

The reactivity of seven Mn-oxides with Cr_{aq}³⁺: A comparative analysis of a complex, environmentally important redox reaction

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ABSTRACT

The interactions between 10^{-4} M Cr_{aq}³⁺ and seven different Mn-oxides (six natural samples, including hausmannite, manganite, romanechite, cryptomelane, lithiophorite, and pyrolusite; and one synthetic sample, birnessite) have been observed in aqueous solution at pH 4.4 (pH 5.2 in the case of hausmannite) and room temperature. For each mineral-solution interaction, the aqueous chemical concentrations of [Mn_{aq}], [Cr_{aq}^T], and [Cr_{aq}⁶⁺] were measured with time. Reacted samples were examined by XPS to determine if and to what extent the surface chemical states of Cr, Mn, and O had changed. Microscopic observations of the reacted surfaces were obtained using AFM and high-resolution, low-voltage FESEM. Cr-uptake onto/into the Mn-oxides is observed to occur in Cr-hydroxide/hydrate undersaturated solutions as a result of adsorption, absorption, and surface precipitation. In addition, the rate and extent of reductive dissolution and Cr_{aq}³⁺ oxidation varied considerably between the seven Mn-oxides. The measured ratios of [Mn]_{aq}: [Cr⁶⁺]_{aq} were in agreement with the values expected from the proposed stoichiometric reactions where they could be easily written. The chromium as detected by XPS on the surface of the reacted Mn-oxides was predominately Cr³⁺, however pyrolusite contained both Cr³⁺ and Cr⁶⁺. Several previous studies have implicated a chromium surface precipitate to be responsible for the cessation of the Cr_{aq}³⁺ oxidation reaction. Our surface sensitive FESEM and AFM observations tend to suggest that Cr uptake is by isolated site binding, and very small (<30 nm) surface clusters. On two of the seven Mn-oxides tested (hausmannite and birnessite), Cr uptake was followed by slow Cr release after a substantial portion of the total aqueous Cr had been converted to Cr_{aq}⁶⁺.

The Mn-oxides that exhibited the greatest and longest lasting Cr³⁺-oxidizing ability were the Mn-oxides containing Mn³⁺, and in particular those containing Mn³⁺ and Mn²⁺. It is believed that the combined presence of a reducible Mn ion (e.g., Mn³⁺) and a highly soluble Mn²⁺ ion facilitates a sustained Cr³⁺-oxidation reaction because fresh Mn³⁺ surface is exposed during the dissolution reaction. Finally, the Cr_{aq}³⁺ reacted Mn-oxides tested showed a partial rejuvenation of their Cr³⁺-oxidizing ability after a period of drying and storage. An assessment of this process will require additional experimentation.