

X-RAY ABSORPTION FINE STRUCTURE SPECTROSCOPY AND  
MOLECULAR DYNAMICS MODELING STUDIES OF ION ADSORPTION  
TO KAOLINITE CLAY SURFACES

Abstract

by

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We used x-ray absorption fine structure spectroscopy to study the local molecular environment of cadmium adsorbed to kaolinite at various pHs and aqueous cadmium concentrations. Quantitative analysis of samples with aqueous cadmium concentration of 100  $\mu\text{M}$  and at pH 7 shows a single hydration sphere around cadmium, suggesting the formation of outer sphere sorption complexes. At pH 9, a clear Cd-M coordination (where M stands for either Si or Al) at second shell distance indicates the formation of inner sphere sorption complexes on the edge sites. The possibility of precipitation of cadmium in the form of solid phases was ruled out due to similar local environment around cadmium in samples prepared under air and nitrogen atmospheres, and by the absence of a Cd-Cd coordination found in the analysis of a 1000  $\mu\text{M}$  sample. Finally, analysis of samples with cadmium aqueous concentration of 3  $\mu\text{M}$ , 10  $\mu\text{M}$ , and 100  $\mu\text{M}$  at pH 9 suggests the formation of inner sphere complexes adsorbed to both silanol and aluminol edge sites in different ratios. In addition, we used molecular dynamics simulation to study the mechanisms involved in the adsorption of various ions to the basal surfaces of kaolinite. Analysis of simulation data indicates that cations and anions

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adsorb preferably on the siloxane and gibbsite surfaces of kaolinite, respectively. We observed strong inner sphere adsorption of chlorine at aluminum vacancies on the gibbsite surface and the occurrence of chlorine-driven inner sphere adsorption of cesium and sodium on the gibbsite surface for high ionic strengths. Cesium ions form strong inner sphere complexes at ditrigonal cavities on the siloxane surface. Outer sphere cesium is highly mobile and only weak adsorption may occur. A small amount of sodium adsorbs on the siloxane surface as inner sphere complexes at diffuse sites. Like cesium, sodium only forms very weak outer sphere complexes on this surface. Inner sphere complexes of cadmium and lead do not occur on either surface. Relatively strong outer sphere cadmium and lead complexes are present on the siloxane surface at ditrigonal cavities.