NAME: Elizabeth Butler  
ORGANIZATION: University of Oklahoma  
PROGRAM AFFILIATION: SBR  
ABSTRACT TITLE: Stability of Iron-Chromium Precipitates for Long Term In-Situ Chromium Immobilization

ABSTRACT: The objective of this research was to identify factors affecting the properties of Fe-Cr precipitates formed in microbial and abiotic anoxic systems. Specific objectives were to: (1) measure the rates of Cr(VI) reduction by Fe(II) minerals and microorganisms; (2) characterize the morphology, crystallinity, and composition of the formed Fe-Cr precipitates; and (3) measure oxidation rates of dissolved Cr(III) in equilibrium with these precipitates by birnessite.

Microbially-active microcosms contained hematite, aluminum substituted goethite (Al-goethite), or iron rich nontronite (NAu-2), and Desulfovibrio vulgaris strain RCH1 (Chakraborty R., http://www.ncbi.nlm.nih.gov/nuccore/CP002297.1) (RCH1). Microcosms containing hematite were prepared with a low and high dilution of the culture to yield faster (hematite/RCH1/fast) or slower (hematite/RCH1/slow) Cr(VI) removal. Abiotic microcosms contained either FeS or dithionite reduced NAu-2. Dissolved Cr(VI) was removed relatively rapidly in all microcosms, with the fastest Cr(VI) disappearance for FeS (30 minutes), and the slowest for hematite/RCH1/slow (one month). Thus, in all systems, Cr(VI) was removed from solution in the time scale of ground water transport.

After the kinetic experiments, the solids were retrieved, washed, and dried. X-ray absorption spectra indicated the presence of mixed Fe(III)-Cr(III) hydroxide phases for all solids. Although the majority of solid phase Cr was in the +III oxidation state, solid phase Cr(VI) was also identified at a relative concentration of 21-25% for RCH1/hematite (slow and fast) and RCH1/Al-goethite, 10-11% for RCH1/NAu-2 and dithionite reduced NAu-2, and 4% for FeS. Transmission electron microscopy (TEM) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) were done to further characterize the solids. The most pronounced morphological changes after reacting with Cr(VI) were observed for RCH1/hematite/fast and FeS. TEM images of RCH1/hematite/fast after reaction with Cr(VI) show jagged edges and pitting, as well as development of a very thin surface layer, suggesting dissolution of hematite and formation of a new phase. TEM and SEM images showed a possible organic film in which nanoparticles with the highest Cr:Fe ratio (approximately 1) were observed. TEM analysis of FeS after reacting with Cr(VI) indicated a poorly crystalline, essentially amorphous material with individual grains difficult to distinguish at the nanoscale. SEM/EDS of this material showed elevated Cr, increased O, and decreased S, suggesting formation of a Cr-Fe hydroxide.

Finally, each solid was equilibrated in the presence of an aqueous suspension of birnessite (along with controls containing no birnessite) for approximately two weeks. We speculated that dissolved Cr(III) in equilibrium with each Fe-Cr solid might be oxidized by the birnessite to Cr(VI), driving further Cr(III) dissolution and oxidation. Solid phase Cr(VI), present at significant quantities in some solids, could also dissolve, regardless of whether birnessite was present. All solids from the microbially-active microcosms showed only minimal release of Cr(VI), and no significant difference in dissolved Cr(VI) concentration in the presence of birnessite compared to the control. FeS and dithionite-reduced NAu-2, on the other hand, showed a steady increase in concentration of Cr(VI) over time, suggesting that these precipitates may be susceptible to re-mobilization of Cr in the subsurface.