

## Sediment remediation of metal and metalloid contaminants with reactive amendments

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Reactive amendments optimized for specific (bio)geochemical site conditions offer a promising remediation technology for high-priority contaminants (As, Hg, Se, Pb, Cu) in sediments by sequestration and stabilization in less reactive and less bioaccessible solids. For subaqueous or subsurface sites where physical removal is impractical or prohibitively expensive, *in situ* stabilization must be designed for long-term immobilization in potentially variable biogeochemical and hydrologic conditions. Amendment technologies are particularly promising when combined with other methods such as sediment capping, reactive barriers, or monitored natural attenuation in an overall risk management approach.

In laboratory experiments supported by equilibrium and kinetic modeling, we are investigating mercury (Hg) and arsenic (As) immobilization with Fe-sulfate and Portland cement amendments. Modeling results indicate formation of hydrated Ca-Si-Al and Ca-Fe ettringite phases within 1-7 d. In the Hg system, experimental data are consistent with model results, showing Mg, Ca, and S concentrations at 1 and 7 d that match predictions. Analyses of reaction products up to 30 d by XRD and SEM/EDS confirm model predictions of secondary phase formation. Mercury uptake measurements and sequential extractions show rapid removal from solution and a decrease in extractable Hg with aging time. In the As system, Fe-sulfate and cement amendment was compared with Fe-sulfate-only (low pH) and cement-only (high pH) treatments of sediments aged for up to 1 y. Similar to Hg, As uptake from solution is rapid (>90% in 1-7 d) and extractable As decreases with aging, although there is variability over the time series. Characterization of reaction products by XRD and XAS indicates arsenic sequestration in either ettringite or Fe-sulfate/arsenate secondary phases by arsenic substitution for sulfate, in contrast to Hg(II), which likely substitutes for Ca in secondary phases. Comparison of laboratory results with field-amended sediments suggest that sulfate-cement mixtures are stable for years if pH and redox conditions remain relatively constant.

## Effects of oxyanions, natural organic matter, and Fe(III) oxide mineralogy on the formation of Fe(II)-bearing secondary mineralization products resulting from the bioreduction of Fe(III) oxides

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### Introduction

The bioreduction of Fe(III) oxides may result in the production of a suite of Fe(II)-bearing secondary mineralization products (Fe(II)SMPs), including magnetite, siderite, vivianite, ferrous hydroxy carbonate (FHC), and green rusts. In an effort to better understand the effects of solution chemistry on the formation of particular Fe(II)SMPs of dissimilatory Fe(III) reduction, we examined the effects of a series of oxyanions and natural organic matter on the bioreduction of Fe(III) oxides by *Shewanella putrefaciens* CN32.

### Experimental Methodology

Defined mineral medium containing 75 mM formate and 80 mM Fe(III), in the form of synthetic Fe(III) oxides, was amended with oxyanions or natural organic matter and inoculated with *S. putrefaciens* CN32. Samples were collected for measurement of Fe(II) and characterization of the Fe(II)SMPs by X-ray diffractions, scanning electron microscopy, and <sup>57</sup>Fe Mössbauer spectroscopy.

### Discussion of Results

With no amendment or with the addition of borate, oxalate, or gellan (an extracellular polysaccharide produced by the bacterium *Sphingomonas elodea*) magnetite and FHC formed. The addition of arsenate, molybdate, phosphate, silicate, tungstate, citrate, humic and fulvic acids, or extracellular polysaccharides from *S. putrefaciens* CN32 resulted in the formation of carbonate green rust.