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 Cm[1].
  - —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 investigated[2].
  - —Micro-XAFS showed that sorbed Pu was predominantly associated with the manganese oxides, not the iron oxides.

[1]J.L. Means *et al*., Geochim. Et Cosmochim. Acta *42*, 1763 (1978).
[2]M.C. Duff *et al*., Environ. Sci. Technol. *33*, 2163 (1999); J. Contam. Hydrol. *47*, 211 (2001).

Background

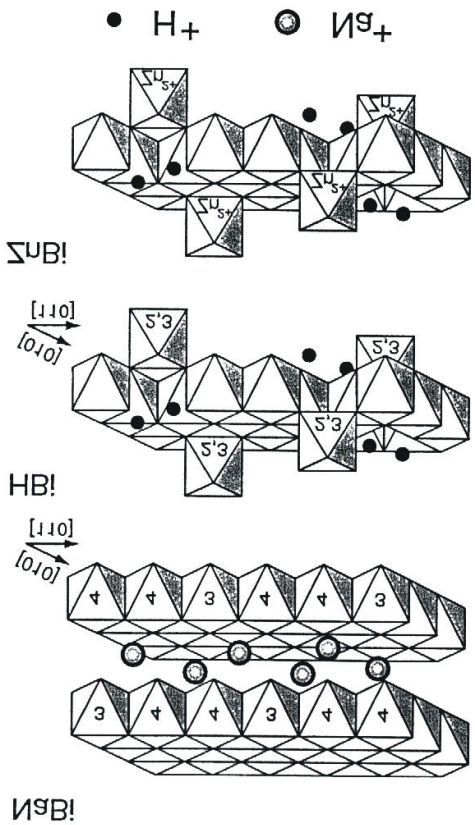
- Based on previous experiments, it is possible that manganese oxides, present as minor phases in the environment, can preferentially sequester Pu species.
- Any risk assessment studies of Pu in the environment will require knowledge of its migration through surrounding geomaterial.
  - If sorption to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

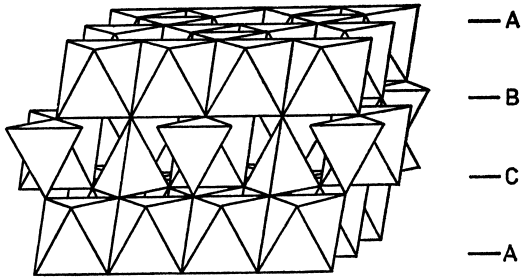
Manganese Oxide/Hydroxide Minerals Show a Variety of Structure

Layer Structure:

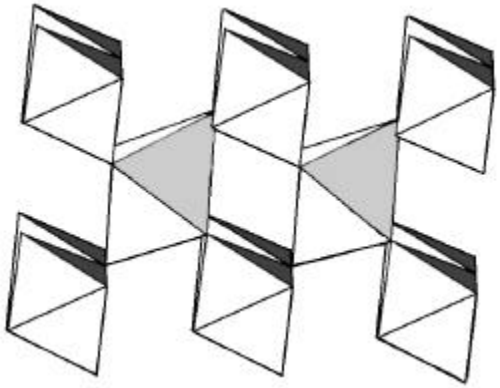


Birnessite (Mn^{4+})

Three-Dimensional Structure:

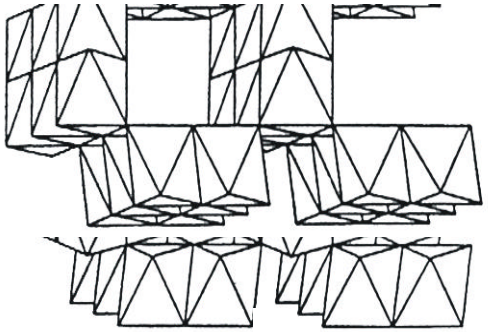


Hausmannite (Mn^{2+}, Mn^{3+})

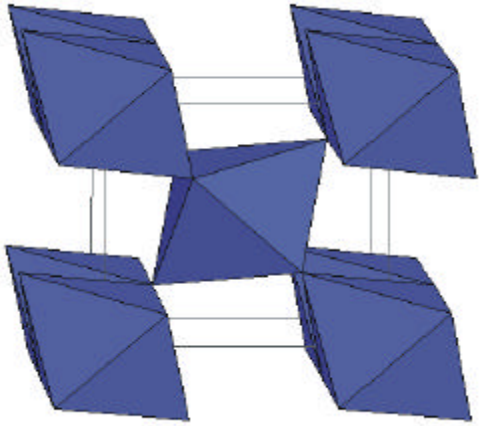


Manganite (Mn^{3+})

Tunnel Structure:

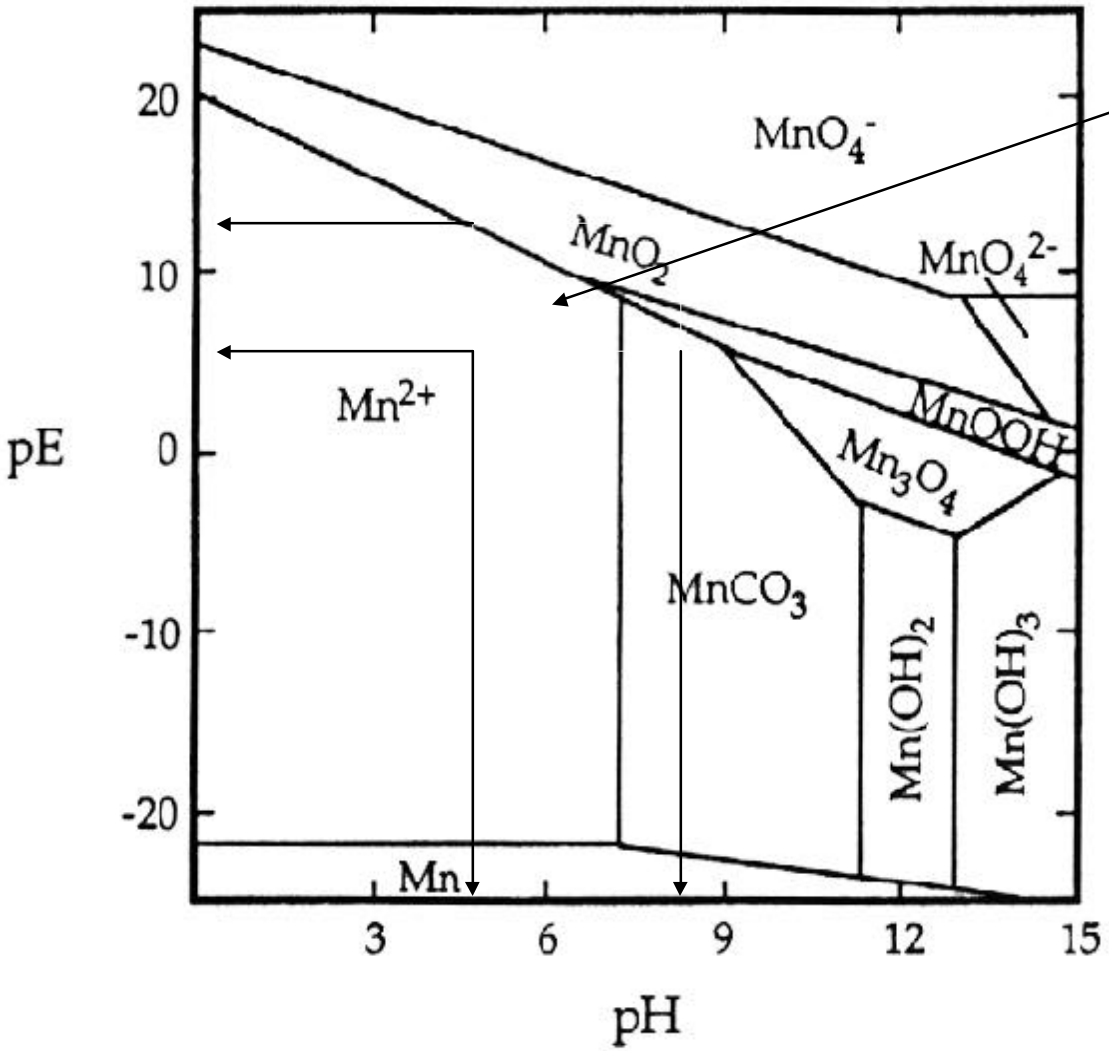


Cryptomelane (Mn^{4+}, Mn^{3+})



Pyrolusite (Mn^{4+})

pE/pH Diagram for Manganese



Eh = 0.4 - 0.8 V

pH = 5 - 8

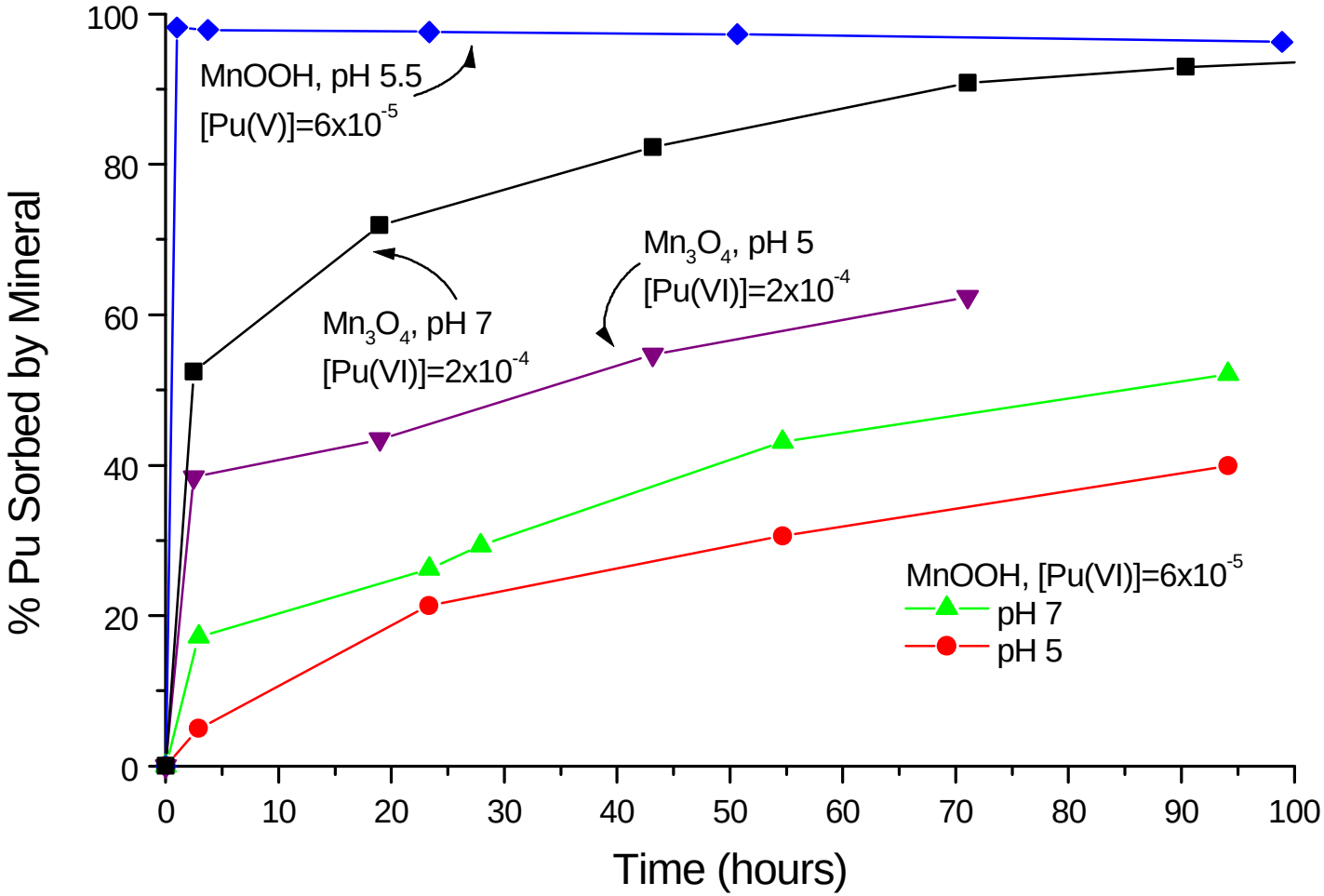
Experimental Procedures

- **Minerals studied so far:**
  - —Manganite, Mn(III)OOH
  - —Hausmannite, $Mn(II)Mn(III)_2O_4$
  - —Cryptomelane, $K(Mn(IV),Mn(III))_8O_{16}$
  - —Pyrolusite, b-MnO_2
- **Mineral characterization**
  - —X-ray diffraction
  - —63 – 212 mm size fraction isolated
  - —pH_{PZC} determined via potentiometric titration
  - —X-ray absorption fine structure spectroscopy (XAFS)
  - —BET surface area

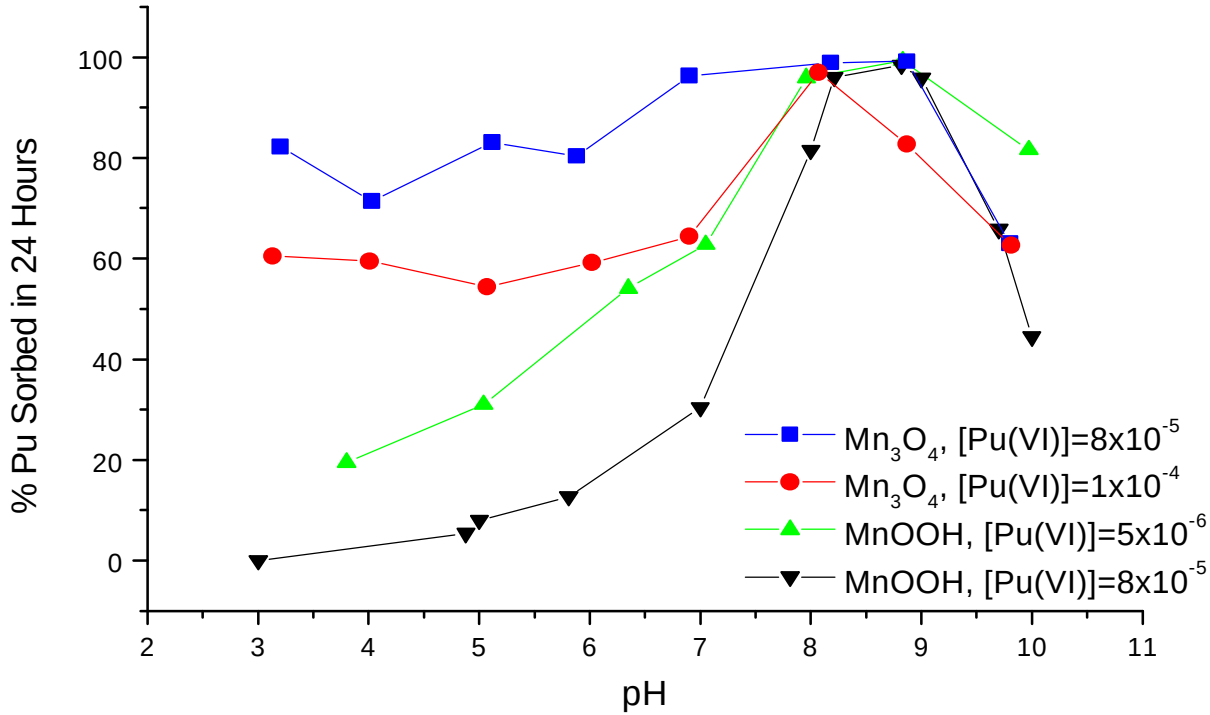
Experimental Procedures

- 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)



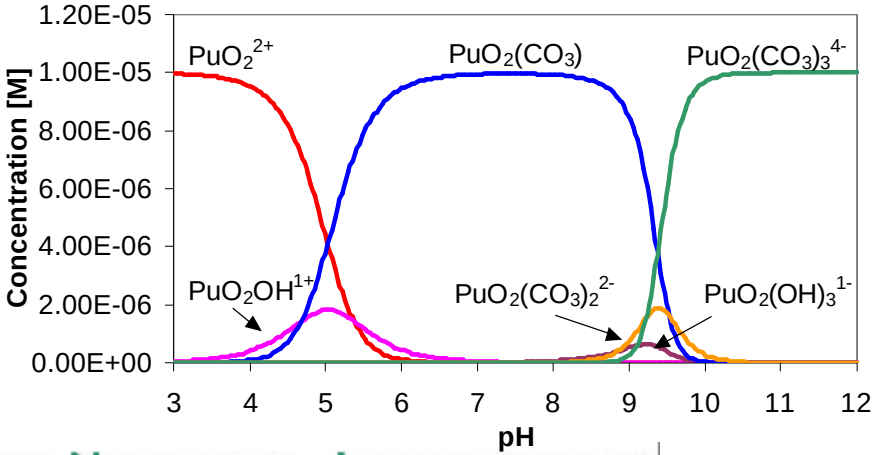
Sorption of Pu(VI)



MnOOH pH_{PZC}=7.4

Mn_3O_4 pH_{PZC}>10

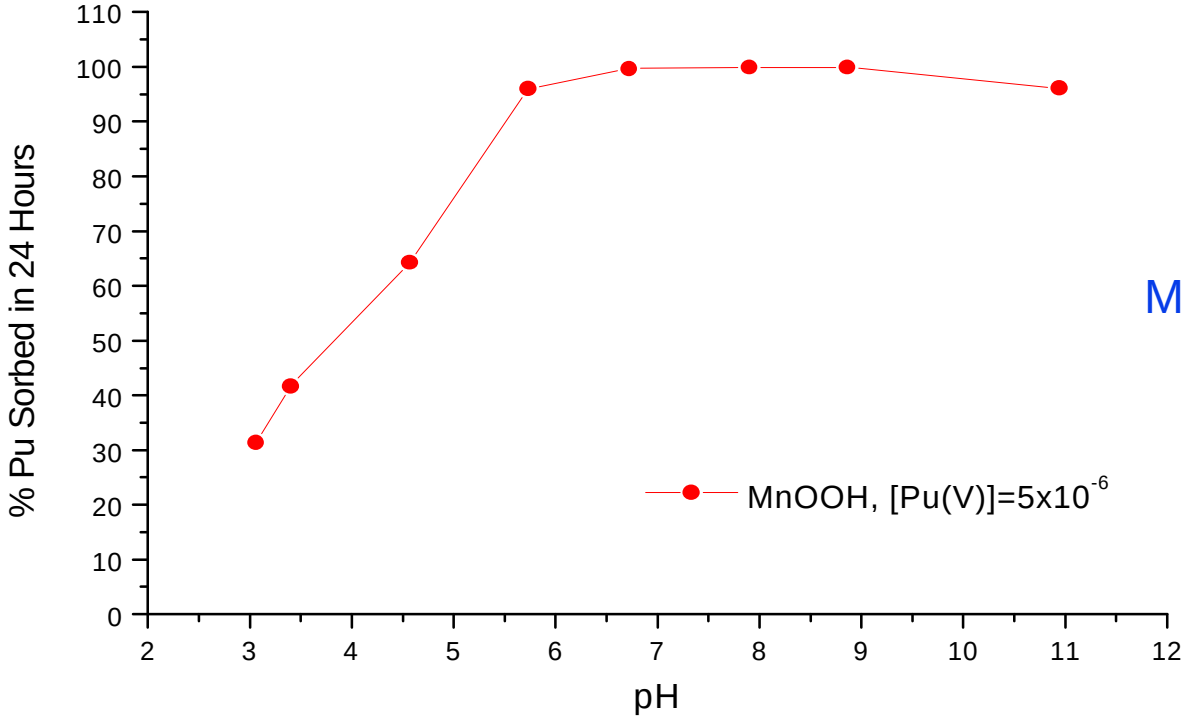
Pu(VI) Speciation



[Pu] 1E-05
[K+] 0.1
[NO3-] 0.1
log pCO2 -3.5

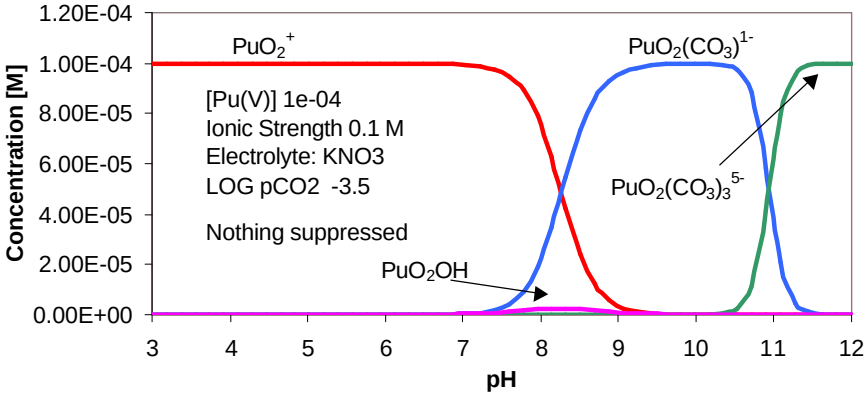
Pu Oligomers Suppressed

Sorption of Pu(V)

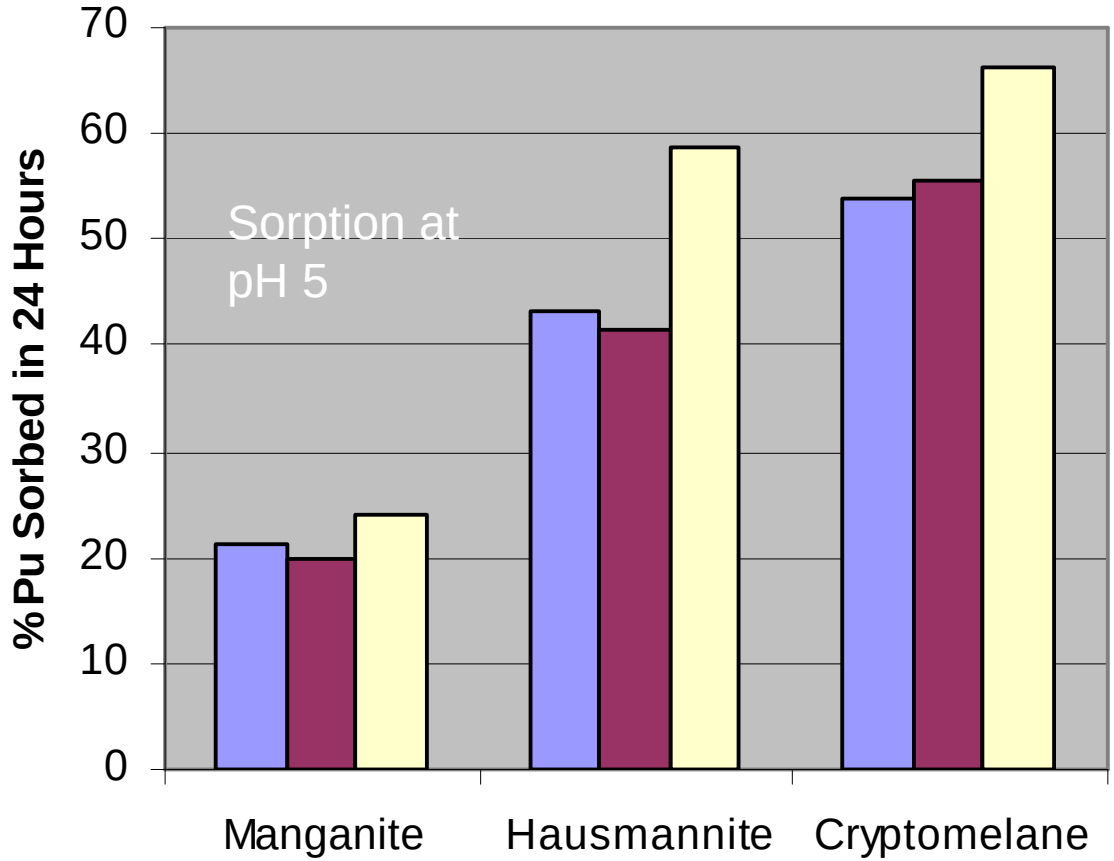


MnOOH pH_{PZC}=7.4

Pu(V) Speciation



Sorption VS. Mineral Surface Area



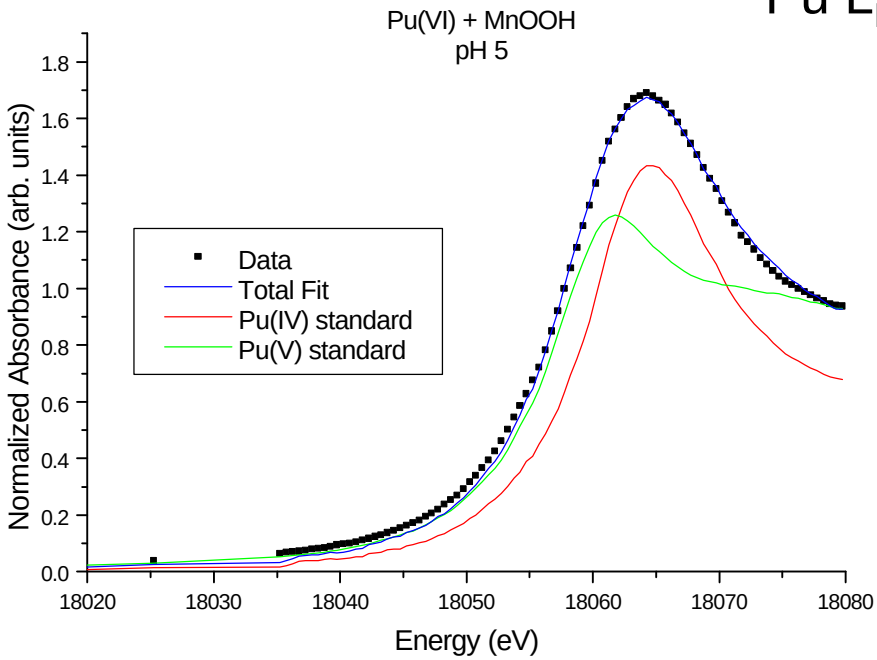
Initial solution concentration and oxidation state :

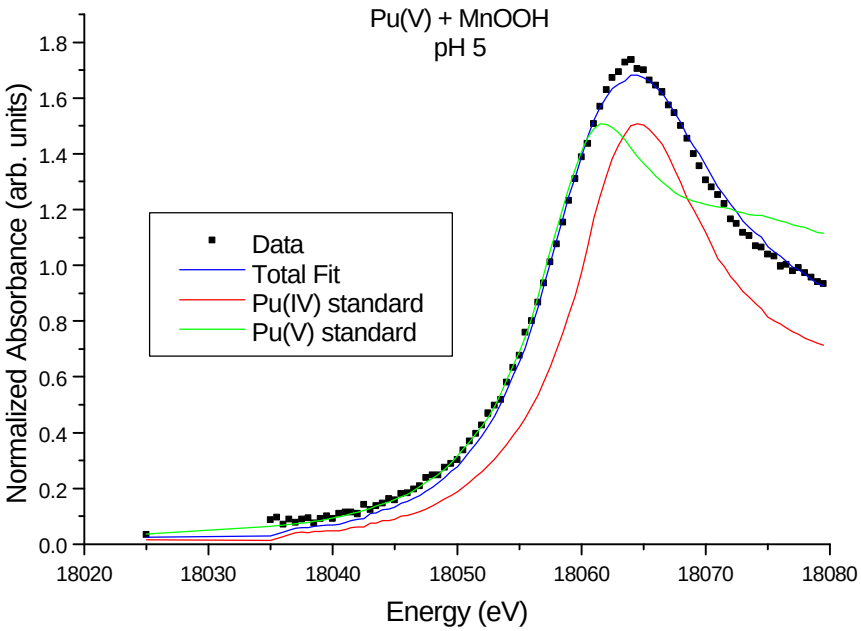
- [Pu(VI)] = 8 x 10^{-5}
- [Pu(VI)] = 1 x 10^{-4}
- [Pu(V)] = 1 x 10^{-4}

	Manganite	Hausmannite	Cryptomelane	
BET Surface Area (m^2/g)	9.5	20.4	187.8	
pH_{PZC}	7.4	> 10	~ 2	

Reduction of Pu by MnOOH

Pu L_{III} XANES

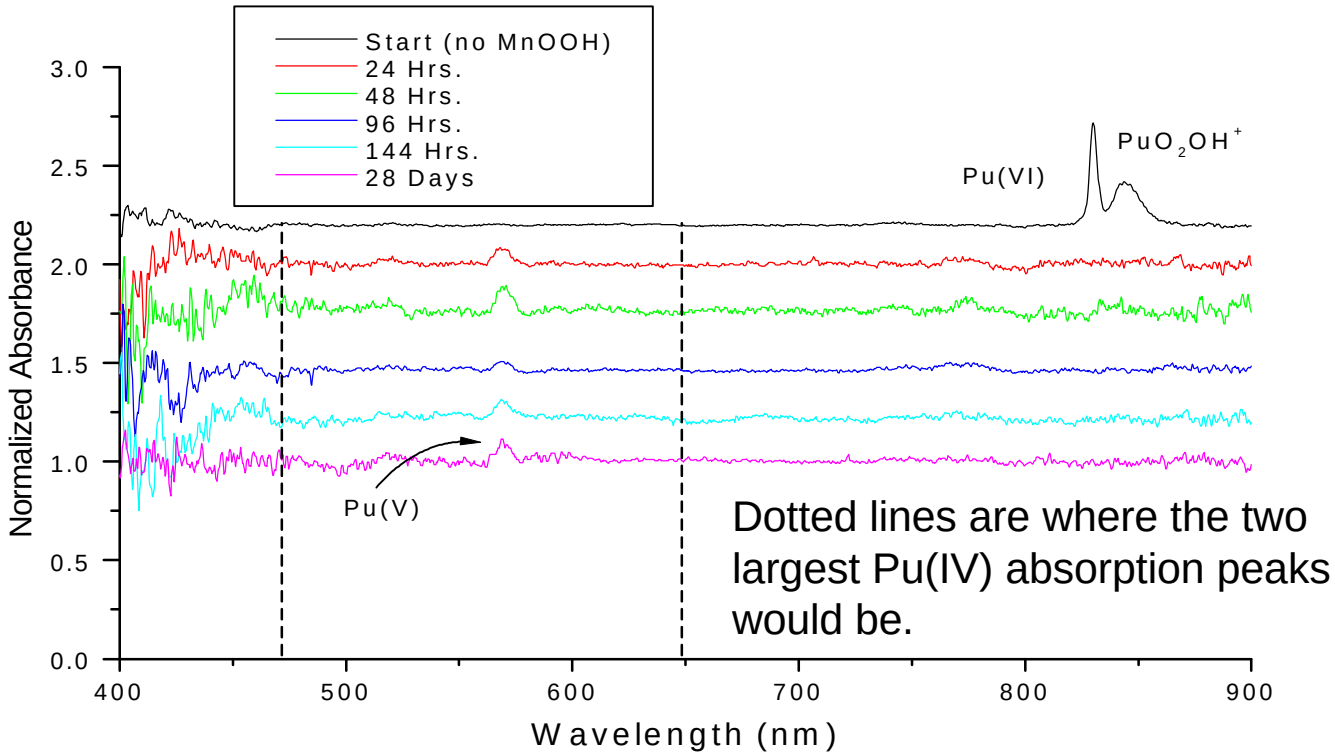




- 24 hour contact time.
- Pu(IV) = 46±2% of total Pu sorbed on the solid.
- Pu(VI) has been reduced by Mn(III)OH.

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

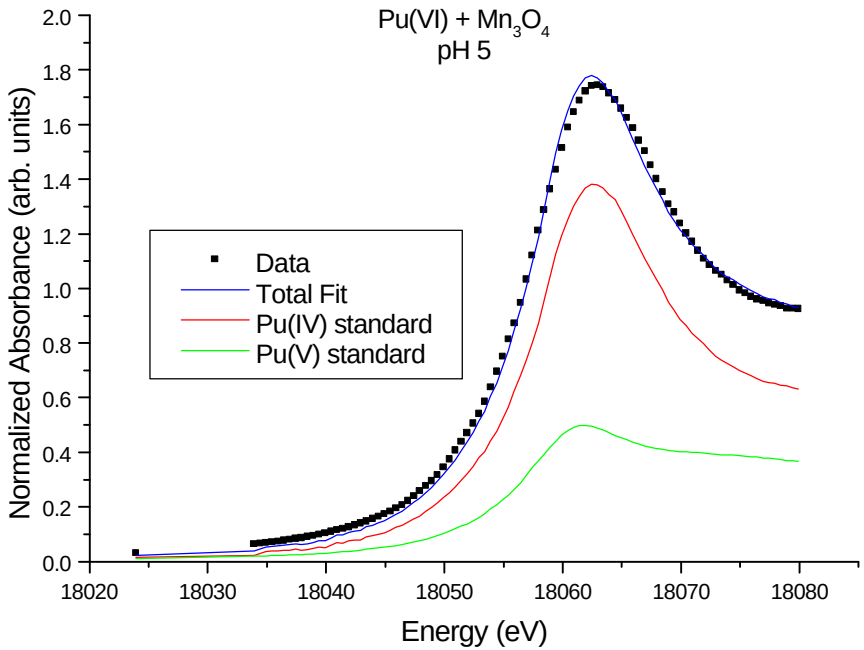
Reduction of Pu(VI) by Manganite

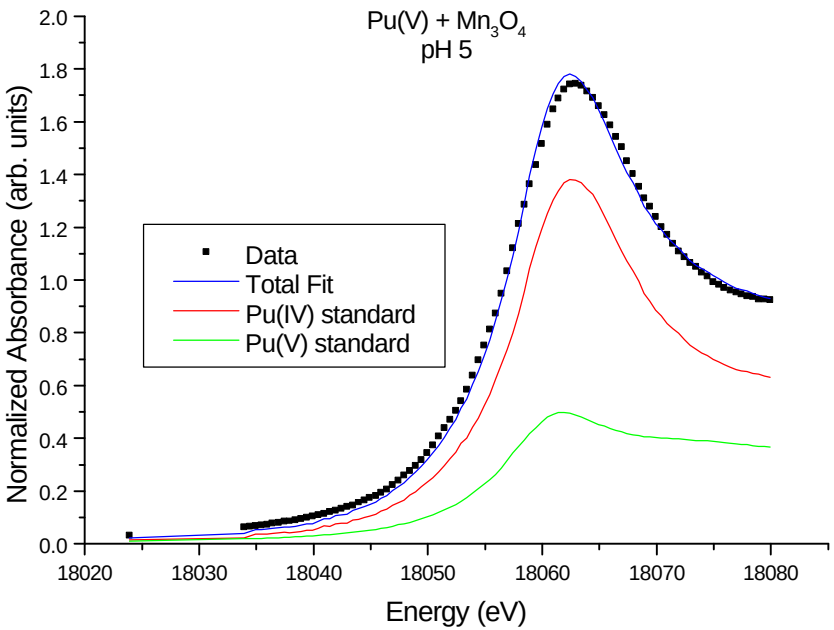


- **Pu(VI) (10^{-4} M) in contact with manganite at pH 5.**
- **Absorption spectra were taken of the <u>solution</u> (minerals were filtered out.)**
- **After 24 hours of contact with manganite, the plutonium in solution has been reduced from Pu(VI) to Pu(V). Pu(VI) without any minerals is stable at 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



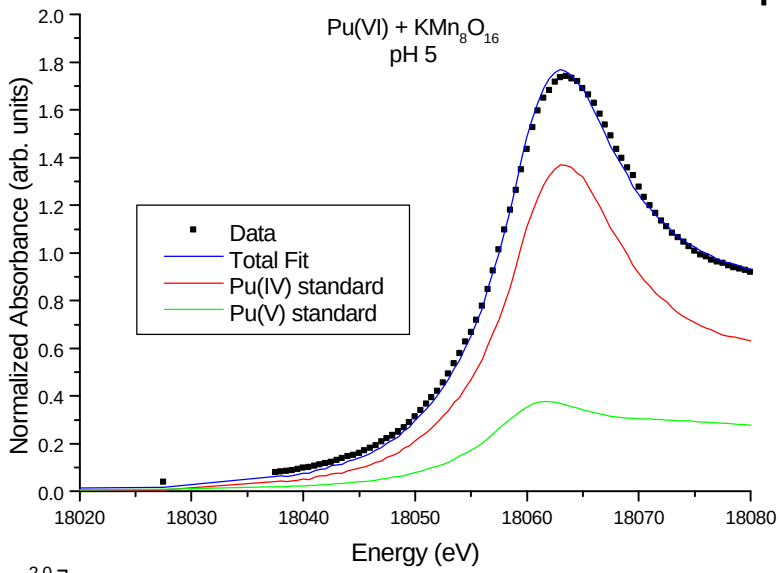


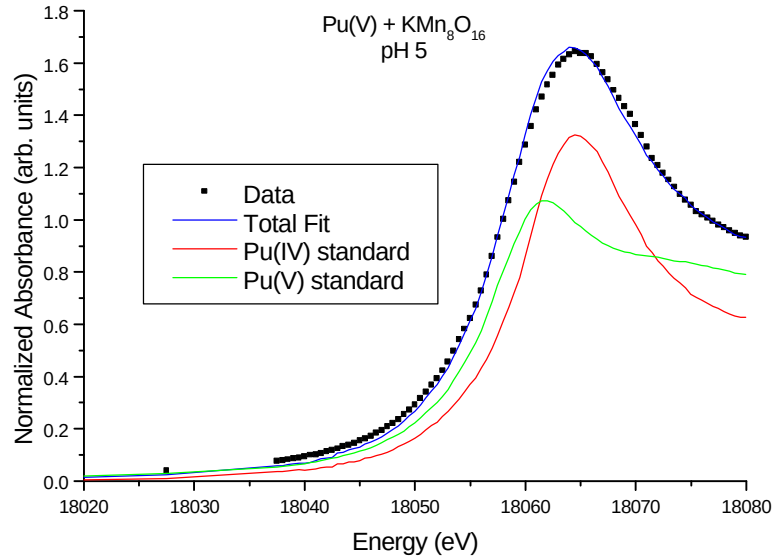
- 24 hour contact time.
- Pu(IV) = 67±2% of total Pu sorbed on the solid.
- Pu(VI) has been reduced by $Mn(II)Mn(III)_2O_4$.

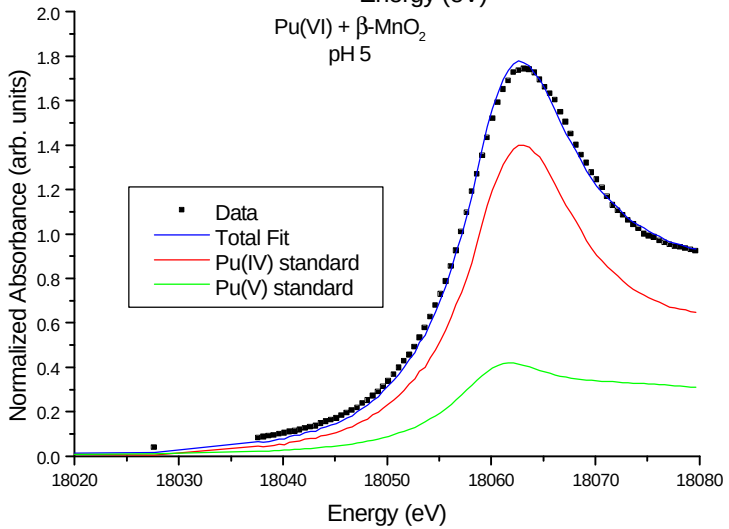
- 24 hour contact time.
- Pu(IV) = 63±2% of total Pu sorbed on the solid.
- Pu(V) has been reduced by $Mn(II)Mn(III)_2O_4$.

Reduction of Pu by Mn^{4+} Minerals

Pu L_{III} XANES







- 24 hour contact time.
- Pu(IV) = 71±2% (upper left)

  48±2% (upper right)

  71±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 d-MnO_2.
- 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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