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Influence of organic potassium biphthalate on Mn oxide nucleation and growth

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Manganese oxides are important stabilizers of organic carbon in soil and aqueous environments. Here, we examined Mn oxide coprecipitation in the presence of phthalate, a non-reactive, widely detected anthropogenic organic contaminant commonly used in plasticizers. Solutions of 0.22 M $MnCl_2$ were mixed with pH ~11 and ~13 NaOH solutions, and bubbled with O_2 (~0.1 L/min). Experiments were conducted with and without potassium biphthalate (KPH) at 1:2 and 3:4 KPH:Mn ratios. Precipitates were characterized with X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and organic elemental analysis. Aqueous Mn remaining in solution was analyzed over time with inductively coupled plasma optical emission spectroscopy.

Most precipitation occurred within 5-100 minutes of reaction. In the absence of KPH, pH ~13 experiments produced primarily the Mn^{3+}-rich, tunnel-structure Mn oxide, manganite, along with minor feitknechtite, manjiroite and hausmannite. At pH ~11, manganite dominated with minor feitknechtite and manjiroite. XPS confirmed a higher fraction of Mn^{3+} in solids formed at pH~13 relative to pH ~11.

The addition of KPH slowed precipitation and reduced solid yield. The precipitates were poorly crystalline, exhibiting broad XRD peaks. XPS showed higher Mn^{4+} fractions in KPH-containing experiments, while Raman indicated increased formation of layered Mn oxides. At pH ~13, increased KPH produced Mn^{4+}-rich layered birnessite and tunnel-structured todorokite. At pH ~11, KPH promoted layered birnessite-like phases with todorokite and cryptomelane. XPS confirmed a significant increase in Mn^{4+}/Mn^{3+} ratios of solids produced from pH~13 solutions with KPH, and a smaller increase at pH ~11. Solids formed with KPH at pH ~13 contained 2.11% - 2.56 wt% C. These results suggest that KPH may inhibit nucleation and growth by blocking reactive surface sites and/or through dissolved Mn complexation. KPH may also promote the oxidation of Mn^{3+} to Mn^{4+} during Mn oxide precipitation, perhaps by slowing precipitation and increasing exposure of Mn to O_2. This may subsequently promote layered Mn oxide formation with higher Mn^{4+} content. Carbon incorporation during coprecipitation highlights how strong mineral-organic associations may impact Mn oxide mineralogy and potential carbon stabilization in natural systems.