

**OXIDATION and SORPTION MECHANISMS  
of HYDROLYZABLE METAL IONS on  
OXIDE SURFACE**

by  
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## ABSTRACT

Metal ion reactions at the solid/solution interface are one of the primary processes which determine their fate in soils and waters. Ascertaining interfacial metal ion reaction rates and mechanisms is essential for determining reaction pathways and conditions which influence these processes. In this study, the sorption and redox reactions of Cr(III) at the oxide/solution interface were investigated by employing an array of sophisticated atomic-resolution experimental techniques and a novel electron paramagnetic resonance spectroscopically monitored stopped-flow (EPR-SF) techniquekinetic technique for studying rapid colloidal reactions *in situ*.

The oxidation of nonhazardous Cr(III) to the hazardous Cr(VI) by Mn-oxide, the only known naturally occurring oxidant of Cr(III), was investigated. The EPR-SF technique was used to determine the redox reaction rate between Cr(III) and  $\delta$ -MnO<sub>2</sub> (birnessite). An overall second-order reaction was ascertained that exhibited a first-order dependence on [Cr(III)]<sub>0</sub> and {MnO<sub>2</sub>}<sub>0</sub>. A four step reaction mechanism was postulated: (i) Cr(III) adsorption, (ii) a two electron transfer, (iii) a single electron transfer and ligand exchange, (iv) and desorption of the reaction products. The adsorption step was rate limiting. At pH > 4, surface precipitation of Cr-hydroxide effectively inhibited oxidation. Aluminum also poisoned the reaction in a similar manner. Surface precipitation was catalyzed in the electrified interface and occurred at an ion activity product 10<sup>3</sup> times lower than would be expected for precipitation in solution.

The surface structure of Cr(III) sorbed on silica was ascertained using extended X-ray absorption fine structure (EXAFS) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopies, along with high-resolution transmission electron

microscopy. A monodentate Cr(III) surface complex formed at surface site occupancies < 20%, while Cr-hydroxide nucleation, with the  $\gamma$ -CrOOH type local structure, occurred at coverages > 20%. At the Cr-Si interface, a shorter corner sharing Cr octahedra distance occurred due to the structural constraints imposed by the silica. The energetics of the strained structure promoted the nucleation growth to progress away from the silica surface rather than across it, i.e., discrete crystalline  $\gamma$ -CrOOH surface clusters formed.