NAME: Bill Burgos
ORGANIZATION: Penn State University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones

ABSTRACT: Hexavalent chromium (Cr^{6+}) is a major contaminant in the environment. As a redox-sensitive element, the fate and toxicity of chromium is controlled by reduction-oxidation (redox) reactions. Previous research has demonstrated the ability of chemically reduced smectite and aqueous Fe^{2+} to reduce Cr^{6+} to Cr(III) as a way of immobilization under natural conditions. However, it is still poorly known whether or not natural or biologically reduced clay minerals exhibit similar reactivity and if so, what are the kinetics and mechanisms of Cr^{6+} reduction by clay-Fe(II). The objective of this study was to determine the kinetics of Cr^{6+} reduction by Fe(II) associated with various common clay minerals and the nature of reduced Cr(III). The reactivity of clay minerals nontronite (NAu-2), montmorillonite (Swy-2), chlorite (CCa-2), and clay-rich sediments from the Ringold Formation of the Hanford site of Washington State towards reduction of Cr^{6+} was studied. Structural Fe(III) in the clay minerals was first bioreduced to Fe(II) by *Geobacter sulfurreducens* with acetate as the sole electron donor and anthraquinone-2,6-disulfate (AQDS) as electron shuttle in select experiments in synthetic groundwater (pH-7). Biogenic Fe(II) was then used to reduce Cr^{6+} at three different temperatures, 10°, 20° and 30°C, in order to determine the activation energy of the redox reaction between Cr^{6+} and clay-Fe(II). The results showed that nontronite was the most effective in reducing Cr^{6+} at all temperatures and chlorite the least. Despite a large amount of Fe(III) bioreduction in chlorite, most bio-produced Fe(II) was not reactive towards Cr^{6+} reduction at 10°C, however at 30°C there was some reduction, which was likely due to released Fe^{2+} from the dissolution of chlorite. For all the clay minerals, the ratio of Fe(II) oxidized to Cr^{6+} reduced was close to the expected stoichiometric value of 3±0.5. Scanning electron microscopy with focused ion beam and transmission electron microscopy with electron energy loss spectroscopy (TEM-EELS) characterization revealed that reduced chromium was Cr(III) and it was closely associated with residual nontronite NAu-2 as micron-scale aggregates. This unique textural association was expected to minimize any chance of Cr(III) reoxidation upon exposure to oxidants. These kinetic results are important for our understanding of how various clay minerals may be used to reductively immobilize heavy metal contaminants such as Cr, Tc, or U from the environment.

We have also been studying the reactivity of clay-Fe(III) towards the oxidation of uraninite. These experiments have focused on the comparing the reactivity of biogenic clay-Fe(II) versus chemically reduced clay-Fe(II). Results obtained with nontronite NAu-2 suggest that only 25 to 35% of the structural clay-Fe(III) can be reduced by a variety of oxidants (including DMRB, quinones, and uraninite). Experiments are now being conducted with nontronite NAu-2, DMRB and nitroaromatic compounds (NACs) to operationally define this thermodynamic endpoint.