

## **From As to U—Central and Complex Controls of Fe and Mn on Contaminant Cycling**

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It is hard to overstate the influence of Fe and Mn on the cycling of metals and metalloids, ranging from As to U. Oxides, oxyhydroxides, and hydroxides of both Fe and Mn serve as primary scavengers of metal(loids), regulating dissolved concentration and transport of contaminants within soils and sediments. The influence of Fe and Mn reaches far beyond sorption processes, however—it includes oxidation, reduction, and aqueous complexation. Moreover, reactive oxygen species generated from Fe(II) and Mn(II) reaction with molecular oxygen results in a broad-range of reaction outcomes for redox active metals such as As, Cr, and U.

The cycling of Cr and U are particularly tied to Mn and Fe. For Cr, Mn(III/IV) oxides represent the only known oxidant of Cr(III) outside of molecular oxygen in hyper alkaline waters. Generation of Cr(VI) from Mn oxides even proceeds with Cr(III) present in sparingly soluble phases. Here, the reaction of Cr(III) with Mn(III/IV) becomes critically dependent on the distance between the two solids, and Mn(II) formation, and then oxidative deposition proximal to Cr(III) phases, become the essential step facilitating the Cr-Mn redox reaction. By contrast, Fe takes the role of nullifying Cr(VI) generation, where even low (micromolar) concentrations of Fe(II) effectively reduce Cr(VI) and render Cr in a sparingly soluble Cr(III)-Fe(III) phase.

Consistent with Cr, U(IV) solids can be oxidized by Mn(III/IV), with the reaction proceeding through a dissolution-redox window. More critical to U, however, is the reduction of dissolved U(VI) by Fe(II). Both solid and aqueous Fe(II) serve as facile reductants of U(VI), with the reaction rate and thermodynamic viability dependent on the uranyl speciation, pH, and Fe phases. The reaction is not, however, singular and rather represents a reaction series that is highly dependent on specific species and concentrations, with divergent product outcomes. Importantly, the final product may differ from the expected U(IV) phases or organic matter complexes and rather involve U(V)-Fe(III) solid products.

In sum, the cycling of metal(loid) contaminants is shaped in large part by reaction with Mn and Fe. The reactions, however, are complex and not always intuitive with our long held assumptions. Here, a series of the complexities driving As, Cr, and U cycling will be illustrated.