KINETICS AND MECHANISMS OF CHROMIUM(III) OXIDATION AND PRECIPITATION ON MANGANESE OXIDES, IN REAL-TIME AND AT THE MOLECULAR LEVEL

by

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ABSTRACT

The initial kinetics of Cr(III) oxidation on mineral surfaces is poorly understood, yet a significant portion of the oxidation process occurs during the first seconds of the reaction. In this study, the initial rates of Cr(III) oxidation on hydrous manganese oxide (HMO) were measured at three different pH values (pH 2.5, 3, and 3.5), using a quick X-ray absorption fine structure spectroscopy (Q-XAFS) batch method. The calculated rate constants were 0.201, 0.242, and 0.322 M^{-1} s^{-1} at pH 2.5, 3, and 3.5, respectively. These values were independent of both [Cr(III)] and [Mn(II)] and mixing speed, suggesting that the reaction was "chemically" controlled and not dependent upon diffusion at the time period the rate parameters were measured. A second-order overall rate was found at three pH values. This represents the first study to determine the chemical kinetics of Cr(III) oxidation on Mn-oxides. The results have important implications for the determination of rapid, environmentally important reactions that cannot be measured with traditional batch and flow techniques. An understanding of these reactions is critical to predicting the fate of contaminants in aquatic and terrestrial environments.

Additionally, this study investigated the kinetics and mechanisms of the reactions occurring during chromium(III) sorption on three hexagonal manganese(IV) oxide surfaces. Bulk Extended X-ray Absorption Fine Structure spectroscopy (EXAFS) analyses show that trivalent chromium binds to the mineral surface in an inner-sphere complex on the edges of the manganese oxide layers, and rapidly oxidizes to Cr(VI), which can weakly bind to the surface in an outer sphere complex,

or diffuse to solution. As more Cr(III) sorbs on Mn(IV)O_2, Cr(III) nucleation occurs on the mineral and simultaneously Cr(VI) oxidation rates decrease. Chromium(III) may precipitate locally on the mineral surface as a γ-CrOOH phase and extend away from the manganese oxide, if the mineral surface is saturated with ions at high ionic strength. Alternatively, Cr(III) can epitaxially nucleate in a α-CrOOH phase on the top of Mn(IV)O_2 layers, due to structural similarities between the surfaces of the Cr(III) precipitate and the manganese oxide. After forming, Cr(III) precipitates can desorb from the mineral surface, since more Cr(III) nucleation products are detected in solution than on the solid phase. Quick X-ray Absorption Fine Structure spectroscopy (Q-XAFS) enables us to measure *in situ* the rates of both surface precipitation formation on manganese oxides and Cr(III) oxidation occurring in the entire batch system. The α-CrOOH phase can quickly form at high pH at the early stage of Cr(III) sorption on manganese oxides, thus competing with the rapid Cr(III) oxidation for free Cr(III) monomers in solution. Additionally, the phase can quickly reach high concentrations in the system, thus acting as a sink for Cr(III) ions. Therefore, since both Cr(III) nucleation and Cr(III) oxidation occur rapidly and potentially have opposite effects on Cr toxicity in the environment, this study, which measures for the first time the rates of Cr surface precipitation on manganese oxide surface using Q-XAFS, demonstrates the need for developing new techniques that can follow the kinetics of rapid reactions occurring in the environment.

Lastly, the speciation of As and Cr in a contaminated soil was studied by micro x-ray fluorescence spectroscopy (μ-XRF), and bulk x-ray absorption spectroscopy (bulk XAFS). The soil was taken from a park in Wilmington, DE, which used to be an important center for the leather tanning industry along the Atlantic

seaboard of the United States, until the early 20th century. The concentrations of As, Cr, and Pb measured at different locations in the park were often far above the background levels of these heavy metals in the State of Delaware. Results from micro x-ray absorption near-edge structure spectroscopy (μ-XANES) and bulk XAFS analyses show that Cr(III) and As(V) are mainly present in the soil, with insignificant amounts of Cr(VI) and As(III). The apparent absence of chromate may be notably due to the association between Cr and Fe in different regions of the soil. Micro x-ray fluorescence spectroscopy (μ-XRF) maps show that these two elements are distributed together in regions where their concentrations are diffuse, and at local spots where their concentrations are high. Iron(II) oxides, which can reduce Cr(VI) to Cr(III), are present at some of these hot spots where Cr and Fe are highly concentrated, based on the results obtained by micro x-ray diffraction spectroscopy (μ-XRD) analyses. Results from bulk extended x-ray absorption fine structure spectroscopy (EXAFS) analyses suggest that As is mainly associated with Al in the soil, and to a minor extent with Fe, which is supported by μ-XRF and μ-XRD results. Arsenate may be sorbed to aluminum oxides, which might have transformed after a long period of time into an As-Al precipitate phase, having a structure and chemical composition similar to mansfieldite. The latter hypothesis is supported by the fact that only a small amount of As present in the soil was desorbed using the characteristic toxicity leaching procedure (TCLP) and the synthetic precipitation leaching procedure (SPLP) tests. This suggests that As is immobilized in the soil.