

Kinetics of Cr(VI) reduction by pyrite surfaces at pH 4 to 9: Surface coverage and passivation effects

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Pyrite is a common constituent of modern anoxic sediments, and may contribute to redox transformations of a range of pollutants including Cr (VI). Previous studies of pyrite oxidation by Cr (VI) have focused primarily on acidic pH conditions [1, 2]; here we present a detailed investigation of the kinetics of Cr (VI) reduction by acid-washed pyrite surfaces over a range of pH (4.0 to 9.0) and surface coverage conditions.

Cr (VI) reduction occurred almost entirely via a surface-reaction pathway, and complete reduction of 7 to 120 μM Cr (VI) by 0.3 to 2.1 m^2/L pyrite suspensions was observed for the pH range 4.0 to 9.0. Timescales for complete Cr (VI) reduction increased significantly with increasing initial Cr (VI) concentration. In general, rates of Cr (VI) reduction increased 5-15 times upon decreasing pH from 9.0 to 4.0, with the greatest pH effect occurring for the highest surface coverage conditions.

A complex dependence of the reaction rate on aqueous Cr (VI) concentration is attributed to a combination of surface-site saturation behavior and declining pyrite reactivity with accumulation of a Cr (III) (hydr)oxide product overlayer. X-ray photoelectron spectra of reacted pyrite surfaces confirmed the presence of a Cr (III) (hydr)oxide overlayer, the accumulation of which limits access of Cr (VI) to reactive surface sites and slows reaction progress. Available reductant (either Fe (II) or S_2^{2-}) at the surface was insufficient for the complete Cr (VI) reduction observed, suggesting a role for cycling of Fe (II)/Fe (III) at the pyrite surface] in regenerating reactive surface sites.

Results of this work indicate that pyrite will rapidly remove μM levels of Cr (VI) from polluted sediment porewaters or groundwaters at circumneutral pH, while surface site limitations or surface passivation will limit rates of Cr (VI) reduction for higher Cr (VI) loadings.

[1] Demoisson *et al.* (2005) *Environ. Sci. Technol.* **39**, 8747–8752. [2] Demoisson *et al.* (2007) *J. Coll. Int. Sci.* **316**, 531–540. [3] Eggleston *et al.* (1996) *American Mineralogist* **81**, 1036–1056.

Biological and biochemical pathways of litter decomposition and soil carbon stabilization

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Current models predict that changes in plant litter chemistry during decomposition are primarily regulated by initial litter chemistry and the stage, or extent, of decomposition. Far less is known about the degree to which decomposer community structure and land use management regimes – including the conversion of grasslands to biofuel crop production – influence litter chemistry during decomposition. Given the recent agricultural intensification occurring globally, our objectives were: 1) to determine the potential effects of agricultural intensification on plant litter chemistry and decomposition rates; and 2) to investigate possible links between ecosystem management, litter chemistry and decomposition, and decomposer communities and activity. After one growing season, conventional-till litter decomposition rates were 20% greater than in old field communities and grass residue in both conventional- and no-till systems was enriched in total polysaccharides relative to the initial litter, while grass litter in old fields was enriched in nitrogen-bearing compounds and lipids. These differences corresponded with differences in decomposer communities. Our results show that agricultural intensification can increase litter decomposition rates, alter decomposer communities, and shift litter chemistry in ways that could have long-term effects on soil organic matter dynamics. We suggest that future efforts to predict soil C dynamics should consider that changes in litter chemistry during decomposition are not merely a function of initial litter quality, but are also strongly influenced by the specific metabolic capabilities of decomposer communities.