

## 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  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{HCO}_3^-$ , given in the order of decreasing observed 4CINB reactivity. In addition, 4CINB was varied from 20  $\mu\text{M}$  to 400  $\mu\text{M}$  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 ( $\text{HCO}_3^-$ ), and changes in sorption capacity and/or the rate constant for a surface reaction ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ).

### 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

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