XANES of Plutonium and Neptunium Solids

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Introduction

The migration of plutonium and neptunium in the subsurface is a key concern at DOE sites where nuclear waste contamination exists. An important factor that determines the overall mobility of these multivalent actinides in the environment is the oxidation state defined by the subsurface redox chemistry. Synchrotron-based methods, such as x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS) can be used to identify oxidation states in these complex "real-system" samples.

An important experimental concern that may limit the use of such synchrotron-based methods is the relative contribution of oxidation state and molecular geometry to the XANES edge position. To address this important issue, we have obtained the XANES of plutonium and neptunium solids containing one oxidation state.[1-3] Additionally, theoretical calculations were performed,[4] in part, to interpret the XANES spectra and establish the effects of geometry on the edge position.

Methods and Materials

Plutonium phases with oxidation states of +3, +4, +5 and +6 were prepared. These are the oxidation states that are most prevalent under environmental conditions. The compounds made were Pu(III)F_3, Pu(IV)O_2, NaPu(V)O_2CO_3, and Ba_3Pu(VI)O_6. A series of Pu(III) solids was also prepared. These, along with the fluoride, were a chloride, bromide, and plutonium sesquioxide phase. The three neptunium phases were Np(IV)F_4, NaNp(V)O_2CO_3, and an amorphous Np(VI) phosphate precipitate.

The samples were analyzed by XANES on the MR-CAT undulator beamline at the Advanced Photon Source (APS) of Argonne National Laboratory. Samples were dried and encapsulated in a polystyrene matrix in a nitrogen glovebox. After encapsulation, the samples were removed from the glovebox and mounted for XANES analysis.

These experimental efforts were complimented by theoretical efforts to calculate XANES spectra. Calculations of the Pu L_{III} XANES of small cluster models of the local Pu environment in PuO_2 have been carried out to compare with the experimental results obtained at the APS. These multiple-scattering calculations used the FEFF7 code with tangent atomic spheres and relativistic corrections for the initial core state.

Results

The shifts in the L_{II} and L_{III} edge positions for a series of plutonium solids that differ in oxidation state are shown in Fig. 1. Here a systematic ~ 2 eV shift was observed as a function of oxidation state. This is consistent with what has been reported for variable oxidation states in aqueous systems. The series of Pu(III) solids analyzed shows that, even though significant differences in the geometry exist, the edge positions do not change (to an uncertainty of ± 0.3 eV).

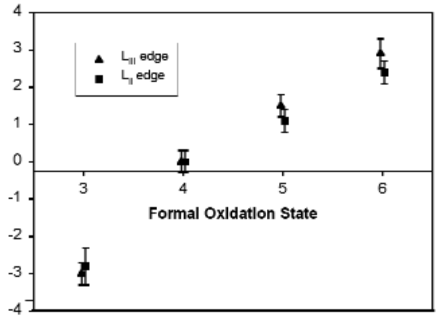

FIG. 1. Shift in XANES edge position for the LII and LIII edges of plutonium solids as a function of the plutonium oxidation state.

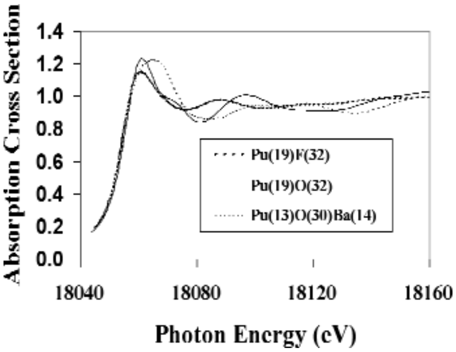

FIG. 2. Calculation of LIII XANES for larger cluster plutonium compounds using the FEFF7 code, and 0.5 nm atomic shells. These calculations do not account for oxidation state effects and show that the molecular geometry differences in these samples do not lead to significant changes in edge position.

Less work has been done with neptunium solids. A ~ 2 eV edge shift was also noted for Np(V) and Np(VI) solids. The edge positions for Np(IV) and Np(V), however, were indistinguishable since they were within experimental uncertainty (± 0.3 eV). This is also consistent with results obtained in aqueous samples. Further work on neptunium solids is in progress.

The L_{III} XANES spectra were calculated for cluster models of PuF_3, PuO_2, and Ba_3PuO_6 (see Fig. 2) in order to study the dependence of the edge position and spectral features on the local coordination of the absorbing Pu atom. The calculated edge positions for the three cluster models vary by no more than 0.5 eV, which is well within the limits of the uncertainties in our theoretical procedure. Thus, our results are consistent with the observation that edge position is determined mainly by the oxidation state of the absorbing atom and depends only very weakly on the local geometry. In agreement with experiment, our results also show the existence of a high-energy shoulder on the edge peak for PuO_2. The width of the edge peak for Ba_3PuO_6 is much greater than for PuF_3 and PuO_2, and there is an asymmetry in the edge peak for Ba_3PuO_6 that correlates well with experimental results.

Discussion

The correlation between the oxidation state and edge position for plutonium solids, and the very small dependence of this position on geometry, indicate that XANES can be used to identify oxidation states in complex samples typical of those obtained in the subsurface at contaminated DOE sites. When the oxidation state is the same, but geometry is varied, we measured a very slight (less than 0.3 eV) shift in the edge position. These results are consistent with those reported for aqueous plutonium systems.

For neptunium, the relationship between oxidation state and edge position is less useful. Although there is a ~ 2 eV shift between Np(V) and Np(VI), the edge positions for Np(IV) and Np(V) are within experimental uncertainty (± 0.3 eV). It is necessary, under these conditions, to rely on the qualitative aspects of the XANES spectrum (e.g., the post-edge features and shoulder) to establish the oxidation state.

Acknowledgments

This work was funded in part by the Nuclear Energy Research Initiative (NERI). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, and Office of Science, under Contract No. W-31-109-Eng-38. The MR-CAT beamline is supported by its member institutions and the U.S. DOE-BES-SC under contracts DE-FG02-94ER45525 and DE-FG02-96ER45589.

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