

Sulfate complexation on iron(III) oxyhydroxide surfaces and in the structure of schwertmannite

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Sulfate is abundant in nature and plays an important role in many geochemical processes. Its mobility is affected by adsorption processes on mineral surfaces. A mechanistic understanding of the adsorption processes requires knowledge of the structure of sulfate adsorption complexes which, however, remains unclear. Here, S K-edge EXAFS spectroscopy was used to directly characterize the sulfate surface complexes on ferrihydrite as well as the sulfate complexes in the schwertmannite (Schw) structure.

Results show that sulfate formed both bidentate-binuclear inner-sphere complexes and outer-sphere complexes on ferrihydrite surfaces under various experimental conditions (pH, ionic strength, and dry or wet status). A comparison of S K-edge XANES spectra suggests that the outer-sphere complex was different from the free sulfate ion in a sodium sulfate solution (pH 5). The inner- and outer-sphere complexes were further quantified using XANES linear combination fitting (LCF) analysis. It was found that with increasing ionic strength, the adsorption loading of the inner-sphere complexes remained almost the same while the outer-sphere complex loading decreased significantly, validating the classic ionic strength effect for a system containing both inner- and outer-sphere complexes.

The sulfate binding environment in Schw has remained enigma. Our results indicate that sulfate mainly formed bidentate-binuclear complexes for air-dried samples while outer-sphere complexes dominated for wet samples. If assuming Schw possesses a tunnel structure as akaganeite and that the sulfate exists mainly in the tunnels, the inner-sphere complexation suggests that there must be some missing Fe on the wall of the tunnel to create exchangeable OH/H₂O surface functional groups for ligand exchange with sulfate.

Our results provide important insights into the complexation reactions between Fe(III) and sulfate that may improve the understanding of sulfate-Fe(III) mineral formation in acidic soils and acid mine drainage-impacted environments.