Inner- and outer-sphere complexation of Pb and Zn on birnessite: EXAFS, density functional theory, and surface complexation modelling

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Sorption by birnessite is the dominant control of Pb and Zn concentrations in marine and terrestrial aquatic environments. We have discovered natural terrestrial birnessites with high concentrations of Pb (>30 wt. %) and Zn (>2 wt. %). EXAFS of these materials show no evidence of surface precipitates or phases such as coronadite or chalcophanite. Using predicted surface complex geometries from ab initio calculations on model clusters, we interpret the EXAFS as the expected tridentate inner-sphere complexes of Pb and Zn forming over vacancy sites on the MnO_6 layer. We find that we can synthesise identical Pb and Zn-bearing birnessites in the laboratory and that these phases can hold extremely high loadings of Pb and Zn. EXAFS of our synthetic materials suggest that loadings above 11 wt. % Pb or 3 wt. % Zn result from the formation of outer-sphere complexes in addition to the inner-sphere vacancy complexes. Outer-sphere complexes, however, are only indicated in EXAFS by a decrease in the average Pb-Mn and Zn-Mn coordination number.

Given that the association of Pb and Zn with birnessite is via surface complexation and not by the formation of a secondary precipitate, we can develop a thermodynamic model (surface complexation model) for sorption by fitting a series of sorption experiments to the equilibrium

$$>Mn_6O_3^{-2} + Zn^{+2} = >Mn_6O_3Zn$$

(with an analogous reaction for Pb) where $>Mn_6O_3^{-2}$ represents a vacancy site. In our surface complexation model, we used a basic Stern model for surface electrostatics and fixed the pK for each vacancy oxygen protonation to be 2.3 (equal to the pH_{pzc}). We used the number of sites as an adjustable parameter; our synthetic birnessite has 0.0025 moles sites/g. This corresponds to ~0.5 times the hypothetical maximum that would be expected for a single MnO_6 layer and is consistent with the near lack of coherent stacking in the c-direction and high surface area of δ-MnO_2. By including a complex with Pb or Zn in the diffuse layer, the basic Stern model also enables us to account for the outer sphere complexation. The exact molecular nature of "outer-sphere" Pb or Zn on birnessite is unclear, however.