Transuranic Interfacial Reaction Studies on Manganese Oxide Hydroxide Mineral Surfaces

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Professor Heino Nitsche, Lawrence Berkeley National Laboratory

Dr. Jeffrey Serne, Pacific Northwest National Laboratory
Dr. David K. Shuh, Lawrence Berkeley National Laboratory
Dr. Glenn A. Waychunas, Lawrence Berkeley National Laboratory

Research Objective

The objective of this project is to provide fundamental knowledge on the interfacial reactions of neptunium and plutonium with manganese oxide and hydroxide mineral surfaces. This information is relevant to the transport of transuranic radionuclide (TRU) contaminants in the vadose zone. Several DOE sites have been contaminated by TRU discharges as a result of weapons activities. Manganese oxides, present as minor phases in the vadose zone, may preferentially sequester TRU and transition metals over iron oxide/hydroxide minerals present in much larger amounts.[1,2] Neptunium and plutonium are highly toxic and potentially mobile in the vadose zone. Transport depends on the physical and chemical reactions between the neptunium or plutonium and the geological material. The data obtained from this project will be used for reactive transport modeling of TRU in the vadose zone, where the processes determining the retardation, immobilization, mobilization and permanence of TRU are poorly understood. Transport modeling will ultimately lead to an improved basis for predicting TRU migration in the vadose zone to adjacent groundwater supplies.

Research Progress and Implications

As of February, 2000, initial sorption experiments have been performed with Pu(VI) on manganite (MnOOH), a manganese oxide/hydroxide mineral with a structure similar to that of rutile. The mineral was first characterized using a combination of powder X-ray diffraction (XRD) and X-ray absorption fine structure spectroscopy (XAFS) on the Mn K edge. Two other manganese oxide minerals, cryptomelane (KMn_8O_{16}) and hausmannite ($Mn(II)Mn(III)_2O_4$), were also characterized with these techniques for use in upcoming sorption experiments. The sorption studies were carried out in batch mode with manganite that was approximately 30-50 µm in size at an ionic strength of 0.1 M. Experiments were performed at two different pH values (5 and 9.5) under atmospheric conditions. The concentration of Pu(VI) in the sorption experiments was 10^{-4} M.

The amount of plutonium sorbed onto the manganite was determined by liquid scintillation measurements taken before and after the addition of the solid. In all samples over 95% of the plutonium was adsorbed after approximately 10 minutes of contact with the manganite. After 24 hours of constant agitation, approximately 50% of the remaining aqueous plutonium was also sorbed onto the manganite. This sorption process is similar to that of other metal oxides where a very fast initial adsorption step is followed by a much slower adsorption step.

The sorption samples were characterized using XAFS on the plutonium L_{III} edge. The oxidation state of the plutonium after having sorbed onto the manganite was determined by comparing XAFS spectra from the sorption samples to aqueous standard solutions of Pu(IV), Pu(V) and Pu(VI). Approximately 90% of the sorbed plutonium at pH 5 remained as Pu(VI) and the other 10% was reduced to Pu(IV). Likewise, only about 30% of the sorbed plutonium at pH 9.5 remained as Pu(VI) and the rest of the plutonium (70%) was reduced to Pu(IV). There was no evidence of Pu(V) at either pH. Figure 1 shows a representative fit to one of the pH 9.5 samples. The fit is constructed from linear combinations of the Pu(IV), Pu(V) and Pu(VI) standards until the errors of the fit are minimized.

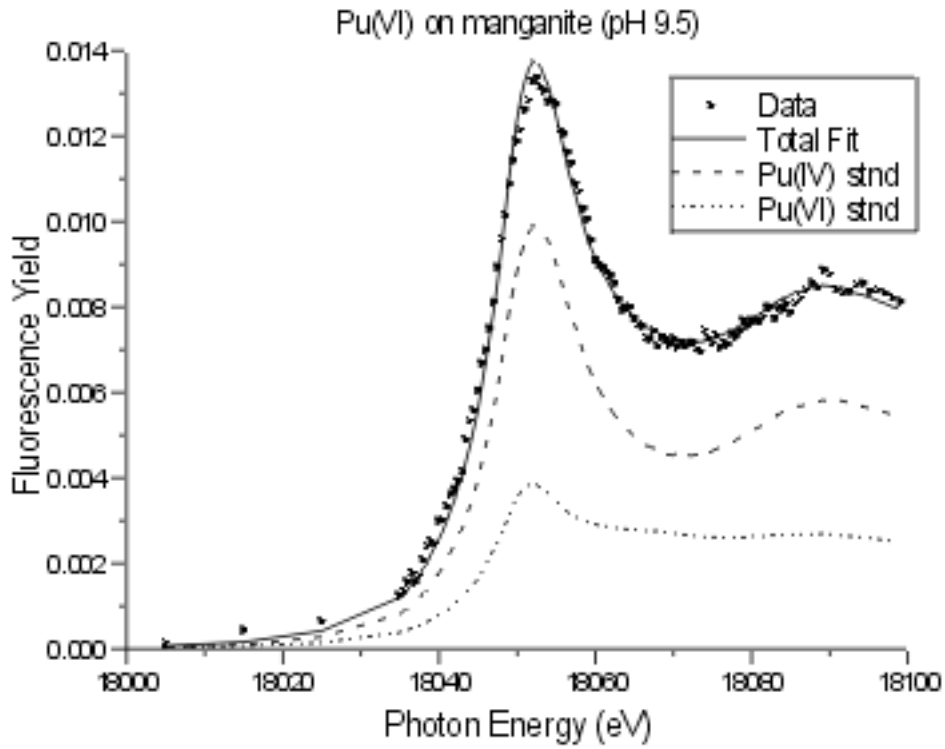

Figure 1. Representative fit to Pu L_{III} XAFS data from the sorption of Pu(VI) on manganite at pH 9.5.

Planned Activities

The manganese minerals will be further characterized to determine their surface area, surface site density and proton exchange capacity. Sorption experiments will be continued to determine the thermodynamic and kinetic parameters governing the sorption of aqueous ions of neptunium and plutonium in well-defined oxidation states on well-characterized mineral surfaces as a function of pH, actinide concentration and ionic strength. These parameters will then be used as input data for reactive transport modeling of TRU in the vadose zone and for the determination of the speciation of neptunium and plutonium in contact with manganese oxide/hydroxide minerals.

References

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2) A. Manceau and J. –L. Hazemann, "ALS work 1998-1999," Personal communication (1999).