Effect of aging on Pb(II) sorption at the calcite-water interface

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Pb(II) sorption experiments with calcite powders were conducted in pH 7.3, 8.2 and 9.4 suspensions equilibrated at atmospheric $P\text{CO}_{2(g)}$ and ~22-25°C. Sorption-desorption experiments and X-ray absorption spectroscopy (XAS) were combined to elucidate the effect of sorption time on trends and dominant mechanisms. At pH 8.2, short-term batch experiments, ≤12 d, reveal the predominance of reversibly bound Pb, attributed to the formation of Pb inner-sphere adsorption complexes as confirmed by XAS. At pH 7.3 and 9.4, macroscopic experiments reveal a component of irreversibly bound Pb indicative of dual sorption mechanisms over the short term. Linear-combination fitting of XANES spectra for 12 d samples confirm ~95% adsorbed and ~5% coprecipitated Pb at pH 7.3, and ~75% adsorbed and ~25% coprecipitated Pb at pH 9.4. The irreversibly bound component as observed in batch experiments was attributed to coprecipitated metal.

For long-term sorption, ≥ 60 d, slow continuous uptake occurs at pH 7.3 and 8.2. Complete reversibility of the sorption process in combination with XAS analysis confirms that additional uptake in these samples proceeds via an adsorption mechanism. At pH 7.3, the ~5% coprecipitated component as observed for shorter sorption times is no longer evident suggesting detection may deoend on surface loading. At pH 8.2 the fraction of desorbed Pb is greater than that predicted from linear isotherms. This implies enhanced susceptibility of adsorption complexes to exchange when sorbed over the long-term. At pH 9.4 no further uptake occurs, and the reversibility of sorption and solid-phase distribution of Pb is commensurate with that for short-term experiments. This suggests that the relatively high fraction of coprecipitated metal (~25%) may affect the calcite surface topography such that further Pb sorption is precluded. The coprecipitated component is not available for exchange with the aqueous phase, and thus this mechanism may be vital for ultimate metal sequestration.

Structure determination of natural and synthetic nanocrystalline phyllomanganates

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In natural phyllomanganates, and especially in those resulting from biological activity, the abundance of random stacking faults leads to the occurrence of extremely disordered structures without three-dimensional ordering (turbostratic stacking). One effective way to characterize the actual structure of these defective solids is the trial-and-error fitting of X-ray diffraction (XRD) patterns using the mathematical formalism described by Drits and Tchoubar (1990).

Even in these most defective phyllomanganates, XRD patterns exhibit noticeable modulations on the high-angle side of the 20,11 and 31,02 scattering bands (~2.45 and ~1.42 Å, respectively – indexing performed assuming a base-centered two-dimensional cell). It will be shown that these modulations can be used to obtain relevant structural information, which includes not only unit-cell parameters but also atomic coordinates and site occupancies. In particular, these modulations were found to be sensitive to the amount of vacant layer sites capped by interlayer metal cations.

The usefulness of this simulation technique will be illustrated with various natural and synthetic (biogenic and abiotic) turbostratic phyllomanganate varieties consisting of diffracting crystallites in the nanometer range. Its complementarity with EXAFS spectroscopy, which is sensitive to the local binding environment of Mn, will be discussed.

Reference

Drits V.A. and Tchoubar C. (1990) X-ray diffraction by disordered lamellar structures. Springer-Verlag.