# Redox Dynamics of Hg and U: Mn(II) as a Reductant of Hg(II) and the Influence of Mineral Surface Sites on the Speciation of U(IV)

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Uranium (U) and mercury (Hg) are contaminants of concern at DOE sites such as Hanford, Rifle, and Oak Ridge. Reductive remediation has been explored extensively for U immobilization, under the premise that mobile U(VI) transforms to less-soluble U(IV) species. As reductive approaches are implemented it is important to understand the effects on other contaminants and components in the system. One of the aims of the Argonne Subsurface SFA project is to provide new insight on the relationship between contaminants of interest (Hg and U), bacteria, and major redox-active elements such as Fe, S, and Mn.

As part of these efforts we have investigated the reduction of Hg(II) by Mn(II). The abiotic reduction of Hg(II) occurs in addition to microbial reduction and is a key component of Hg biogeochemical cycling. Although reduction to Hg(0) is thermodynamically favorable when coupled to the oxidation of Mn(II), to date the redox reactivity between Hg(II) and Mn(II) has not been documented. Here, we use synchrotron X-ray Absorption Spectroscopy (XANES and EXAFS) to demonstrate that Mn(II) can reduce Hg(II) under environmentally relevant conditions. The reactivity, the reaction pathways, and the reduced Hg products depend on pH and the complexing ligands or the mineral loading in the system. At pH 7.5 Hg(II) was reduced to Hg(0) within hours. Hg(II) reduction was coupled to the oxidation of Mn(II) to sparingly-soluble Mn(IV) oxides. Minerals such as Al2O3 and TiO2 inhibited the rate of Hg(II) reduction. Complexing ions such as sulfate-stabilized Hg(I) intermediates, which transformed to Hg(0) over an extended period of time.

In addition, we are continuing to investigate the factors responsible for the non-uraninite U(IV) speciation observed in reduced field-site sediments. We have shown previously that phosphate and Ti(IV) inhibit uraninite formation, resulting instead in complexed U(IV) in the solid phase. Here, we demonstrate that the ratio of U to the high affinity surface sites in a system affects the speciation of U(IV) produced by reduction of U(VI). At low U:surface ratios that are typical of natural environments, the presence of minerals such as TiO2 and Fe3O4 leads to the stabilization of adsorbed U(IV) species, whereas higher U:surface ratios that are more typical of laboratory experiments lead to the predominance of uraninite. These results expand the set of biological and abiotic factors known to control non-uraninite U(IV) speciation and suggest the need to modify current geochemical models to include this complexity for more accurate predictions of U transport.