296 - Cation effects on Mn²⁺ oxidation by nanoparticulate d-MnO₂

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 $Mn^{(III,IV)}$ -oxides can coexist with dissolved Mn^{2+} in the environment, such as in a redox reaction where Mn^{2+} is produced by $Mn^{(III,IV)}$ reduction or oxidized to form $Mn^{(III,IV)}$ -oxides. In this study, d- MnO_2 , a nanoparticulate layered $Mn^{(IV)}$ -oxide, was reacted

with 1 mM Mn^{2+} at pH 7.8 in a stirred-flow reactor in the presence of Na⁺ (50 mM), Ca²⁺ (16.7 mM), Ni²⁺ (0.1mM) and Zn²⁺ (0.1mM), respectively. The reacted solids were characterized using XRD, XAS and TEM. Results indicate that feitknechtite (b-

 $Mn^{III}OOH$) was the predominant mineral phase formed in the presence of Na⁺, Ca²⁺ and Ni²⁺, whereas hetaerolite (ZnMn^{III}₂O₄) is

the product in the presence of Zn^{2+} . The four types of cations exhibit different inhibitory effects on the reaction rate in the increasing order of Na⁺, Ca²⁺, Zn²⁺ and Ni²⁺. The strong Ni²⁺ inhibitory effect is likely due to its ability to enter vacant sites and/or adsorb on edge sites of d-MnO₂.

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