

Effects of dissolved oxygen on the interaction between $\text{Cr}(\text{OH})_3(\text{s})$ and birnessite

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Hexavalent chromium ($\text{Cr}(\text{VI})$) is the 2nd most common inorganic contaminant after lead at hazardous waste sites driven by various applications of Cr for industrial purpose. In addition to the anthropogenic contamination, soil and groundwater contamination by $\text{Cr}(\text{VI})$ without any anthropogenic source has been reported around the world. Under natural environments, the geochemical processes for $\text{Cr}(\text{VI})$ generation would likely be associated with the oxidation of $\text{Cr}(\text{III})$ since Cr generally exists in the oxidation state of +III as a trace constituent in various aluminosilicate minerals. Previous studies have suggested that the principal oxidant of $\text{Cr}(\text{III})$ would be Mn oxides of natural origin. This study examines the effects of dissolved oxygen (DO) on $\text{Cr}(\text{VI})$ generation from the oxidative dissolution of $\text{Cr}(\text{OH})_3(\text{s})$ mediated by birnessite, which is one of the most common Mn oxides in the environment.

For the purpose of this study, $\text{Cr}(\text{OH})_3(\text{s})$ and birnessite were synthesized and reacted to each other under oxic or anoxic conditions. 1.0 g/L of each solid was mixed in 50 mM NaNO_3 adjusted to pH 7, 8 or 9 with a buffer (Na-MOPS for pH 7 and 8, CHES for pH 9). $\text{Cr}(\text{OH})_3(\text{s})$ was readily oxidized by birnessite under both oxic and anoxic conditions. Especially, the oxidation of $\text{Cr}(\text{OH})_3(\text{s})$ was considerably boosted at all pH conditions in the presence of DO. In addition, the effects of DO increased with increasing pH. These results indicate that the overall reaction between $\text{Cr}(\text{OH})_3(\text{s})$ and birnessite would likely be catalyzed by DO and thereby follow different pathways under oxic conditions from those in the absence of DO.