

As(III) oxidation by delta-MnO₂: Kinetics, Mechanisms, and Inhibition

MATTHEW GINDER-VOGEL^{1,2*}, BRANDON LAFFERTY^{2,3}, AND DONALD L. SPARKS²

¹Present Address: Environmental Chemistry and Technology, Dept. of Civil and Environmental Engineering, University of Wisconsin – Madison, Madison, WI 53706, mgindervogel@wisc.edu

²Dept. of Plant and Soil Sciences, Delaware Institute for the Environment, University of Delaware, Newark, DE 19711

³United States Army Corps of Engineers, Engineer Research and Development Center, 3909 Halls Ferry Rd, Vicksburg, MS 39180

Abstract

In the environment, chemical reactions at the mineral/water interface occur over a range of temporal scales, ranging from microseconds to years. Many important mineral surface processes (e.g., adsorption, oxidation-reduction, precipitation) are characterized by a rapid initial reaction on time-scales of milliseconds to minutes, and are often limited by the formation of secondary mineral phases. Knowledge of these initial reaction rates combined with detailed characterization of secondary phases is critical to determining chemical rate constants, and reaction mechanisms.

Here we describe the reactions controlling the oxidation of As(III) by δ -MnO₂ (a poorly crystalline form of hexagonal birnessite) over time-scales ranging from sub-second to hours. Initial As(III) oxidation rates (< 30 s) were measured using batch reactions and quick-scanning X-ray absorption spectroscopy (Q-XAS). Longer-term reaction dynamics were examined using a combination of column and stir-flow reactors combined with molecular-scale characterization of the resultant solid-phases with both Q-XAS and traditional XAS. While the aqueous As(V) and As(III) concentrations were determined using LC-ICPMS analysis.

Q-XAS studies reveal that As(III) oxidation occurs most rapidly during the initial 30 seconds of reaction, followed by slow oxidation over the next several minutes, and that traditional analysis (i.e., ex-situ analysis of As(III/V)_{aq}) may underestimate As(III) oxidation rates due to As(V) removal from solution due to sorption on the HMO mineral surface.

In column and stirred-flow experiments, As(III) oxidation by δ -MnO₂ is also initially rapid but slows appreciably after several hours of reaction. Mn(II) is the only reduced product of δ -MnO₂ formed by As(III) oxidation during the initial, most rapid phase of the reaction. However, it appears that observed Mn(III) is a result of comproportionation of Mn(II) sorbed onto Mn(IV) reaction sites rather than from direct reduction of Mn(IV) by As(III). The only evidence of arsenic (As) sorption during As(III) oxidation by δ -MnO₂ is during the first 10 h of reaction, and As sorption is greater when As(V) and Mn(II) occur simultaneously in solution. Our findings indicate that As(III) oxidation by poorly crystalline δ -MnO₂ involves several simultaneous reactions and reinforces the importance of studying reaction mechanisms over multiple time-scales with multiple techniques.