

CHROMIUM(III) INDUCED SOLID PHASE TRANSFORMATION OF δ -MnO₂

Fendorf S.E.* and Sparks D.L.

Dept. of Plant & Soil Science, Univ. of Delaware, Newark DE 19717-1303

In order to evaluate the hazard of heavy metals it is necessary to determine their reaction pathways in surficial environments. Chromium is a heavy metal which is stable in two oxidation states under surface environmental conditions, Cr(III) and Cr(VI). The trivalent form is benign and rather immobile in soil and water systems due to its low solubility in all but acidic conditions, in addition to its high affinity for solid surfaces. In contrast, Cr(VI) is more toxic and very mobile in the environment as it readily forms anionic species. Therefore, to assess the hazard of Cr in a system one must determine the speciation of Cr and any reaction pathways which will allow for transformations between oxidation states (redox reactions).

Manganese oxides appeared to be the oxidant of Cr(III) present in the soils (1), and are the only naturally occurring substances which are capable of oxidizing Cr(III) under commonly occurring environmental conditions (2). Various phases of Mn-oxides have the capacity to oxidize Cr(III) (2-4). Amacher and Baker (4) used a commonly occurring form of Mn-oxide, δ -MnO₂, to investigate the oxidation of Cr(III). Chromium(III) was readily oxidized by the δ -MnO₂, but the oxidation rate decreased with increased pH--contradicting thermodynamically expected trends. It was hypothesized that Mn(II) liberated in the redox reaction was reabsorbing on the surface and inhibiting Cr(III) sorption and subsequent oxidation by the oxide. However, Mn(II) was shown not to inhibit the oxidation of Cr(III) (5); Fendorf and Zasoski (3) hypothesized that the decrease in extent and rate of Cr(III) oxidation by δ -MnO₂ with increasing solution pH values and Cr(III) concentrations was due to the formation of a surface precipitate of Cr(OH)₃. The Cr-hydroxide precipitate thus induced a barrier to the electron transfer between Cr(III) and δ -MnO₂, and was itself thermodynamically redox stable. The resulting electrophoretic mobilities of the conglomerated colloid were representative of the Cr-hydroxide as opposed to the δ -MnO₂.

The hypothesized formation of a surface precipitate has been based on macroscopic data; therefore, the inhibition mechanism of Cr(III) oxidation remains in question. Here, we have used high resolution transmission electron microscopy (HRTEM) to investigate the possible formation of a surface precipitate at higher solution pH values and Cr(III) concentrations. High-resolution TEM images show that the unreacted MnO₂ was partially crystalline (6). Interspersed with amorphous material, there are layers of parallel atomic planes exhibiting severe bends and twists which in some cases form distinctive needle-shaped protrusions characteristic of synthetic birnessites. Conventional selected area electron diffraction yields patterns show well defined but rather broad rings having prominent 2.4 Å and 1.4 Å spacings, and a spacing of roughly 7.3 Å can also be discerned. After reacting with Cr(III), HRTEM images of the δ -MnO₂ show a marked change in the crystal structure. Electron diffraction confirms this, producing patterns containing sharp, well defined rings throughout. A dramatic change in the crystal structure is apparent after the oxidation/reduction reaction of Cr(III) and MnO₂. The solid surface post-reaction is not redox reactive and thus Cr(III) oxidation is terminated upon its formation. The results of these findings have important implications for environmental quality. The highly redox reactive δ -MnO₂ is transformed into a redox stable crystalline solid; thus, the potential for Cr(III) oxidation to the more hazardous Cr(VI) species is eliminated. Currently work is underway to determine the identity of this newly formed solid phase resulting from the Cr(III)/MnO₂ reaction.

References

- (1) Bartlett, R.J., and B. James. 1979. *J. Environ. Qual.* 8:31-35.
- (2) Eary, L.E., and D. Rai. 1987. *Environ. Sci. Technol.* 21:547-552.
- (3) Fendorf, S.E., and R.J. Zasoski, 1991. *Environ. Sci. Technol.* In Press.
- (4) Amacher, M.C., and D.E. Baker. 1982. DE-AS08-77DPO4515. Inst. for Res. on Land and Water Res., Penn State Univ, PA.
- (5) Fendorf, S.E., R.J. Zasoski, and R.G. Burau. 1991. Submitted to: *Environ. Sci. Technol.*
- (6) Fendorf, M., Fendorf, S.E., Sparks, D.L., and Gronsky, R. 1991. *Proceedings of the 49th Annual Meeting of the Electron Microscopy Society of America*, (ed. Bailey, G.W.) In Press. (San Francisco Press, Inc., San Francisco, 1991).