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Effect of organic ligands on Cr(III) oxidation by δ-MnO_2

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The oxidation of Cr(III) to the more toxic, carcinogenic and mobile Cr(VI) is an important process increasing in the context of pollutant mobilization in soil, water and air. The oxidation of Cr(III) by manganese oxides is considered one of the most important oxidation mechanisms. Since the solubilities of Cr(III) bearing phases and Mn oxides under oxic conditions and circum-neutral pH are typically very low, dissolution of low concentrations of Cr(III) from stable solid phases, diffusion towards Mn oxides and oxidation at the Mn oxide surfaces are considered important steps in the dominant oxidation mechanism. This was driven home in a study by Pan et al. (2019) using split reactor experiments with a dialysis membrane prohibiting direct contact between Cr(III) hydroxides and MnO_2 to show that the low solubility of Cr(III) at alkaline pH strongly reduces diffusion to MnO_2 and therefore inhibits the oxidation reaction.

As part of a study of Cr isotope fractionation by ligand complexation, we investigated the effect of organic ligands on diffusion-controlled Cr(III) oxidation by MnO_2. In this study, we compared the effect of structurally different organic ligands on Cr(III) oxidation by MnO_2 in mixed batch experiments and compared it to rates in a similar split reactor setup as the one employed by Pan et al (2019). We generally observed inhibitory effects of organic ligands on oxidation rates in mixed batch systems. However, in split reactor experiments where diffusion rates are limiting oxidation in the absence of a ligand, we observed significant acceleration of the oxidation rates depending on the ligand structure and reactivity. In this presentation we interpret these observations based on mechanistic differences and discuss their relevance for contaminated systems.

References

1. Pan, Liu, Catalano, Wang, Qian, Giammar (2019). ACS Earth Space Chem 3, 357-365.