Arsenic Oxidation by Hausmannite: Effects of Metal Impurity and Mn Oxide Mixtures

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The reactivity of manganese (Mn) oxides with heavy metals of concern in the environment has almost exclusively been examined using pure, well-defined individual Mn oxide through controlled laboratory batch experiments. However, natural mineral samples typically have trace metal impurities, either incorporated into their structures or present on surfaces, and mixed mineral phases are exceedingly common. Yet the effects of metal impurities and Mn oxide mixtures in regards to their reactivity have not been fully understood.

In this study, we aim to address part of this knowledge gap by comaring pristine hausmannite ($Mn^{II}Mn^{III}{}_2O_4$) nanoparticles to those with Ni(II) impurities, either structurally incorporated (up to 20 w.t.%) or surface-sorbed, in regards to their oxidation potential for arsenite (As(III)). We also compared the As(III) oxidation rate of hausmannite and bixbyite ($Mn^{III}{}_2O_3$) mixtures with that of individual Mn oxide. Total As and Mn concentrations in batch reactions over 8 hr were measured by inductively coupled plasma optical emission spectroscopy, and arsenate (As(V)) by ion chromatography. We also applied attenuated total reflectance Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy to determine surface complexes formed on the various mineral surfaces, and to assess changes to the hausmannite morphology. Pristine hausmannite presented the highest As(III) oxidation rate (~87 % of added As(III) to As(V)), followed by Ni-sorbed and Ni-substituted hausmannite. Ni(II) subsitutition in the structure caused ~20% reduction in As(III) oxidation. Reaction products, Mn(II) and As(V), were predominently found in solution versus bound to the mineral surfaces and the pseudo-octahedral hausmannite changed to almost spherical after 8 hr. The As(III) oxidation rate by hausmannite and bixbyite mixtures was almost comparable to that by pristine hausmannite only. The result of this study showcases the importance of metal impurities and mineral mixed phases in Mn oxide reactivity with As(III), and further, helps better predict the behavior of As in the environment.