron barriers.

Effects of Co-solutes on bioaugmented granular iron systems

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Rationale

Previous work has demonstrated the utility of iron and bioaugmented granular iron systems for the remediation of many groundwater contaminants. Although progress has been made towards understanding the mechanisms and effectiveness of the degradation process, factors governing variations in the performance of these systems have thus far received significantly less attention. This work focused on elucidating the effects of bioaugmentation and groundwater co-solutes on granular iron reactivity.

Experimental

Studies were conducted using columns packed with untreated sieved iron that were fed with simulated groundwaters containing various co-solutes and the model contaminant trichloroethylene (TCE). Furthermore, the columns were bioaugmented by inoculating them with the metal reducing bacterial strains *Shewanella alga* BRY and *Geobacter sulfurreducens*. Thereafter, bacterial growth and distribution profiles were monitored. Other chemical parameters such as TCE, Fe^{II}, HCO₃⁻, TOC, and H₂ concentrations were obtained from sampling ports located down the length of the columns.

Results and Discussion

Evaluations of individual contaminant and daughter product profiles and pore water velocities suggest that significant differences in column reactivity result from variations in the types and quantities of co-solutes present. In addition, the bioaugmented columns exhibited behavior that varied considerably from that observed in the non-augmented columns. Surface analyses suggest formation of different iron oxide species dictated by the presence of the co-solutes and by bacterial activity. These results extend our understanding of the 'passivation' process that iron barriers undergo.

Geochemical dynamics in Fe(0)-PRB's: H₂ evolution and passivation

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In order to assure the acceptance of Fe(0)-PRB's (permeable reactive barriers) as a remediation strategy for groundwater pollution, data about the long-term performance are needed [1]. The impacts of hydrogen (H₂) evolution and passivation due to the build-up of secondary minerals have received only minor attention up to now [2, 3].

We conducted horizontal column experiments with Fe(0) under varying geochemical conditions for over 2 years. Results indicate that H₂ evolution and reactivity loss due to passivation may cause severe problems regarding the performance of PRB's. While for columns fed with deionized water mean H₂-evolution rates of 0,02-0,2 mmol H₂/d*kg Fe were determined, the presence of 1 g/l HCO₃⁻ increased H₂-evolution rates to 2,5-3,5 mmol H₂/d*kg Fe. Before the onset of iron passivation maximum rates of up to 14 mmol H₂/d*kg Fe were determined. H₂-evolution did not exhibit a linear relationship in regard to varying feed concentrations of HCO₃⁻, complicating predictions of field corrosion rates with natural groundwaters. With increasing experimental duration a loss of reactivity due to the build-up of passivating precipitates was observed. This reactivity loss caused a decrease in H₂-evolution as well as in contaminant degradation. The progression of the passivation front could be described with the development of a completely unreactive zone combined with a reactivity loss in the still active sections. Geochemical equilibrium modeling based on experimental data enabled us to calculate the amount and general type of precipitates formed in the column systems. Since gaseous H₂ was collected individually for different sections in the column systems, we were able to describe spatial differences in corrosion rates and precipitate build-up, and their development with progressing experimental duration.

References

- [1] EPA (2003), EPA/600/R03/045a, 156 p.
- [2] Reardon, E.J. (1995), *Environ. Sci. Technol.*, 2936-2945.
- [3] Klausen, J.; P.J. Vikesland; T. Kohn; D.R. Burris; W.P. Ball & A.L. Roberts *Environ. Sci. Technol.*; 1208-1218.

Uranium oxides generated from armored vehicles perforated by ammunition composed of depleted uranium metal

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Munitions of armor-piercing depleted-uranium (DU) metal were used by the U.S. Department of Defense (DoD) on the battlefield for the first time during the 1991 Operation Desert Storm. Since then, they were used by NATO in the Balkan conflicts and by DoD in the recent 2003 Operation Iraqi Freedom. DU munitions that impact hard targets or are enveloped in fire undergo oxidation to form DU oxide particles and agglomerations. Spent DU penetrators on firing ranges or on battlefields also corrode in the natural environment to yield DU oxides. In response to questions raised after the Gulf War about the health significance of exposure to DU, the U.S. Department of Defense initiated the Capstone DU Aerosol Study to quantify and characterize DU aerosols collected inside, on, and near to Abrams tanks and Bradley Fighting Vehicles struck by DU penetrators. XRD analysis determined that the aerosols were primarily a combination of U_3O_8 and UO_3 phases, though intermediate phases resembling U_4O_9 and other oxides were prominent in some samples. SEM analyses showed some large DU particles that appear to have fractured, perhaps as a result of abrasion and comminution. Others were spherical, occasionally with a dendritic or lobed surface structures. SEM/EDS analysis of the aerosols identified the presence of oxides of U, Al, and Fe, and lesser amounts of Cu, Zn, Ti, Si, Ca, and Mg. Other studies by PNNL and others show that oxidation of these aerosol products and of spent DU penetrators in the natural environment ultimately results in a mixture of metaschoepite and schoepite. With continued exposure to pore water in soils, the schoepite phases will likely continue to alter to less soluble U(VI) phases, such as becquerelite, uranophane, soddyite, autunite, and related U(VI) minerals. The results from the Capstone study provide additional data about aerosols generated by the impact of armored vehicles by DU munitions and an improved scientific basis for assessing health risks and environmental fate of DU fragments, aerosol and corrosion products in soil systems.

Mineral precipitation and corrosion in a long-term zero-valent iron reactive barrier

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Zero-valent iron (ZVI) permeable reactive barriers (PRB) have been effective in the remediation of certain contaminants (i.e. uranium) from groundwater. However, long-term corrosion of ZVI filings and mineral precipitate accumulation may decrease the effectiveness of a ZVI PRB to mediate groundwater. Notable changes in mineral precipitates, cementation and corrosion of ZVI filings within the Oak Ridge Reservation Y-12 in-situ PRB have occurred after about 2.5 yrs of operation.

Discussion of Results

Iron (oxy)hydroxides, maghemite/magnetite and aragonite occurred throughout the PRB. Goethite, lepidocrocite, mackinawite, siderite, aragonite and calcite were associated with oxidized and cemented areas, while green rusts were present in reduced zones. Since an earlier study of this PRB after about 1.2 yrs of operation there were 1) increases in iron (oxy)hydroxides, and calcium and iron carbonate minerals, 2) increases in cementation, as shown in the figure below where the iron filings are cemented with calcium carbonate, and 3) increases in oxidation, corrosion, and disintegration of ZVI filings, especially in cemented areas.

Conclusions

If the amount of corrosion and cementation that occurred from about 1.2 to 2.5 yrs after installation continues, certain areas of the PRB (i.e. up-gradient entrance of PRB to groundwater) may last less than 5 more years; thereby, decreasing the effectiveness of the PRB to mitigate contaminants.

