Title: Photochemically-induced formation of manganese oxide nanoparticles by reactive halogen radicals in briny water

Authors: Zhenwei Gao, Charlie Skurie, Jing Liu, and Young-Shin Jun*

Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, Missouri 63130, United States

**ysjun@wustl.edu*

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Abstract: In meeting rapidly growing demands for energy and clean water, engineered systems such as unconventional oil and gas recovery and desalination processes produce large amounts of briny water. In the environment, these highly concentrated halides can be oxidized and transformed to reactive halogen radicals, whose roles in the degradation and transformation of organic pollutants have been studied. However, redox reactions between halogen radicals and heavy metal ions are still poorly understood. In this work, we found that aqueous manganese ions (Mn^{2+}) could be oxidized to Mn oxide solids by reactive halogen radicals generated from reactions between halide ions and hydroxyl radicals or between halide ions and triplet state dissolved organic matter. In particular, more Mn^{2+} was oxidized by Br radicals generated from bromide ion (Br^-) than by Cl radicals generated from chloride ion (Cl^-), even though the concentrations of Br^- in surface waters are much lower than Cl^- concentrations. In addition, the highly concentrated halides greatly increased the ionic strength of the solution, affecting Mn^{2+} oxidation kinetics and the crystallinity and oxidation state of the newly formed Mn oxides. These newly discovered pathways involving Mn^{2+}(aq) and reactive halogen radicals aid in understanding the generation of abiotic Mn oxide solids and forecasting their redox activities. Moreover, this work emphasizes the critical need for a better knowledge of the roles of reactive halogen radicals in inorganic redox reactions.