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Complexation and Redox Interactions Between Aqueous Plutonium and Manganese Oxide Interfaces

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The sorption of Pu(VI) and Pu(V) onto manganite (MnOOH) and Hausmannite (Mn_3O_4) was studied at pH 5. Manganite sorbed 21-24% from a $1x10^{-4}$ M plutonium solution and the hausmannite removed between 43-66% of the plutonium. The increased sorption by hausmannite results from its larger surface area (about twice that of manganite) plus a larger number of active surface sites. X-ray absorption near-edge structure (XANES) spectra taken at the Pu L_{III} edge were compared to standard spectra of plutonium in single oxidation states. Based on these spectra, it appears that both manganite and hausmannite reduce the higher valent plutonium species to Pu(IV). Between 53-59% of the plutonium was present as Pu(IV) in the manganite samples while 55-61% of the plutonium complexed to the hausmannite had also been reduced to Pu(IV). The exact mechanism behind this redox interaction between the plutonium and the manganese needs to be identified.

KEYWORDS: Plutonium, manganese, manganite, hausmannite, XANES

I. Introduction

Several U.S. Department of Energy sites have been contaminated by plutonium as a result of weapons related activities. Plutonium is highly toxic and potentially mobile in aquatic environments. To predict its potential hazards, reliable models of plutonium migration through the vadose zone to nearby groundwater supplies are required. Fundamental knowledge of the interfacial reactions between plutonium and the surrounding geomaterial is essential for understanding its transport in the environment.

Previous studies have illustrated that plutonium will sorb to iron oxyhydroxides and other naturally occurring materials, possibly retarding its migration through the environment.[1,2] Recent synchrotron based X-ray microprobe studies have shown that manganese oxides, present as minor phases in the environment, can preferentially sequester plutonium over iron oxides present in larger quantities.[3-5] Based on these developments, it is essential that the interactions between plutonium and manganese oxyhydroxides be thoroughly understood to design effective transport models and efficient plutonium remediation systems.

We have begun a systematic study of the interfacial reactions between plutonium and manganese oxyhydroxide mineral surfaces. The interaction of Pu(V) and Pu(VI) with manganite (Mn(III)OOH) and hausmannite ($Mn(II)Mn(III)_2O_4$) has been studied using several analytical methods. Manganite and hausmannite were chosen as representative examples of minerals typically found in vadose zone conditions underneath the Hanford tank farm.[6,7] The information gained from these investigations will ultimately be incorporated into models that will be used to predict the migration of plutonium contaminants in the environment.

II. Experimental Procedure

Manganite and hausmannite were supplied by Chemetals, Incorporated (Baltimore, MD) as dry powders and were used without additional treatment. The minerals were crushed and the 63-212 μm size fraction was collected. Powder X-ray diffraction patterns taken with a Siemens D-500 diffractometer showed that no impurities or alternate mineral phases were present within the detection limits of the method. The mineral surface areas were determined

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using a standard B.E.T. method with an out-gassing temperature of 150°C.

Pu(VI) was prepared by refluxing a stock solution of plutonium in concentrated $HClO_4$ at 190° for 4 hours. Any traces of organic materials were destroyed before the addition of $HClO_4$ by evaporating the solution with concentrated HNO_3 to near dryness. Pu(V) was formed by electrochemically reducing Pu(VI) according to the method of Cohen.[8] Plutonium oxidation states were verified prior to use through optical absorption spectroscopy measured with an Ocean Optics S2000 fiber optic spectrometer.[9] Samples were prepared by shaking diluted plutonium stock solutions with either 250 mg of manganite or 100 mg of hausmannite in 0.1 M $NaClO_4$. pH values were adjusted using NaOH or $HClO_4$ of various concentrations. After 24 hours of contact, the samples were filtered onto 3μm cellulose membrane filters, which were then placed in heat-sealed polyethylene bags for containment.

X-ray absorption near-edge structure (XANES) spectra were collected on the Pu L_{III} edge at the Stanford Synchrotron Radiation Laboratory (SSRL) on wiggler beam line 4-1 using a half-tuned Si (220) double-crystal monochromator. Fluorescence yield spectra were collected with a four-pixel Ge fluorescence detector.[10] Energy calibrations were performed simultaneously by measuring transmission data from a PuO_2 reference. The pre-edge background was removed such that the absorption well above the Pu L_{III} edge followed a Victoreen formula. All data from the Ge detector were corrected for dead time prior to data reduction.

III. Results and discussions

Figure 1 illustrates the **(a)** manganite and **(b)** hausmannite mineral structures. Manganite has a structure similar to that of rutile[11] and is composed of rows of edge-sharing $Mn(O,OH)_6$ octahedra.[12] Unlike rutile, the octahedra are considerably distorted. Hausmannite has a tetragonally-distorted spinel structure[12] with most Mn(III) in octahedral sites and Mn(II) in tetrahedral coordination. In solution, the surface functional groups of both minerals are hydroxyl groups, which can be protonated or deprotonated depending on the pH of the solution.

Pu(VI) and Pu(V) were sorbed to manganite and hausmannite at a pH of 5 from an initial plutonium concentration of $1x10^{-4}$ M. Before the preparation of the XANES samples described above, the amount of plutonium complexed with the minerals was determined via liquid scintillation counting by measuring the plutonium remaining in solution. After 24 hours of contact, the manganite sorbed 21±1% of the Pu(VI) and 24±1% of the Pu(V). Likewise, the hausmannite removed 43±1% of Pu(VI) and 66±1% of Pu(V) from the solution. Previous kinetic experiments had shown that the uptake of plutonium was complete after 24 hours of contact time.

The hausmannite sorbed approximately 2-3 times the amount of plutonium than the manganite under the same conditions. This is due to the larger surface area of hausmannite, which was found using the B.E.T. method to be 20.4±0.8 m^2/g compared to 9.5±1.4 m^2/g for manganite. There are more available surface sites per unit area for binding to plutonium, resulting in a larger overall amount of plutonium sorption with hausmannite.

XANES measurements were also collected on standard solutions containing either Pu(IV), Pu(V), or Pu(VI). The oxidation state of the plutonium was verified using optical absorption spectroscopy. The incident x-ray energies for

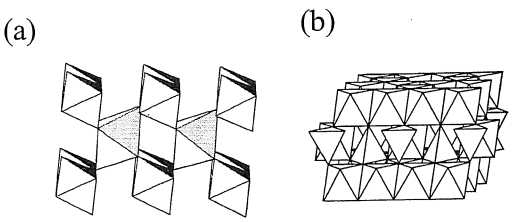

Fig. 1 Structures of (a) manganite and (b) hausmannite.

the data of these standard solutions were also calibrated to the PuO_2 reference. Plutonium oxidation states can be determined by comparing the main L_{III} absorption energy to known standards.[13] In addition to the energy shifts between the Pu(IV), Pu(V), and Pu(VI) standards and the PuO_2 reference (1.88±0.01 eV, 0.17±0.01 eV, and 2.33±0.01 eV, respectively, taken from the peak in the first derivative), there is a feature on the high energy side of the white line in the Pu(V) and Pu(VI) spectra due to multiple scattering between the plutonium and the axial oxygens of the plutonyl structure. This anomalous energy shift between the Pu(IV) and Pu(V) standards has been observed previously.[14] These differences in energy and shape allow for the determination of plutonium oxidation states in the sorption samples by fitting a linear combination of the standard spectra to the experimental data between 18,000 and 18,080 eV. The small energy shift and nearly identical shape of Pu(V) and Pu(VI) make it difficult to quantify the amount of each of these oxidation states present in the unknown spectra. However, we can determine whether there is any of the plutonyl structure present without being able to distinguish between Pu(V), Pu(VI), or a combination of the two. The fits presented below represent our preliminary results.

Figure 2 shows the XANES spectra taken after Pu(VI) **(a)** and Pu(V) **(b)** were in contact with manganite for 24 hours, and the resulting fits to the data. The plutonium standards used in the fits are also shown for comparison. 68±5% of the initial Pu(VI) sorbed to the manganite has been reduced to Pu(IV), and approximately 67±5% of the original Pu(V) has also been reduced to Pu(IV). The best agreements were achieved by fitting the residual plutonium as Pu(V), but as discussed above, it is also possible that this residual could be Pu(VI) or a combination of both Pu(V) and Pu(VI). Likewise, **Fig. 3(a)** and **(b)** shows the results of the interaction of Pu(VI) and Pu(V) with hausmannite and the comparison to the plutonium standards. In these samples, 71±5% of the original Pu(VI) and 61±5% of the

Pu(V) were also reduced to Pu(IV) after 24 hours of contact. The best fits were achieved by fitting the residual plutonium in each case as Pu(V). There was something wrong with the absolute energy calibration in Fig. 3(b) such that all of the plutonium standards needed to be shifted 0.92 eV to correctly line up the references of the plutonium standards to the reference from the data. In all four spectra, however, the characteristic high-energy plutonyl feature is missing. This indicates that the plutonyl cation (either Pu(VI) or Pu(V)) is mostly reduced and is instead sorbed to the mineral surfaces as Pu(IV). Extended x-ray absorption fine structure (EXAFS) data, which will be presented in a future publication, also give evidence for the reduction to Pu(IV).[15] Fits to the EXAFS show that the nearest oxygen neighbors have bond lengths resembling what would be expected for Pu(IV).

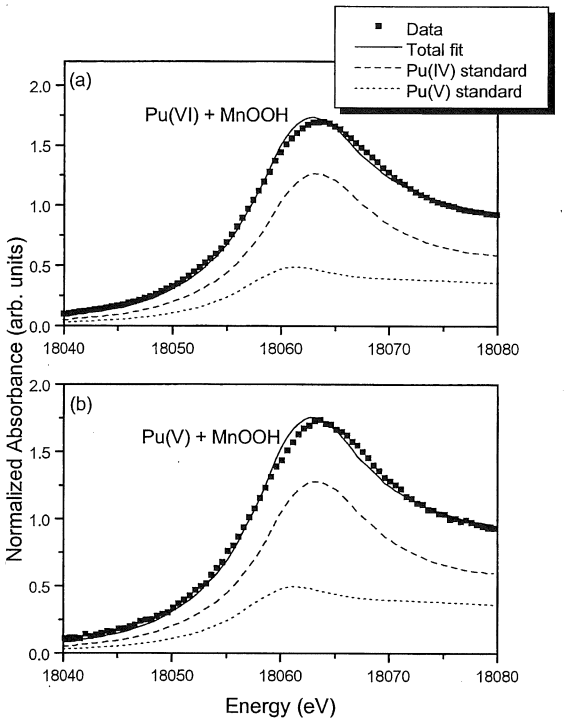

Fig. 2 XANES spectra of (a) Pu(VI) and (b) Pu(V) solutions in contact with MnOOH at pH 5 for 24 hours. The plutonium standards used to fit the spectra are also shown in their relative amounts.

The exact mechanism behind the reduction of plutonium is currently unknown, however one possibility is that Mn(III) (or Mn(II) in the case of hausmannite) is directly reducing the plutonium (and therefore becoming oxidized in the process) on the mineral surface or when the plutonium in solution is in close contact with the surface. Another possibility is that the Mn(III) in these minerals is undergoing disproportionation after contact with the solution into Mn(II) and Mn(IV). Mn(II) (which is already present in hausmannite) is highly soluble and would likely dissolve into solution immediately after formation. The Mn(II) in solution could reduce the plutonium in solution to Pu(IV), which would then sorb to the mineral surfaces.

IV. Conclusions

Manganite and hausmannite, which represent typical Mn(III) minerals found in vadose zone conditions under the Hanford tank farm, have been shown to sorb Pu(VI) and Pu(V) at pH 5. The hausmannite sorbs approximately 2-3 times the amount of plutonium than the manganite due to its larger surface area. The comparison of XANES spectra taken at the Pu L_{III} edge to standard solutions containing a

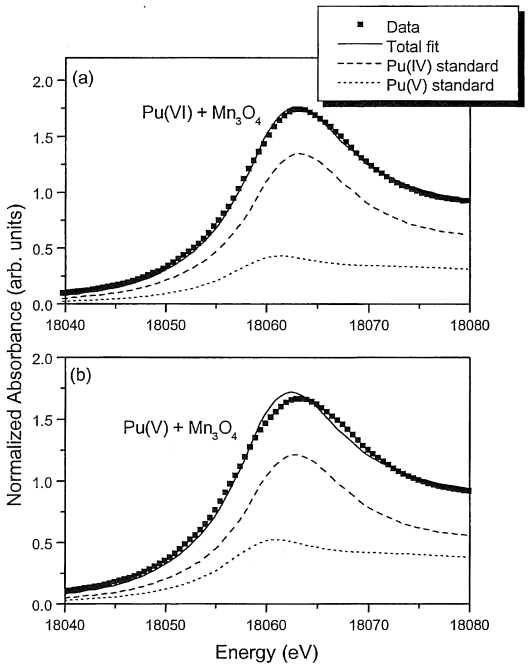

Fig. 3 XANES spectra of (a) Pu(VI) and (b) Pu(V) solutions in contact with Mn_3O_4 at pH 5 for 24 hours. The plutonium standards used to fit the spectra are also shown in their relative amounts. The absolute energy calibration was unreliable for the data set in (b), and an overall energy shift of 0.92 eV was allowed for the plutonium standards in the fit.

single plutonium oxidation state shows that both manganite and hausmannite reduce Pu(VI) and Pu(V) to Pu(IV) after 24 hours of contact. The mechanism responsible for the plutonium reduction could be attributed to direct reduction by Mn(III) or Mn(II) on the mineral surfaces or possibly from Mn(II) in solution, which would be formed as the result of disproportionation of Mn(III). Regardless of the exact mechanism governing this redox interaction between manganese and plutonium, the reduction to Pu(IV) has important environmental ramifications. For instance, Pu(IV) forms insoluble colloids, which carry a positive surface charge and have a tendency to adsorb on various

surfaces including minerals.[16] The plutonyl cations are much more soluble and therefore more likely to migrate through the vadose zone to nearby groundwater supplies. These results are important for designing effective environmental stabilization and remediation systems because the formation of insoluble plutonium species that have a tendency to adsorb to mineral surfaces could retard its migration through the environment.

In addition to studying the mechanism governing the manganese – plutonium redox system, we are also conducting sorption studies at additional pH values and with other representative manganese oxyhydroxide minerals. All of these results will be incorporated into surface complexation models that will used to predict the transport of plutonium contaminants in the environment.

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References

1) A. L. Sanchez, J. W. Murray, and T. H. Sibley, "The adsorption of plutonium IV and V on goethite," Geochim. Cosmochim. Acta **49**, 2297 (1985).
2) W. L. Keeney-Kennicutt and J. W. Morse, "The redox chemistry of $Pu(V)O_2^+$ interaction with common mineral surfaces in dilute solutions and seawater," Geochim. Cosmochim. Acta **49**, 2577 (1985).
3) M. C. Duff, D. B. Hunter, I. R. Triay, D. T. Reed, C. R. Cotter, P. M. Bertsch, J. Kitten, G. Shea-McCarthy, S. J. Chipera, and D. T. Vaniman, "Mineral associations and average oxidation states of sorbed Pu on tuff," Environ. Sci. Technol. **33**, 2163 (1999).
4) M. C. Duff, M. Newville, D. B. Hunter, P. M. Bertsch, S. R. Sutton, I. R. Triay, D. T. Vaniman, P. Eng, and M. L. Rivers, "Micro-XAS studies with sorbed plutonium on tuff," J. Synch. Rad. **6**, 50 (1999).
5) A. Manceau and J. –L. Hazemann, Personal communication (1999).
6) B. M. Tebo, W. C. Ghirose, L. G. van Waasbergen, P. L. Siering, and R. Caspi in *Geomicrobiology Reviews in Mineralogy* (Mineralogical Society of America, Washington, D. C., 1997), Vol. 35, p. 225.
7) R. J. Serne, J. L. Conca, V. L. LeGore, K. J. Cantrell, C. W. Lindenmeier, J. A. Campbell, J. E. Amonette, and M. I. Wood, "Solid-waste leach characteristics and contaminant-sediment interactions. Volume 1: Batch leach and adsorption tests and sediment characterization," PNL-8889 (PNNL, 1993).
8) D. Cohen, "Electrochemical studies of plutonium ions in perchloric acid solutions," J. Inorg. Nucl. Chem. **18**, 207 (1961).
9) D. Cohen, "The absorption spectra of plutonium ions in perchloric acid solutions," J. Inorg. Nucl. Chem. **18**, 211 (1961).
10) J. J. Bucher, N. M. Edelstein, K. P. Osborne, D. K. Shuh, N. Madden, P. Luke, D. Pehl, C. Cork, D. Malone, and P. G. Allen, SRI '95 Conference Proceedings. Rev. Sci. Inst. **67**, 1 (1996).
11) H. Dachs, "Neutronen- und Röntgenuntersuchungen am Manganit, MnOOH," Zeits. Kristallogr. **118**, 303 (1963).
12) G. A. Waychunas in *Reviews in Mineralogy* (Mineralogical Society of America, Washington, D. C., 1991), Vol. 25, p. 11.
13) S. D. Conradson, I. Al Mahamid, D. L. Clark, N. J. Hess, E. A. Hudson, M. P. Neu, P. D. Palmer, W. H. Runde, and C. D. Tait, "Oxidation state determination of plutonium aquo ions using x-ray absorption spectroscopy," Polyhedron **17**, 599 (1998).
14) P. G. Allen, J. J. Bucher, D. K. Shuh, N. M. Edelsetin, and T. Reich, "Investigation of aquo and chloro complexes of UO_2^{2+}, NpO_2^+, Np^{4+}, and Pu^{3+} by x-ray absorption fine structure spectroscopy," Inorg. Chem. **36**, 4676 (1997).
15) D. A. Shaughnessy, C. H. Booth, H. Nitsche, D. K. Shuh, G. A. Waychunas, R. E. Wilson, H. Gill, K. J. Cantrell, and R. J. Serne, "Investigation of molecular interfacial reactions between Pu(VI) and Pu(V) with manganese oxide minerals manganite and hausmannite," to be published.
16) J. M. Cleveland, The Chemistry of Plutonium (American Nuclear Society, Illinois, 1979), p. 82.