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Structure of heavy-metal sorbed birnessite: Part 1. Results from X-ray diffraction

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ABSTRACT

The structure of heavy-metal sorbed synthetic birnessites (MeBi) was studied by powder X-ray diffraction (XRD) using a trial-and-error fitting procedure to improve our understanding of the interactions between buserite/birnessite and environmentally important heavy metals (Me) including Pb, Cd, and Zn. MeBi samples were prepared at different surface coverages by equilibrating at pH 4 a Na-rich buserite (NaBu) suspension in the presence of the desired aqueous metal.

Two main types of experimental XRD patterns were obtained as a function of the Me cations sorbed from solution, which exert a strong control on layer stacking sequence, as well as on the location and coordination of Me: (1) CdBi and PbBi samples correspond to a one-layer hexagonal (1H) structure, $AbC_{b'A'}\,{}^{C'b'}AbC$…, and (2) ZnBi exhibits a one-layer monoclinic (1M) structure in which adjacent layers are shifted by +**a**/3, $AbC_{b'A'c'}BcA_{c'B'a'}CaB_{a'C'b'}AbC$.

Simulated XRD patterns show that octahedral layers contain 0.833 Mn cations (Mn^{4+} and Mn^{3+}) and 0.167 vacant octahedra; $Mn^{3+}_{interlayer}$ and adsorbed $Me_{interlayer}$ compensate for the layer charge deficit. $Mn^{3+}_{interlayer}$ is octahedrally coordinated in all samples and is located above or below vacant layer octahedra sharing three O_{layer} with neighboring Mn_{layer} octahedra to form a triple-corner surface complex (^{VI}TC sites). In ZnBi and CdBi samples, $Me_{interlayer}$ is also located in TC sites; all Cd is octahedrally coordinated whereas about 30% of Zn is tetrahedrally coordinated (^{IV}TC sites). In PbBi samples, all Pb is octahedrally coordinated, most of these cations (~75%) being located in TC sites. Additional Pb is located above or below empty tridentate cavities, sharing three edges with neighboring Mn_{layer} octahedra (^{VI}TE sites).

Structural formulae calculated for each sample show that during the NaBu-to-MeBi structural transformation, interlayer Na^+ and Mn^{2+} are replaced by Me and H^+ adsorbed from solution, whereas $Mn^{3+}_{interlayer}$ resulting from the equilibration of NaBu at low pH is less affected. Sorption of divalent Me above and below vacant layer sites provides optimal conditions for local charge compensation in MeBi.