

## Surface Precipitation of Hydrolyzable Metal Ions on Oxide Surfaces

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Heavy metal retention on solid surfaces is a primary determinant in affecting the environmental hazard of these elements. Mechanistic models are necessary to accurately assess the potential binding of metals, and thus their potential mobility. Numerous thermodynamic models have been proposed to explain the metal sorption process. However, these models have been based on macroscopic data and do not give direct evidence for the sorption mechanisms. Increasingly, surface spectroscopic and microscopic techniques have been used to ascertain the binding structure of sorbed ions. In this research, we have used high-resolution transmission electron microscopy (HRTEM) coupled with static studies to discern the mechanism of Al(III) and La(III) sorption on MnO<sub>2</sub> and TiO<sub>2</sub> near and beyond monolayer coverage. Surface precipitation of Al(III) and La(III) was observed on MnO<sub>2</sub>, but was not apparent on TiO<sub>2</sub> nor in bulk solution. Al(III) formed a surface precipitate at lower concentrations and pH values than La(III). We conclude that surface precipitation can occur prior to bulk solution and is dependent on the type of surface and metal ion present. Mechanistic models need to incorporate such processes since the formation of a surface precipitate encapsulates the oxide and the resulting conglomerated colloid exhibits the properties of the metal hydroxide.