

Applying quantum chemistry to interpret XAS and NMR of Cd(II) adsorbed onto gibbsite and kaolinite

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Understanding how toxic metals such as cadmium (Cd^{2+}) adsorb to mineral surfaces could lead to improved methods for attenuating contaminants in surface and groundwater. Metals may adsorb preferentially to particular mineral surfaces; for example, Cd^{2+} could adsorb more favorably to the (100) surface of gibbsite than it does to the (001) surface.¹ If so, then synthetic gibbsite accentuated (100) surfaces could be used to diminish Cd^{2+} contamination in the environment. Experimental methods for studying adsorption have difficulty differentiating the sites of preferential adsorption onto minerals. However, computational chemistry techniques can provide results to compare with experimental data to distinguish which surface sites are most reactive towards adsorbing metals.¹

This study presents results from periodic planewave density functional theory (DFT) calculations of the (001) and (100) surfaces of gibbsite and kaolinite, respectively. Cd^{2+} was added to the surface models through mono-, bi-, or tridentate inner-sphere or outer-sphere interactions. The effects of surface charge (i.e., protonation) and hydration were used as variables to determine their effects on the calculated energies and structural results. Here, we report the calculated Cd–Al distances, relative energies, and adsorption energies for Cd^{2+} adsorbed onto the (001) and (100) surfaces of gibbsite and kaolinite models; it is possible to compare the former results with XAFS data.²

In addition, ongoing work involves the calculations of XANES and NMR properties of suitable candidate structures extracted from optimized periodic models. The results are compared with appropriate data.

[1] Kubicki *et al* (2008) *Geochem. Trans.* **9**(4). [2] Gräfe *et al* (2007) *J. Colloid Interface Sci.* **315**, 21-32.