Transuranic Interfacial Reaction Studies on Manganese Oxide Hydroxide Mineral Surfaces

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Operated by Battelle for the U.S. Department of Energy

Project No. 70176
FY 2000 Award

Background

Objectives

Knowledge of the interfacial reactions of the transuranic radionuclides (TRU) neptunium and plutonium with manganese oxide and hydroxide mineral surfaces is needed to understand the mobility of these contaminants in the vadose zone.

The processes determining the retardation, immobilization, and permanence of TRU in the vadose zone are poorly understood. The transport properties depend strongly on the physical and chemical interactions between the TRU and the surfaces of the geomaterials.

Recent investigations have indicated that manganese oxides and hydroxides, present as minor phases in the vadose zone, can preferentially sequester TRU over iron oxide/hydroxide minerals present in much larger amounts.[1,2]

In order to develop accurate reactive transport models that predict the migration of TRU through the vadose zone, surface interactions between TRU and manganese oxide/hydroxide minerals present in the vadose zone must be modeled correctly.

Thermodynamic and kinetic parameters governing the sorption of TRU, specifically neptunium and plutonium, in well-defined oxidation states on well-characterized manganese oxide/hydroxide mineral surfaces as a function of pH, actinide concentration, and ionic strength are being investigated. These data will be used to develop surface interaction models between TRU and manganese oxide/hydroxide mineral surfaces.

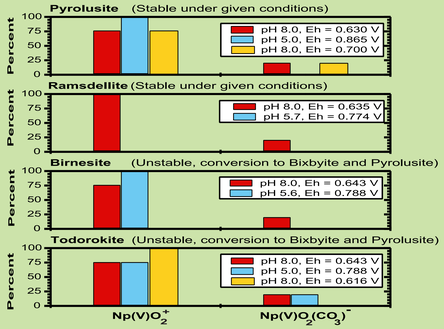
Significance to DOE

- Several U.S. Department of Energy sites within the nuclear weapons complex have been contaminated with TRU resulting from the discharge of contaminated liquids directly into the ground. Manganese oxides have been identified in the areas around these contaminated sites.[3]
- Predicting the potential hazards of these TRU to humans requires reliable transport models of TRU through the vadose zone and the underlying groundwater.
- Understanding the interactions between TRU and manganese oxyhydroxides is essential to creating reliable reactive transport models of TRU from contaminated DOE sites to adjacent water supplies.

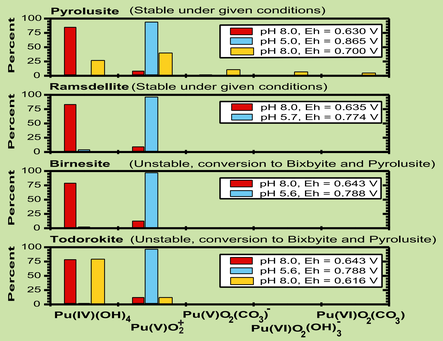
Actinide Properties

Aqueous Actinide Speciation

- Neptunium can exist in three oxidation states (4+, 5+, 6+) and plutonium can exist in four oxidation states (3+, 4+, 5+, 6+) in natural aqueous environments.
- Low pH values tend to favor lower oxidation states while higher oxidation states become more accessible as the pH is increased.
- Species distributions of neptunium and plutonium in contact with manganese minerals were calculated assuming actinide concentration = 10^{-6} M, ionic strength I = 0.01 M and the system is open to air and in equilibrium with CO_2.



Speciation calculation results for neptunium in contact with selected manganese oxides/hydroxides.[4]

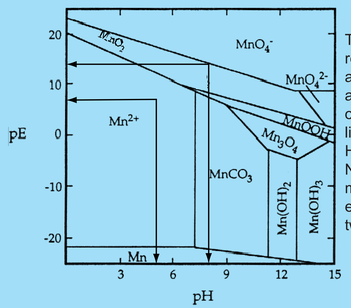


Speciation calculation results for plutonium in contact with selected manganese oxides/hydroxides.[4]

Properties of Manganese Oxide Hydroxide Minerals

Stability of Manganese Minerals in the Vadose Zone

Changes in chemical conditions can widely alter the Eh and pH of vadose zone liquids. Such changes may affect the solubility and stability of mineral phases, as shown in the diagram below.[5]

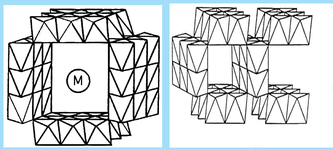


The arrows represent approximate pE and pH conditions of vadose zone liquids from the Hanford waste site. Notice that several mineral phases exist between the two arrows.

Structure of Manganese Oxide Hydroxide Minerals

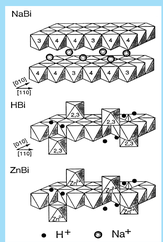
Manganese oxide/hydroxide minerals form a variety of structures with tunnels, layers, and other topologies, resulting in a wide range of reactive sites for the incorporation or binding of metal species.

Tunnel Structures:



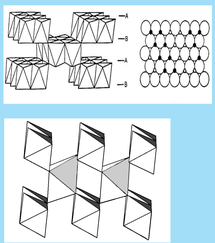
Todorokite (I)
Cryptomelane (r)

Layer Structures:



Birnessite

Three Dimensional Structures:



Ramsdellite (top), Manganite (bottom)

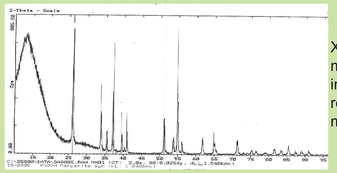
Initial Results

Experiment

Investigation of the sorption properties of plutonium(VI) on manganite (MnOOH). Plutonium concentration = 10^{-4} M (0.05 mg) and ionic strength I = 0.1 M. Samples were prepared at several pH values with 200 mg MnOOH (M/V = 100 g/L) under atmospheric conditions in $NaClO_4$ background electrolyte.

Mineral Characterization

- X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS).
- BET surface area measurement and particle size determination.
- Potentiometric titration (point of zero charge, pH_{PZC}).

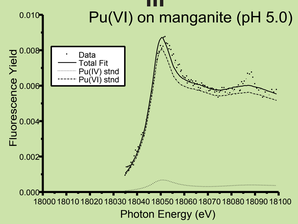


XRD pattern of manganite. The lines in the spectrum represent ideal manganite peaks.

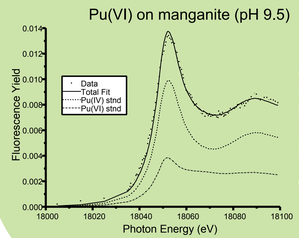
Plutonium Sorption

- Uptake curve determination (amount of plutonium sorbed onto manganite with time.)
- Over 95% of plutonium sorbed onto manganite after initial contact.
- Fast initial sorption step followed by a much slower sorption step.

Plutonium L_{III} XAFS



At pH 5, approximately 90% of the sorbed plutonium remains as Pu(VI) and the other 10% is reduced to Pu(IV). There is no apparent evidence of Pu(V).



At pH 9.5, approximately 30% of the sorbed plutonium remains as Pu(VI) and the other 70% is reduced to Pu(IV). There is no apparent evidence of Pu(V).

Research in Progress

Initial Conclusions

- At pH 5 and pH 9.5 there is a complete uptake of 10^{-4} M Pu(VI) by manganite.
- The Pu(VI) sorbed onto manganite at pH 9.5 has been reduced to Pu(IV).

Current Experiments

- Further characterization of additional manganese oxide/hydroxide minerals.
- Batch experiments to determine the sorption of plutonium and neptunium on manganese minerals as a function of time, pH, concentration, oxidation state and ionic strength.
- XAFS studies to determine the local structure of the sorbed plutonium/mineral complexes.

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Acknowledgements

This work was supported by the Office of Science and Technology, within the U.S. Department of Energy, under the Office of Environmental Management's Science Program at the Ernest Orlando Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF0098.

Some of this work was performed at the Stanford Synchrotron Radiation Laboratory, which is operated by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Division of Chemical Sciences.

The authors thank Corwin Booth for assistance with analyzing the XAFS data and Dana Caulder and Wayne Lukens for assistance with collecting the XAFS data.