

ROLE OF Fe-MINERALS ON RADIONUCLIDE MOBILITY IN SUBSURFACE

R.K.Kukkadapu¹, T.S.Peretyazhko¹, J.M.Zachara¹, Y.Bi², and K.F.Hayes²

¹Pacific Northwest National Laboratory, Richland, WA 99352, USA

²University of Michigan, Ann Arbor, Michigan, MI,48103, USA

The U.S. Department of Energy faces the challenge of cleaning up groundwater plumes contaminated by radioactive metals, e.g., uranium and technetium. The mobility of these metals in contaminated aquifers is governed by a complex assortment of site-specific biogeochemical and hydrological properties, sediment Fe-mineralogy, and redox status. Among other effects, there is a particular interest in understanding the role of Fe(III)-(oxyhydr)oxides and Fe-containing clay minerals, ubiquitous in soils and sediments, on metal attenuation. Secondary Fe(II)-minerals, such as Fe-sulfides and Fe-carbonates generated under reducing conditions by (bio)transformation of the Fe(III)-(oxyhydr)oxides convert oxidized soluble contaminants to sparingly soluble phases, e.g., Tc(VII)_{aq} to Tc(IV)-oxide. Reduced clays also are reactive toward soluble contaminants. However, upon the return of oxic conditions, these Fe minerals are vulnerable to oxidative mineral transformation. Thus, the temporal fate of the contaminants in the subsurface is, in part, a function of the Fe-redox state.

Two case studies regarding the role of Fe-minerals on radionuclide mobility under different scenarios are presented here. In the first example, sediments obtained at different depths from the Columbia River corridor (WA State, USA) were reacted with soluble Tc(VII) to gain insights into the nature of reactive Fe(II). Detailed Mössbauer spectroscopy measurements, coupled with Tc-extended X-ray absorption fine structure (EXAFS), microscopic observations, and selective chemical extraction studies, have shown the Fe-mineralogy of the transect varied with the depth, and Tc reactivity of the sediment is dependent on the Fe(II)-mineral suite of the sample. Sediments containing siderite, FeCO₃, exhibited the highest reactivity toward Tc. Figure 1 shows Mössbauer spectra of a siderite-rich sample before and after Tc reaction.

Biogenic Fe-sulfide minerals have been reported to slow down the oxidation of U(IV)O₂ precipitate to soluble U(VI). However, the delaying effect of Fe-sulfides on UO₂ oxidative dissolution and its implication for long-term U immobilization is not well understood. To understand the mechanistic details of the role of Fe-sulfide on UO₂ dissolution, products of laboratory-synthesized mackinawite (Fe(II)S_{0.9}) and UO₂ mixture reacted with dissolved oxygen (DO) were studied. Mössbauer spectroscopy, X-ray diffraction (XRD), and solution analysis indicated: a) Fe(II)S_{0.9} effectively scavenges DO and inhibits UO₂ oxidation until Fe(II)S_{0.9} is completely depleted, and b) Fe(II)S_{0.9}

is converted to nanogoethite and lepidocrocite via an Fe(II)/Fe(III) intermediate product state that was not readily discernible from XRD (Figure 2).

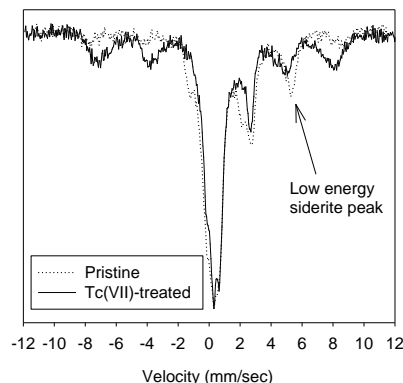


Figure 1. 12 K spectra of pristine and Tc(VII)-treated sediments showing siderite oxidation by Tc(VII) to a new Fe(III)-phase.

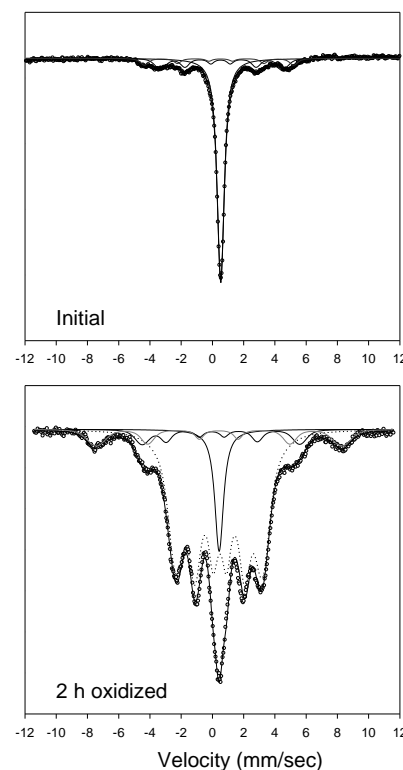


Figure 2. 4.5 K Mössbauer spectra of initial and 2-h oxidized FeS_{0.9} samples. The singlet in the initial sample is due to low-spin Fe(II) in a tetrahedral environment in mackinawite. Bulk transformation of the singlet occurred within 2 hours. The inner sextets are due to Fe(II) and Fe(III) in modified mackinawite structure. The outer sextet is due to ferrihydrite