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XPS Study of Reductive Dissolution of Synthetic Birnessite by Humate

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Redox reactions play an important role in many of the geochemical and biological processes, and are particularly important for mobilisation of transition metals in sediments. Most of such reactions occur at the mineral-solution interface, hence study of reactions at such interfaces is critically important for the understanding of transition metal behaviour in natural systems.The present study investigates the surface reactions of synthetic birnessite [$Mn(II)_{0.05}Mn(III)_{0.25}Mn(IV)_{0.7}O_{1.7}(OH)_{0.25}$] when reacted with dilute (5 x 10^{-4}M) Na-humate solution using X-ray Photoelectron Spectroscopy (XPS).

Mn2 p, C1s and O1s spectra of reacted surfaces reveal that Mn(IV) of birnessite is reduced to Mn(III) while humate is oxidised to CO_2. Initially rapid production of CO_2 results in accumulation of CO_2 at the reaction interface. After about 15 minutes, the reaction rate decreases to the point where desorption keeps pace with accumulation (no appreciable change in adsorbed CO_2 content between 15 min and 2.5 hr). The rate of CO_2 production continues to decrease with time until after 5 hr of reaction CO_2 is not detected at the reaction surface. Reduction of Mn(IV) of birnessite to Mn(III) indicates that MnO_2-oxalate redox reaction proceeds as transfer of one electron per metal centre.

There is no XPS evidence for reduction of Mn(III) of the solid to Mn(II) in the presence of humate. Whereas this reaction proceeds in presence of other ligands (like arsenite), the carboxylate group of humate inhibits this step, probably through formation of a strong Mn(III)-carboxylate surface complex (either monodentate or bidentate). This postulate is consistent with Mn^{3+}(aq) stabilisation by oxalate in aqueous solutions. Further study using X-ray absorption spectroscopy (XAS) is required for a better understanding of the structure of the surface complexes.

Rate of release of soluble Mn(II) to dilute humate solutions is lower by more than two orders of magnitude compared with rate of release to aerated, distilled water at similar pH. Apparently, the process of proton promoted dissolution of the soluble Mn(II) component of birnessite in distilled water is impeded by the addition of humate. This is probably due to the formation of strong, multinuclear surface complexes between Mn(II, III) and adsorbed carboxylate groups.