Use of X-ray Absorption Spectroscopy to Distinguish Between Inner And Outer-sphere Pb Adsorption Complexes on Montmorillonite

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Adsorption behavior of Pb on montmorillonite as a function of pH was highly dependent on ionic strength. At I = 0.1 M the removal of Pb from solution increased from ~40% to ~80% at pH = 6 and pH = 7, respectively. This pH dependent behavior suggests inner-sphere complexation on the functional groups at the edges of the montmorillonite. At I = 0.002 M Pb absorption was less dependent on solution pH, with ~97% removed from solution at pH = 4 and nearly 99% removed from solution at pH = 7. The lack of pH dependence at I = 0.002 M suggests that adsorption is primarily via an outer-sphere mechanism. The XANES spectrum of Pb sorbed on montmorillonite at pH = 4.40 (I = 0.002 M) was similar to the XANES spectrum of a Pb²⁺ (aq) sample, suggesting that the adsorbed Pb is coordinated by water molecules. At pH = 6.40 (I = 0.002 M and I = 0.1 M) the XANES spectra for Pb sorbed on montmorillonite are similar to a Pb solution containing predominantly [Pb₄ (OH)₄]⁴⁺ complexes, indicating that sorbed Pb is predominantly coordinated by OH⁻ ligands.