



Transuranic Interfacial Reaction Studies on Manganese Oxide Mineral Surfaces

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Background



- **Manganese oxide soil components have been shown to strongly bind metal cations including Co, Ra, Th, Pu, Am, and Cm¹.**
 - Manganese oxides preferentially sorb Co over iron oxyhydroxides present in larger concentrations.
- **The sorption of Pu onto Yucca Mountain tuff containing both iron and manganese oxides has been investigated².**
 - Micro-XAFS showed that sorbed Pu was predominantly associated with the manganese oxides, not the iron oxides.

¹J.L. Means *et al.*, *Geochim. Et Cosmochim. Acta* 42, 1763 (1978).

²M.C. Duff *et al.*, *Environ. Sci. Technol.* 33, 2163 (1999); *J. Contam. Hydrol.* 47, 211 (2001).



Background



- Based on previous experiments, it is possible that manganese oxides, present as minor phases in the environment, can preferentially sequester Pu species.
- Any risk assessment studies of Pu in the environment will require knowledge of its migration through surrounding geomaterial.
 - If sorption to manganese oxides is retarding Pu migration, this interaction must be thoroughly investigated as part of site remediation studies.



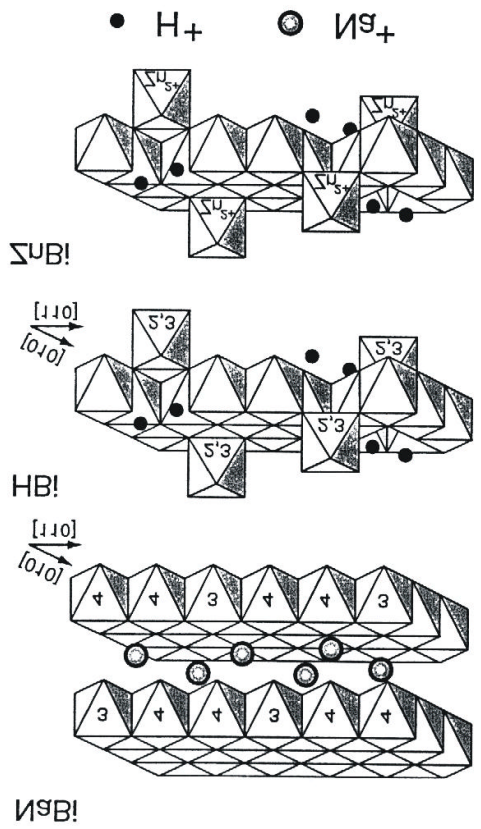
Objectives



- **Fundamental understanding of the interfacial reactions between plutonium and manganese oxide hydroxide minerals.**
 - Relevant to the transport of contaminants in the vadose zone.
 - Determine whether Pu will be immobilized by the minerals present at contaminated sites.
- **Incorporate this data into surface complexation models.**
 - Predict migration of contaminants to nearby water supplies.
 - Design effective and efficient Pu extraction systems for site remediation.

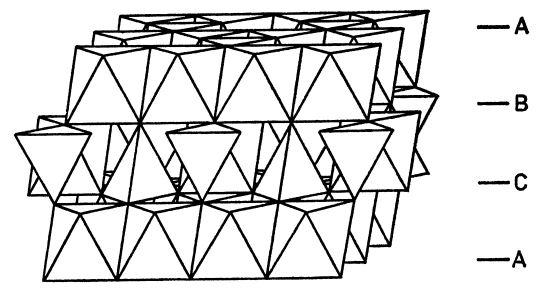
Manganese Oxide/Hydroxide Minerals Show a Variety of Structure

Layer Structure:

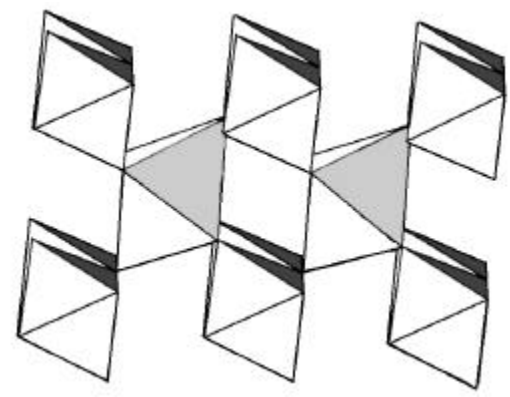


Birnessite (Mn^{4+})

Three-Dimensional Structure:

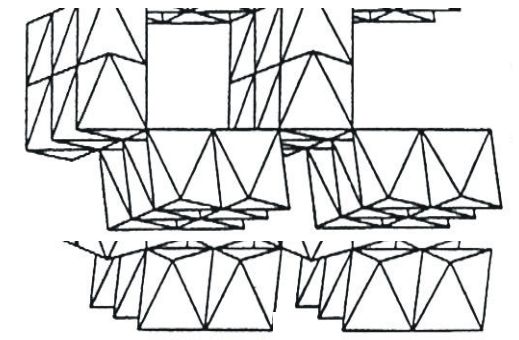


Hausmannite (Mn^{2+} , Mn^{3+})

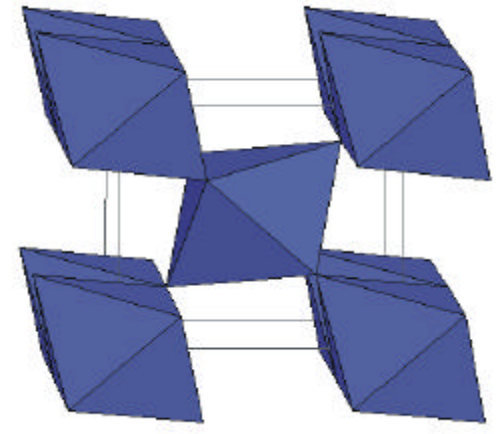


Manganite (Mn^{3+})

Tunnel Structure:

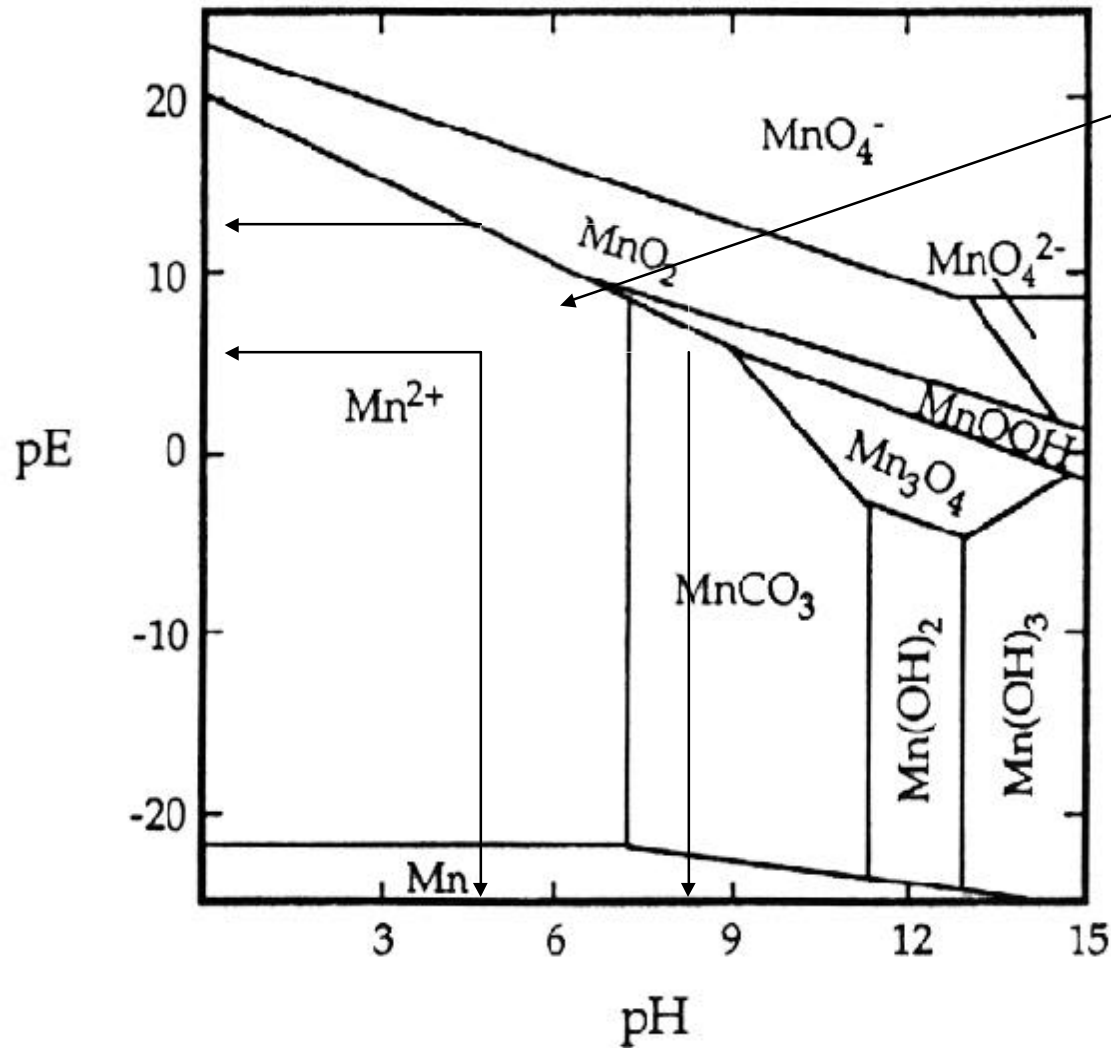


Cryptomelane (Mn^{4+} , Mn^{3+})



Pyrolusite (Mn^{4+})

pE/pH Diagram for Manganese



Eh = 0.4 - 0.8 V
pH = 5 - 8



Experimental Procedures



- **Minerals studied so far:**
 - Manganite, Mn(III)OOH
 - Hausmannite, $\text{Mn(II)Mn(III)}_2\text{O}_4$
 - Cryptomelane, $\text{K(Mn(IV),Mn(III))}_8\text{O}_{16}$
 - Pyrolusite, b-MnO_2
- **Mineral characterization**
 - X-ray diffraction
 - 63 – 212 nm size fraction isolated
 - pH_{PZC} determined via potentiometric titration
 - X-ray absorption fine structure spectroscopy (XAFS)
 - BET surface area

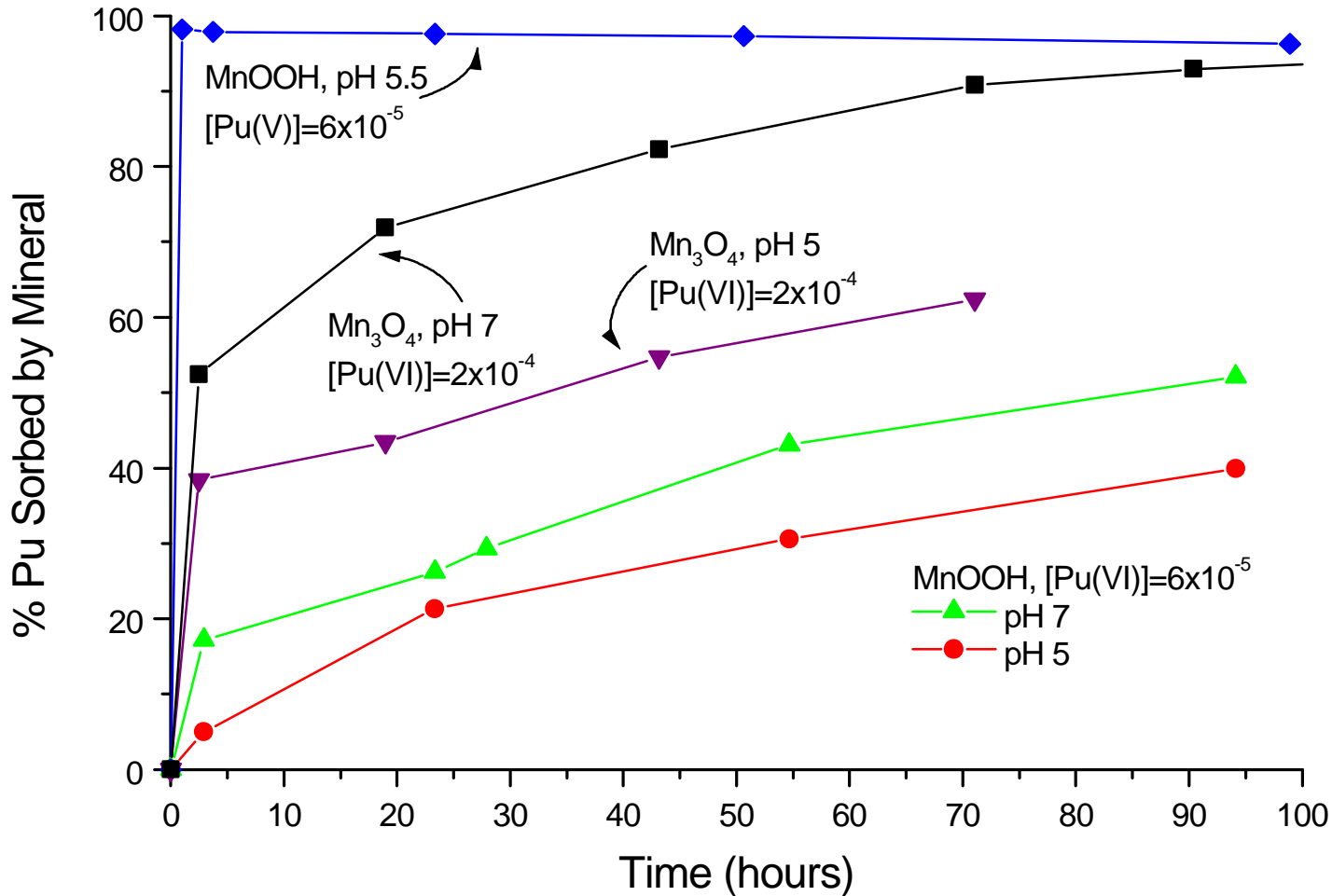


Experimental Procedures

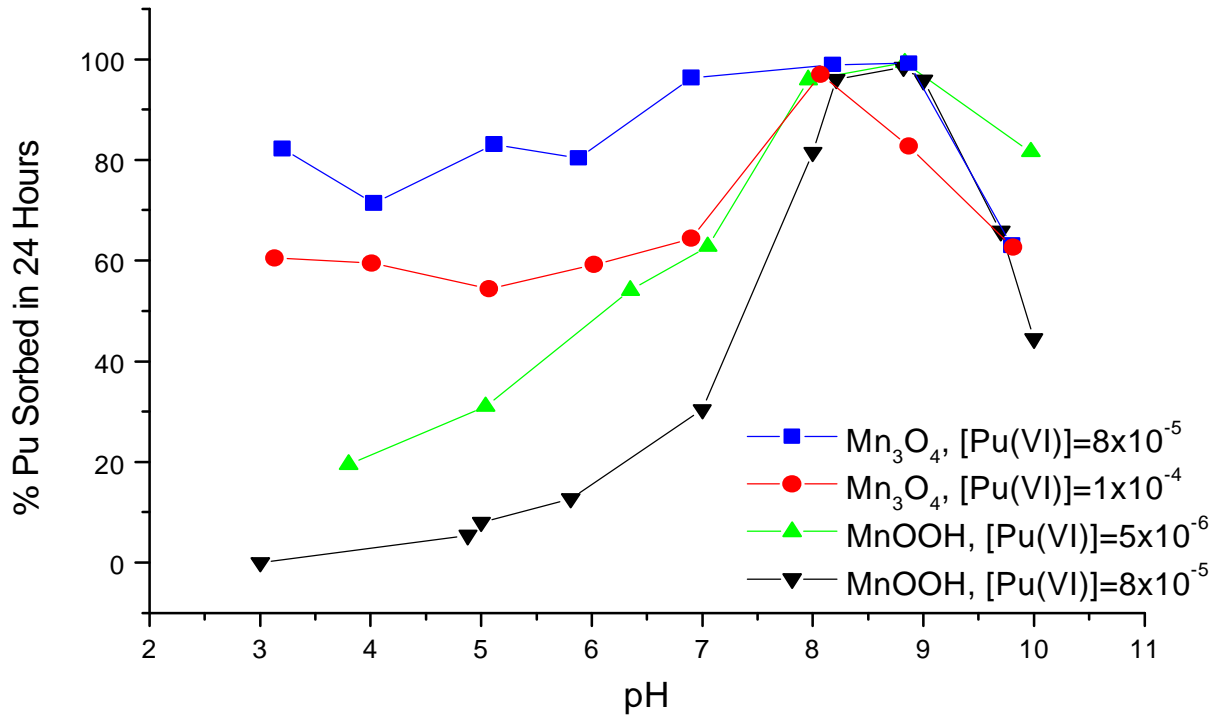


- **Batch sorption studies with Pu(VI) and Pu(V)**
 - Oxidation states verified spectrophotometrically
 - Carbonate added to high pH samples to equilibrate with air
 - Ratio of solid mass to total sample volume optimized for each mineral
 - 10 mg/mL manganite
 - 4 mg/mL hausmannite
 - 2 mg/mL pyrolusite
 - 1 mg/mL cryptomelane
 - Amount of sorption determined by measuring filtered assays via liquid scintillation counting

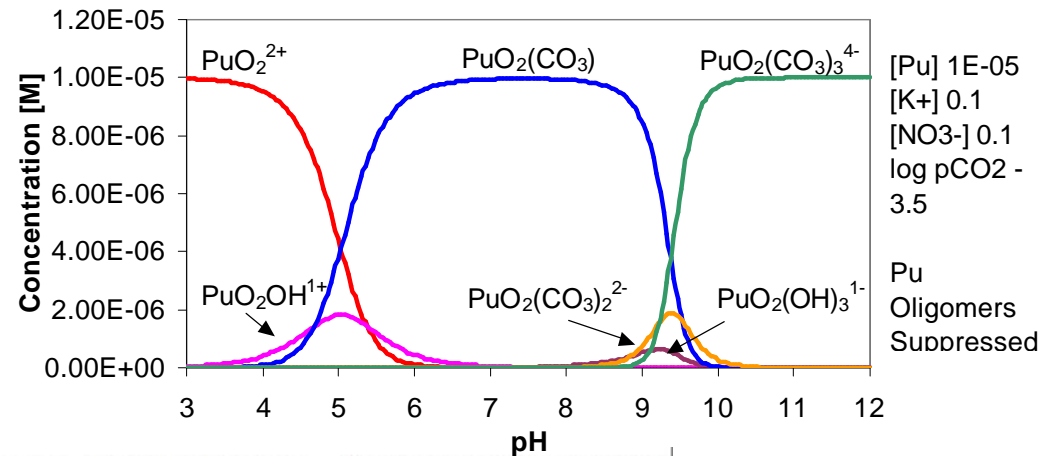
Sorption Kinetics – Pu(VI) and Pu(V)



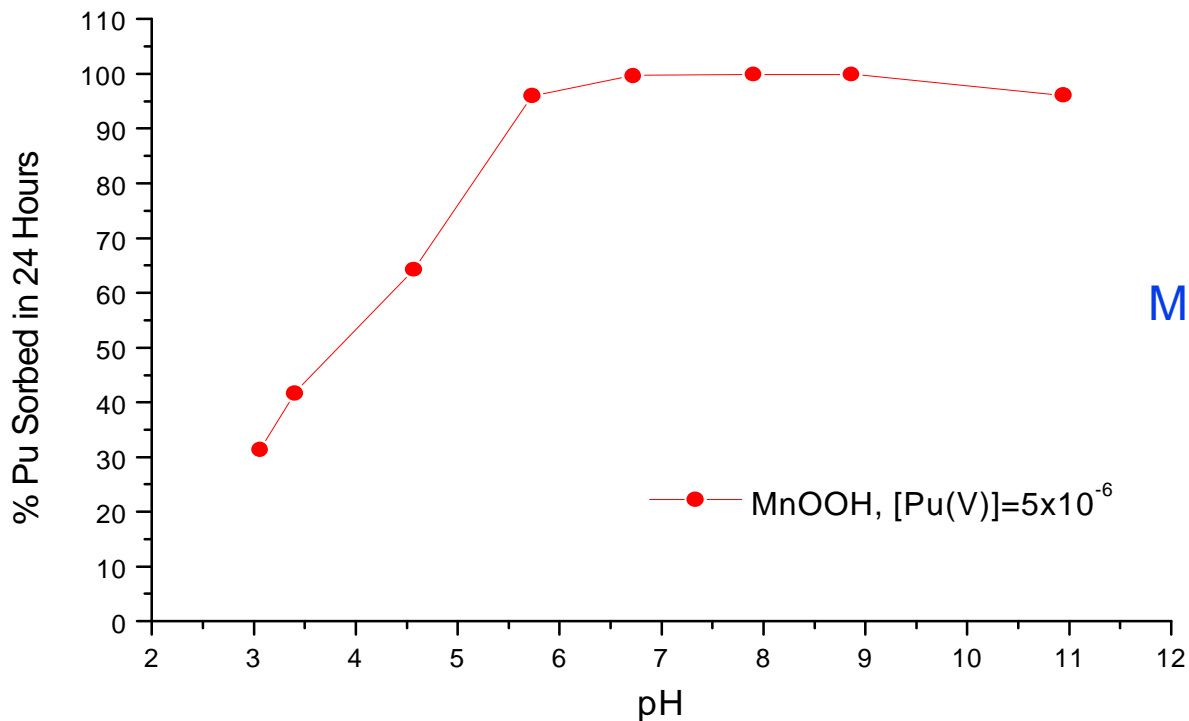
Sorption of Pu(VI)



Pu(VI) Speciation

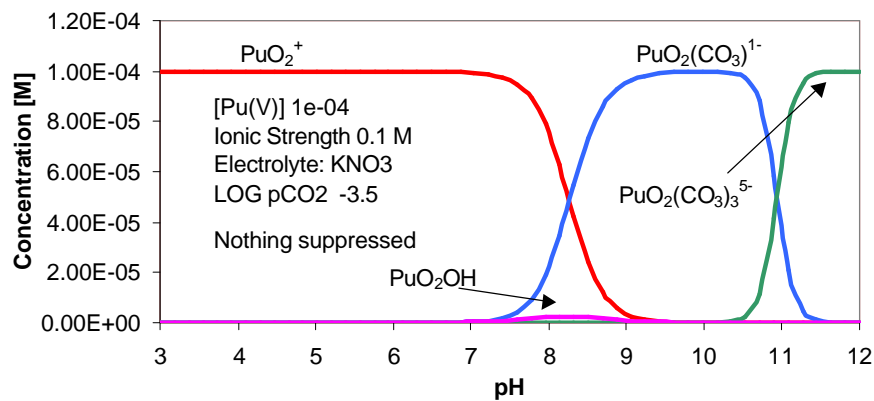


Sorption of Pu(V)

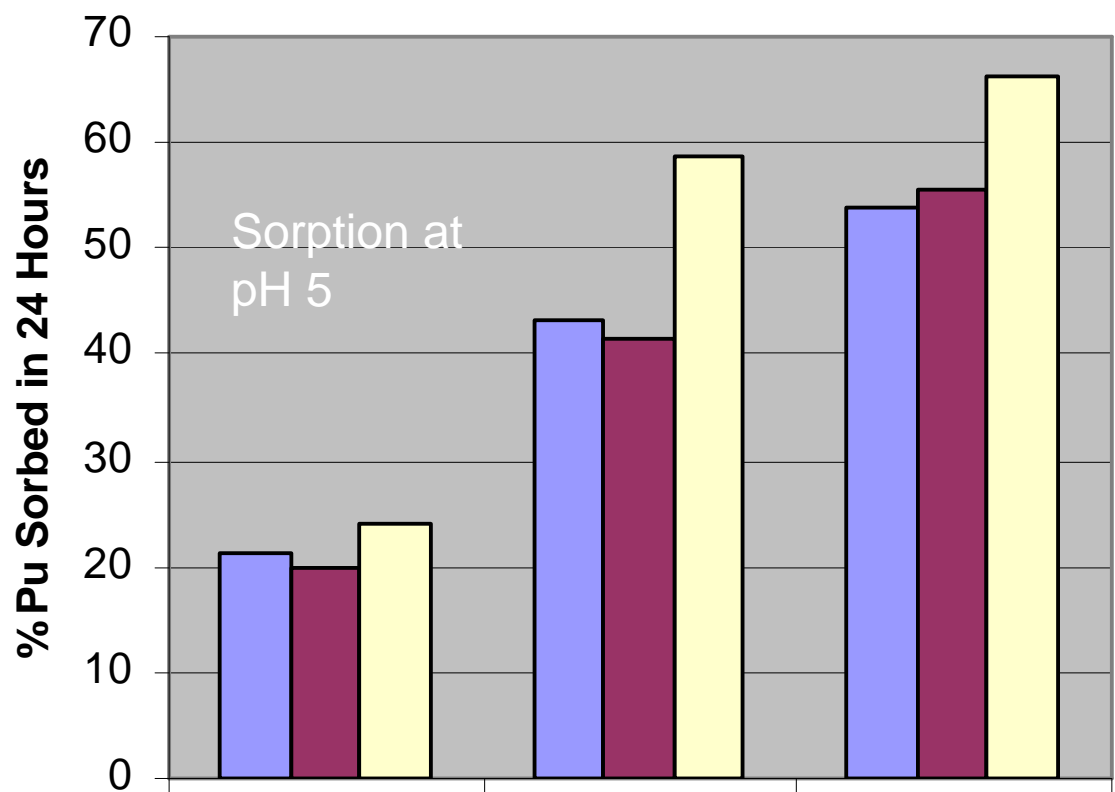


MnOOH $pH_{PZC} = 7.4$

Pu(V) Speciation



Sorption VS. Mineral Surface Area



Initial solution concentration and oxidation state :

- [Pu(VI)] = 8 x 10⁻⁵
- [Pu(VI)] = 1 x 10⁻⁴
- [Pu(V)] = 1 x 10⁻⁴

Manganite Hausmannite Cryptomelane

9.5 20.4 187.8

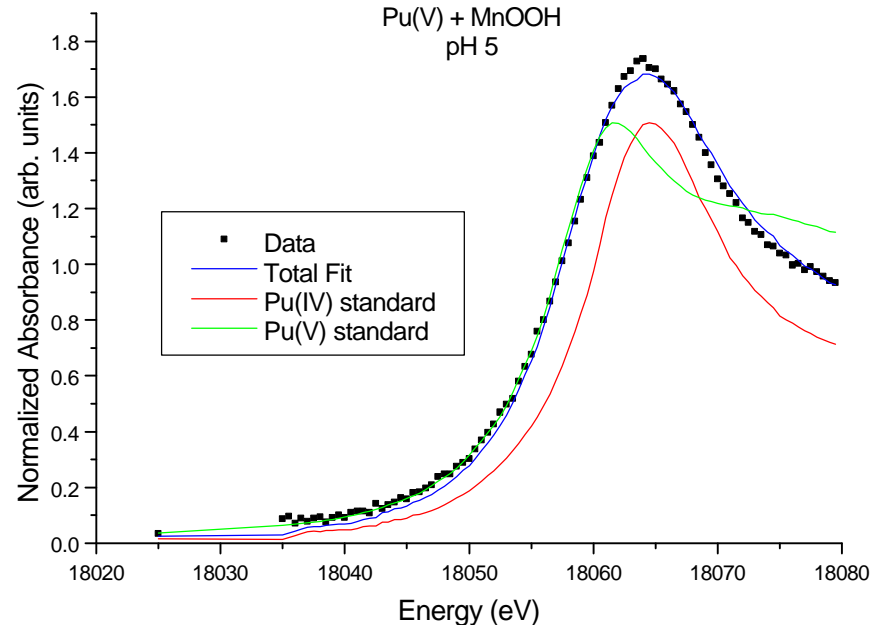
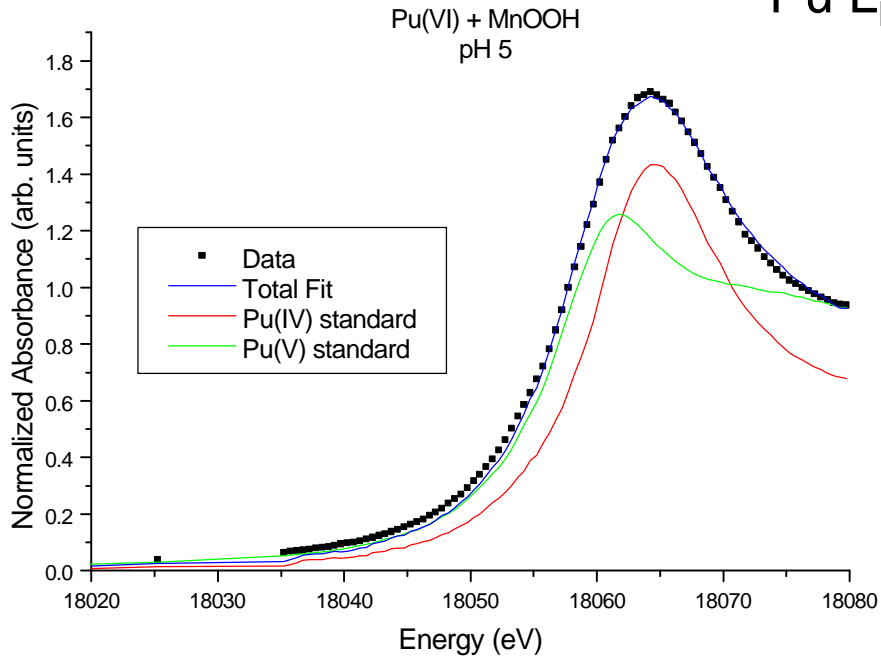
7.4 > 10 ~ 2

BET Surface Area (m²/g)

pH_{PZC}

Reduction of Pu by MnOOH

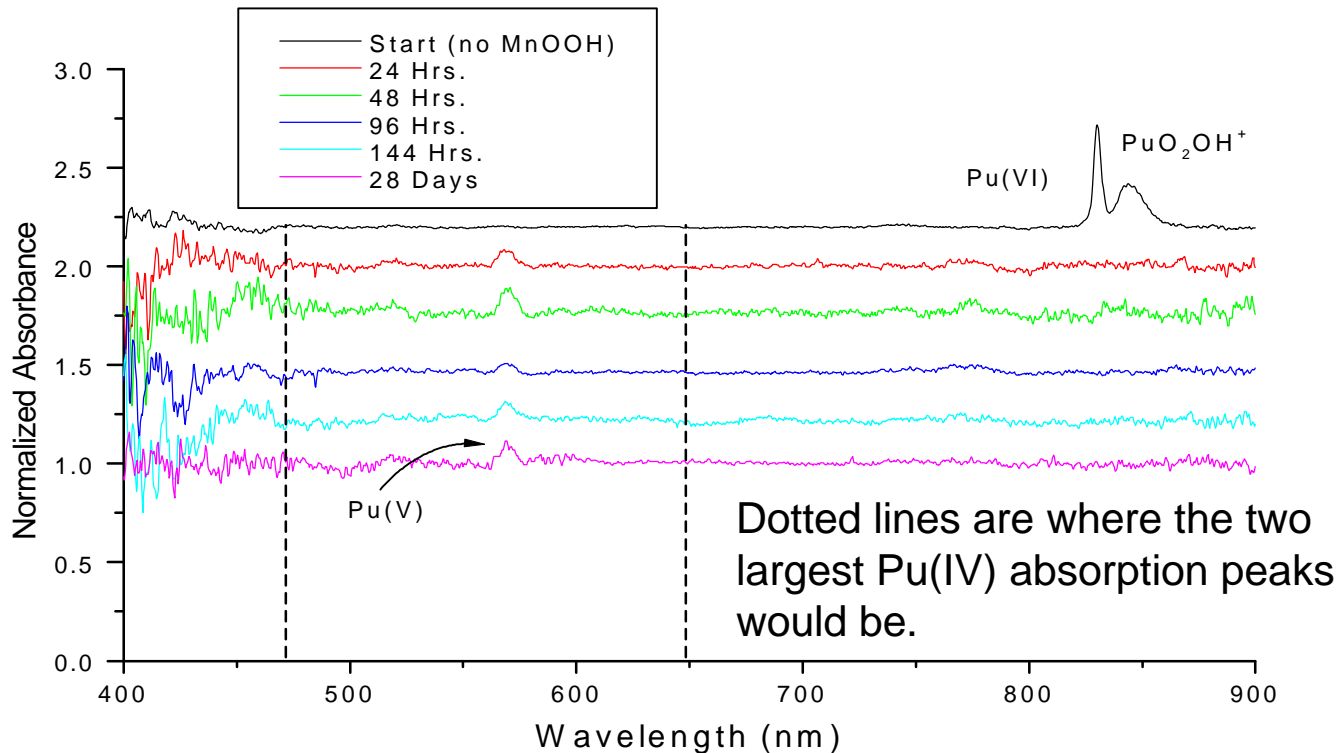
Pu L_{III} XANES



- 24 hour contact time.
- Pu(IV) = 46±2% of total Pu sorbed on the solid.
- Pu(VI) has been reduced by Mn(III)OH.

- 24 hour contact time.
- Pu(IV) = 43±2% of total Pu sorbed on the solid.
- Pu(V) has been reduced by Mn(III)OH.

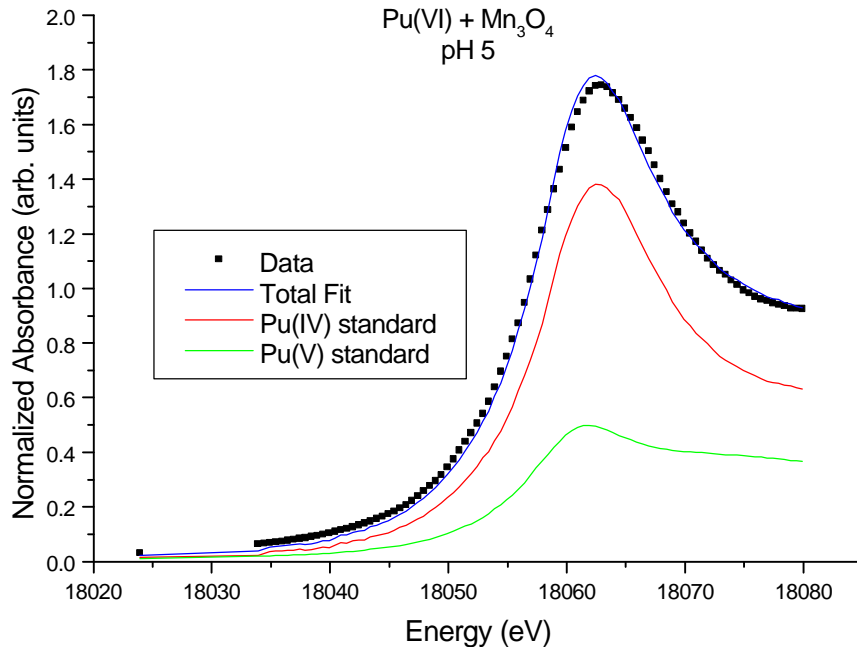
Reduction of Pu(VI) by Manganite



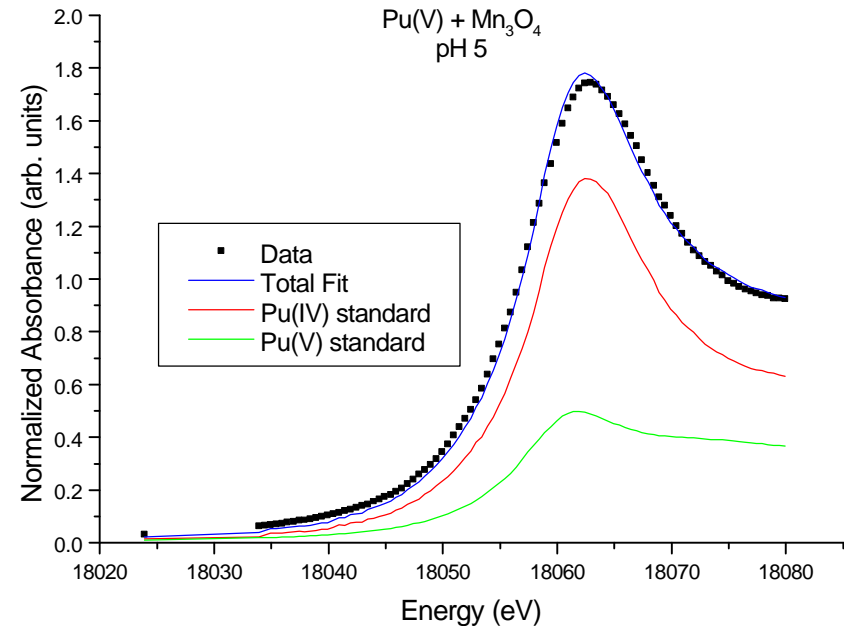
- Pu(VI) (10^{-4} M) in contact with manganite at pH 5.
- Absorption spectra were taken of the solution (minerals were filtered out.)
- After 24 hours of contact with manganite, the plutonium in solution has been reduced from Pu(VI) to Pu(V). Pu(VI) without any minerals is stable at pH 5 for an extended period.
- The same results were also observed for hausmannite.

Reduction of Pu by Mn_3O_4

Pu L_{III} XANES



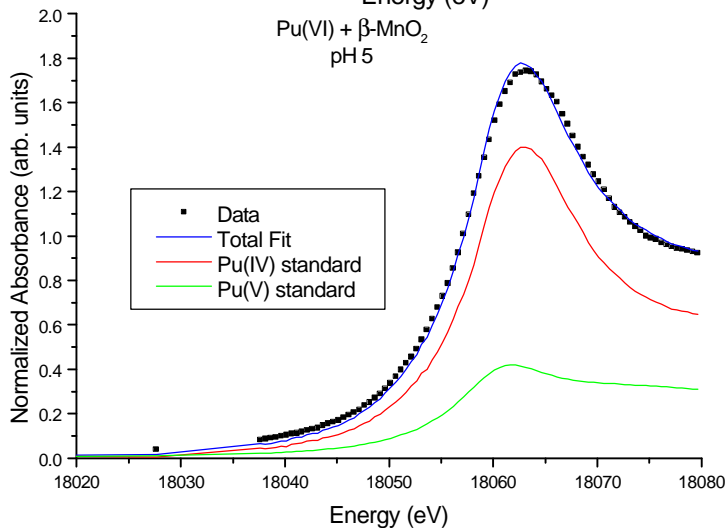
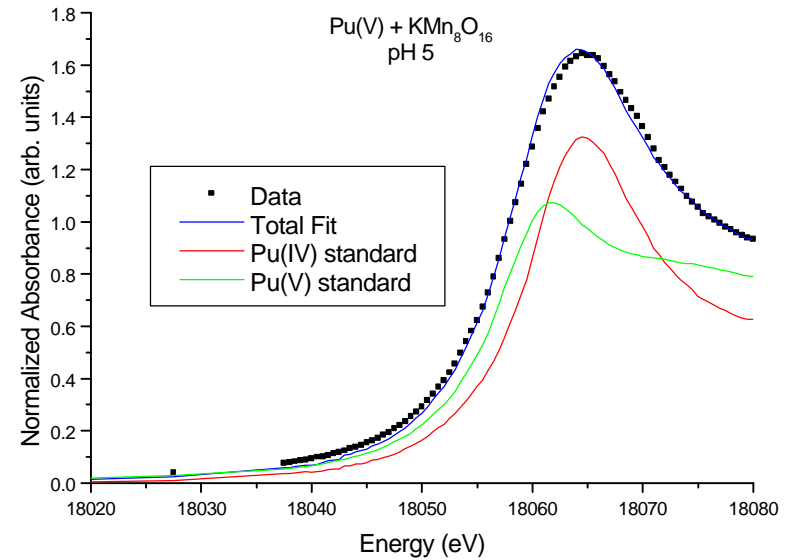
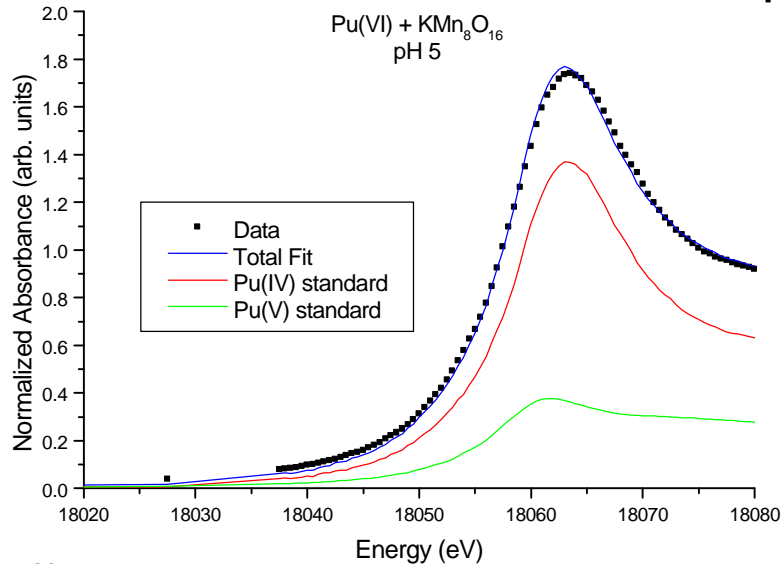
- 24 hour contact time.
- Pu(IV) = $67 \pm 2\%$ of total Pu sorbed on the solid.
- Pu(VI) has been reduced by $Mn(II)Mn(III)_2O_4$.



- 24 hour contact time.
- Pu(IV) = $63 \pm 2\%$ of total Pu sorbed on the solid.
- Pu(V) has been reduced by $Mn(II)Mn(III)_2O_4$.

Reduction of Pu by Mn⁴⁺ Minerals

Pu L_{III} XANES



- 24 hour contact time.
- Pu(IV) = $71 \pm 2\%$ (upper left)
 $48 \pm 2\%$ (upper right)
 $71 \pm 2\%$ (lower left)



Summary



- **Manganese oxide hydroxide minerals show a large sorption capacity for Pu(VI) and Pu(V). Sorption increases:**
 - with increasing mineral surface area
 - with increasing pH
 - with decreased Pu concentration
 - at pH values below the formation of Pu-carbonato anions.
- **Manganese minerals reduce Pu(VI) and Pu(V) to Pu(IV)**
 - Process appears to be independent of the mineral structure or manganese valence
- **XAFS measurements indicate that Pu sorbs to these minerals in an inner sphere configuration (not shown)**



Experiments in Progress



- SEM on minerals to characterize surface changes vs. pH.
- Determine whether Mn(III) disproportionation is driving Pu reduction.
- Sorption of Pu(VI) and Pu(V) on birnessite and δ -MnO₂.
- Tritium exchange on minerals to determine density of active sites.
- XAFS measurements to determine structure of sorbed Pu – Mn complexes.



Plans for the Future



- **Grazing incidence XAFS (GIXAFS) on the mineral surfaces**
 - Better understanding of the structure of the Pu – mineral surface complex
 - Determine surface Mn oxidation states
- **Sorption on other manganese oxide minerals**
 - Different mineral structures and manganese valence states.
- **Need to study sorption when competing species are present.**
- **Sorption of Np(V) on Mn oxide mineral surfaces.**
- **Develop surface complexation models with existing data.**



Implications for Waste Cleanup



- **Manganese oxide minerals have a large sorption capacity**
 - Even if present as minor phases, these minerals can preferentially sequester Pu
 - Manganese may be the controlling system for retarding Pu migration through the vadose zone
- **Redox reactions between the manganese and the plutonium are occurring**
 - Changes in Pu oxidation state could affect its mobility through the environment
 - The Pu is reduced to more insoluble Pu(IV), which could be sequestered by the surrounding geomaterial.
 - These interactions can prevent the migration of Pu to nearby water supplies and make site remediation easier



Acknowledgments



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- The authors would also like to thank Richard Wilson for producing the Pu speciation diagrams.

Research Objective: Several DOE sites have been contaminated by transuranic radionuclide (TRU) discharges including neptunium and plutonium. Their interaction with the surrounding geological media can affect the transport and remediation of these radionuclides in the environment. Manganese based minerals, present as minor phases in the vadose zone, can preferentially sequester TRU over other minerals present in larger quantities. The objective of this project is to understand the interactions between plutonium and neptunium and manganese oxyhydroxide minerals to predict potential hazards they represent to the environment, as well as to provide important scientific information for the design of effective remediation strategies for contaminated DOE sites.

Research Progress and Implications: This report summarizes our results after one-and-a-half years of a three-year project. This research began with the study of plutonium sorption on representative manganese oxyhydroxides. Four manganese oxides representing a variety of manganese valence states present in the environment were chosen for plutonium sorption studies: manganite (Mn(III)OOH), hausmannite (Mn(II)Mn(III)₂O₄), cryptomelane (K(Mn(IV),Mn(III))₈O₁₆), and pyrolusite (β-Mn(IV)O₂). The minerals were characterized using X-ray diffraction, X-ray absorption spectroscopy (XAS), and potentiometric titration. The sorption experiments were performed with solutions of plutonium prepared electrochemically in single oxidation states verified spectrophotometrically. In addition, our collaborators at PNNL have made calculations using the program MINEQL to determine the plutonium speciation in our solutions.

Sorption of Pu(VI) and Pu(V) on Mn(III) minerals. Experiments were started with Pu(VI) to study the kinetics of sorption. Samples were prepared at an ionic strength of 0.1 M (adjusted with NaClO₄) at various pH values and were equilibrated with air. Figure 1 shows the sorption of Pu(VI) on hausmannite. It was determined from these experiments that the initial, fast sorption step, which sequesters between 20% and 80% of the initial plutonium, was complete

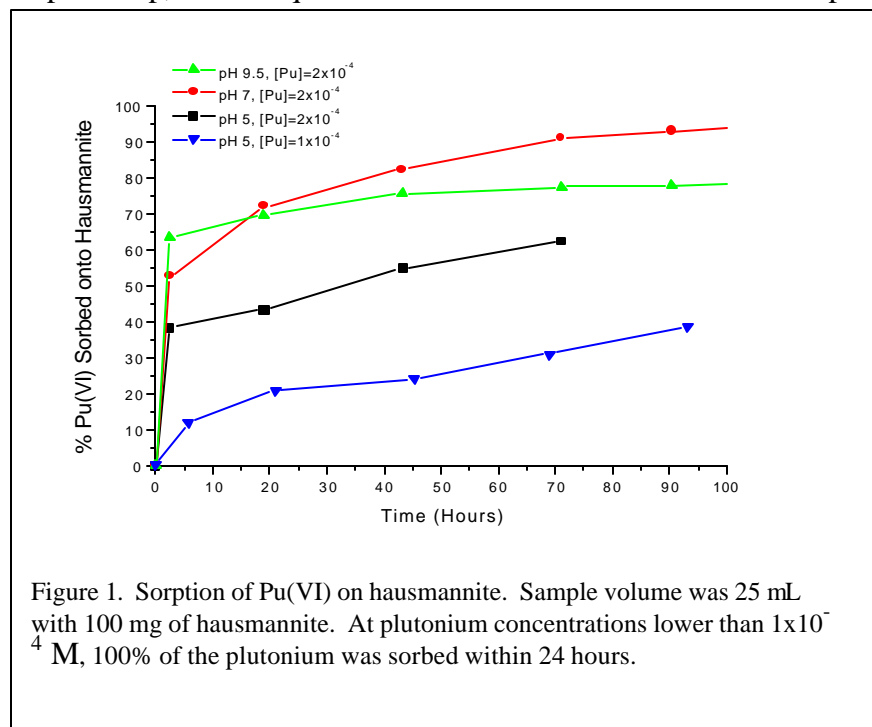
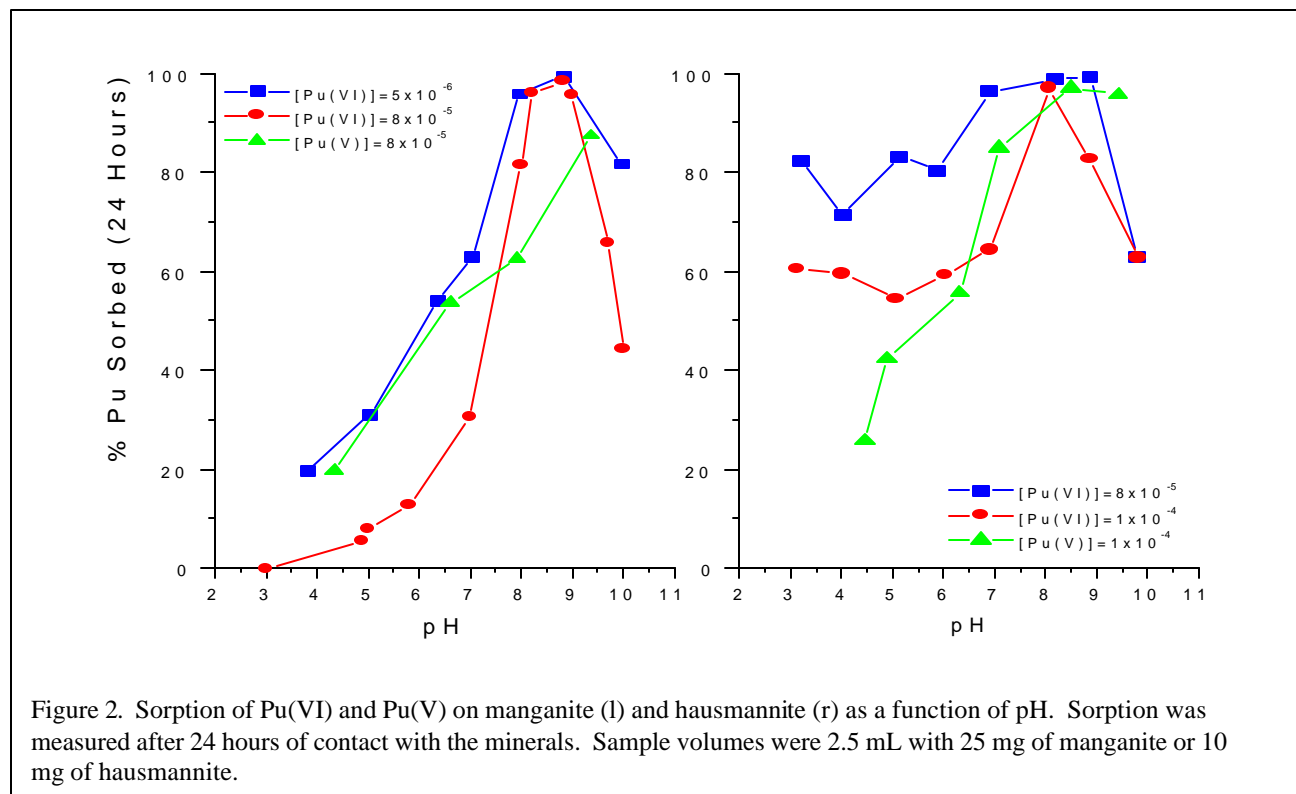


Figure 1. Sorption of Pu(VI) on hausmannite. Sample volume was 25 mL with 100 mg of hausmannite. At plutonium concentrations lower than 1x10⁻⁴ M, 100% of the plutonium was sorbed within 24 hours.

after 24. A slower sorption process occurs over the course of several days and follows this initial sorption step. Subsequent experiments measured the sorption of Pu(VI) and Pu(V) as a function of pH (Figure 2.)

The pH where the manganite surface is electrically neutral (the point of zero charge or pH_{PZC}) is 6.4±0.3 based on the results of potentiometric titrations. Figure 2 shows that the amount of plutonium sorbed by the manganite increases rapidly after the pH_{PZC}. At a pH

higher than the pH_{PZC} , the surface has a net negative charge, resulting in a greater tendency for the manganite surface to sorb positively charged plutonium ions. The pH_{PZC} of hausmannite was determined to be between 8 and 11. Figure 2 shows an increase in the amount of plutonium sorbed at pH values near 8. Figure 2 also shows a larger overall sorption of plutonium with hausmannite compared to manganite. This can be related to the surface area of the minerals. The surface area of manganite was determined using B.E.T. to be $9.5 \pm 1.4 \text{ m}^2/\text{g}$, and hausmannite



has a surface area of $20.4 \pm 0.8 \text{ m}^2/\text{g}$, about twice as large as manganite. This larger surface area means that there are a greater number of surface sites available for plutonium binding, and there is a larger overall sorption on hausmannite. Figure 3 shows plutonium sorption over 24 hours as a function of mineral surface area. In addition, it was determined that there was no difference in plutonium sorption onto manganite or hausmannite at varied ionic strength values, which means that the sorption process is independent of the ionic strength of the solution and does not follow an ion-exchange mechanism.

Oxidation state of the sorbed plutonium. The oxidation state of the sorbed plutonium was determined using XAS and optical absorption spectroscopy. XAS measurements taken at the plutonium L_{III} edge showed that Pu(VI) and Pu(V) are reduced to Pu(IV) when sorbed onto manganite or hausmannite at pH values from 5 to 9.5 after 24 hours of contact. Absorption spectra taken of the solutions after the minerals had been removed by filtration showed that there was no Pu(IV) in solution, only Pu(V). Thus, the initial Pu(VI) is completely reduced in solution to Pu(V) by the minerals. Since the sorbed plutonium species was Pu(IV), the Pu(V) in solution must be further reduced to the tetravalent state, which then binds to the mineral surface. These systems are being investigated further to explore the redox processes occurring between the plutonium and the manganese.

Structure of the sorbed plutonium species. XAS measurements were also used to determine the structures of the sorbed plutonium – manganese species. These data are currently under analysis, but initial results of Pu(VI) sorbed onto hausmannite at pH 5 show that the plutonium

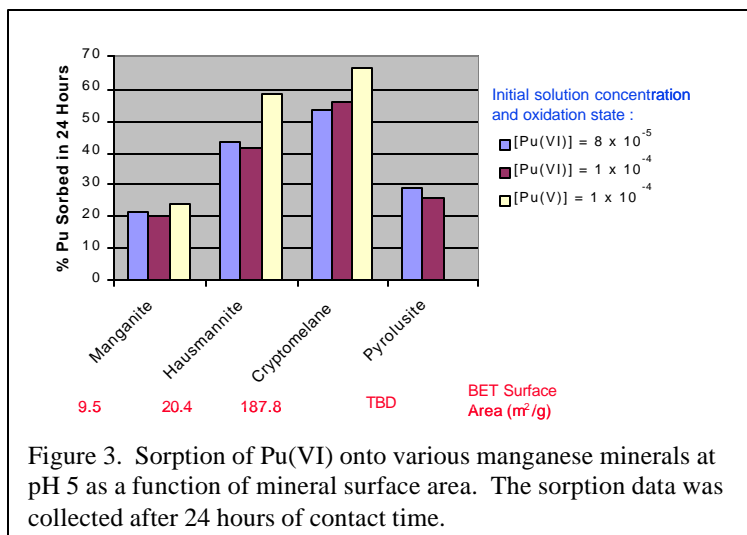


Figure 3. Sorption of Pu(VI) onto various manganese minerals at pH 5 as a function of mineral surface area. The sorption data was collected after 24 hours of contact time.

binds to the mineral surface in an inner-sphere complex configuration, which means that the plutonium is bound directly to the mineral surface without any intervening water molecules. Figure 4 shows the data and resulting fits to the XAS data of Pu(VI) sorbed to hausmannite. The plutonium has two oxygen nearest neighbors at 2.21 Å and 2.37 Å that most likely correspond to oxygen groups on the mineral surface bound to the plutonium. There are two different manganese sites in hausmannite, one

tetrahedral and the other in an octahedral arrangement. The plutonium also interacts with two manganese neighbors at 3.37 Å and 3.66 Å, which correspond to these two different manganese sites in the mineral. There is no evidence of any Pu – Pu interactions indicating that there is no

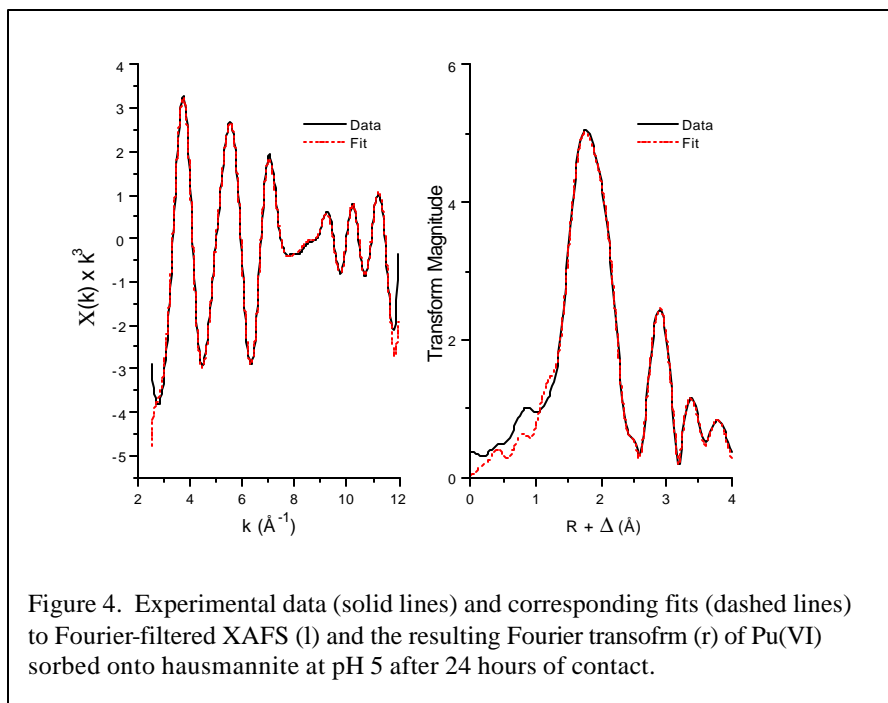


Figure 4. Experimental data (solid lines) and corresponding fits (dashed lines) to Fourier-filtered XAFS (l) and the resulting Fourier transform (r) of Pu(VI) sorbed onto hausmannite at pH 5 after 24 hours of contact.

precipitation of PuO₂ at the surface. The sorption must therefore be a surface effect and not due to precipitation occurring at plutonium nucleation sites. The data also indicate that Pu(VI) sorbed to manganite and Pu(V) sorbed to both hausmannite and manganite are bound in an inner sphere coordination as well.

Summary. Our results to date indicate that manganese oxide hydroxides, which show a variety of structure

and manganese valence states, have large sorption capacities for Pu(VI) and Pu(V). Sorption increases as a function of mineral surface area and pH, especially at pH values above the pHPZC where the mineral has a net negative surface charge. In addition, manganite and hausmannite (both predominantly Mn(III) minerals) reduce Pu(VI) and Pu(V) to Pu(IV), which then sorbs to

the mineral. Pu(V) does not appear to bind to the surface, but instead remains in solution. There are redox reactions occurring between the plutonium and the manganese both in solution and on the minerals. XAS measurements show that plutonium is bound to these minerals in an inner sphere configuration and that there is no evidence of PuO₂ precipitation on the surface. Based on these initial results, if plutonium contaminants in the environment were to come into contact with manganese oxide hydroxide minerals, the plutonium could be sequestered through sorption at the mineral surface under certain conditions.

Planned Activities: We have already begun sorption experiments on Mn(IV) based minerals such as pyrolusite and birnessite. We plan to monitor the plutonium oxidation state both in solution and on the mineral surfaces to see how the redox reactions between plutonium and Mn(IV) differ from those with Mn(III). Initial results show that the plutonium in solution remains as Pu(VI) instead of being reduced to Pu(V) as with Mn(III) systems. We will also measure the redox potentials between manganese and plutonium in these systems, enabling us to possibly predict preferred plutonium oxidation states based on the minerals present under various environmental conditions.

Another project that has already begun is the development of a grazing incidence XAS (GIXAFS) system for use with plutonium. This is a powerful tool for measuring surface species. With XAS, one sees an average structure that includes not only surface components but bulk ones as well. GIXAFS eliminates contribution from the bulk leaving only surface species.

Our collaborators at PNNL have begun experiments to determine the behavior of these minerals under environmental conditions. The manganese in these minerals can disproportionate or be released into solution, which means that there may be manganese cations as well as plutonium in solution competing for potential surface sites. The minerals will be studied to determine their solubility, surface valence states, and rate of disproportionation.

The experiments described above have either already begun or will be started during the year 2001. Once the sorption mechanism is better understood, the data we have collected will be used to model the surface complexation with the program FITEQL. The modeling will primarily be performed at PNNL. Looking ahead even farther, we plan to study the sorption of neptunium so that a more complete model of TRU migration can be developed.