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Distribution & Solubility of Radionuclides & Neutron Absorbers in Waste Forms for Disposition of Plutonium Ash & Scraps, Excess Plutonium, and Miscellaneous Spent Nuclear Fuels

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Research Objective

The objective of this research is to gain a fundamental understanding of the distributions and the solubility limits for actinides Pu and U and rare earth neutron absorbers such as Gd and Hf in waste forms. This will be accomplished by systematically studying the local structural environments of these constituents in representative waste forms such as glass, ceramics, and vitreous ceramics. Basic knowledge of these issues will provide a technical and scientific basis that can be used by the U.S. Department of Energy (DOE), Environment Management (EM) Program in developing, evaluating, and selecting waste forms for the safe disposal of Pu, spent nuclear fuel, and other transuranic wastes. The work presented here is a summary of our research activity from November 1997 to May 1998. The elucidation of the correlations between the local structural environments of actinides and rare earth neutron absorbers in waste forms as functions of waste form compositions, and waste form processing conditions will also advance basic material science.

Research Progress and Implications

The work presented here is a summary of our research activity from November 1997 to May 1998. Currently being studied is the effect of the Pu oxidation state on its solubility in borosilicate-based glasses. When glasses are melted in ambient atmosphere, Pu(IV) has been shown to be the dominant oxidation state as determined by ultraviolet-visible-near infrared spectroscopy (UV-VIS-NIR) and x-ray absorption fine structure (XAFS) techniques. However, no literature data are available for glasses containing Pu predominantly as Pu(III) nor the solubility for Pu(III) in the glass. The results of our study demonstrate that in borosilicate glass, Pu(III) is significantly more soluble than Pu(IV). Using x-ray diffraction analysis the solubility of Pu(III) as oxide was determined to be at least

25 mass% in the reduced glass, while it was no greater than 10 mass% in the same glass under oxidizing conditions (glass melting temperature was 1400°C). The oxidation states of Pu in the glasses were determined by XAFS analysis using the Pu L_{III} edge as shown in Figure 1. Using standard reference XAFS spectra of Pu(IV) and Pu(III), we estimated that about 90 % of the Pu was present as Pu(IV) in the oxidized glass and about 95% of the Pu was Pu(III) in the reduced glass.

In contrast to the redox effect on the solubility limit of Pu, the solubility of U in soda-lime (SL) silicate glass is favored under oxidizing conditions or glass with high Na_2O concentration. In ambient atmosphere at 1500°C, the solubility, in terms of UO_3, is found to be 30 mass% in the baseline glass (SRM 1830 from NIST) and at least 40 mass% in the baseline glass with additional Na_2O.

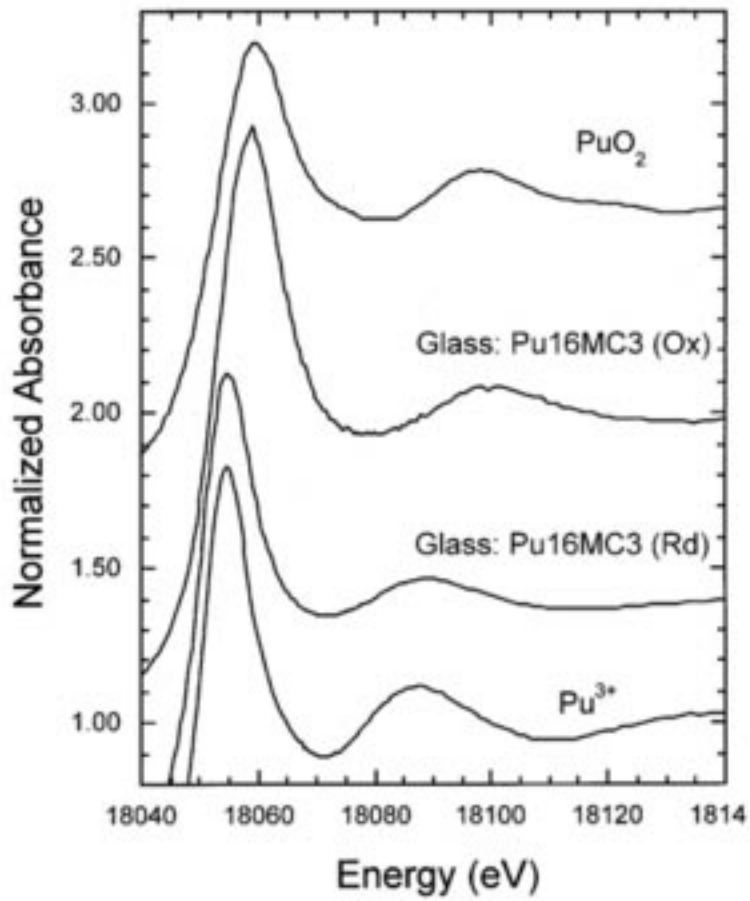

Figure 1. **Normalized Pu L_{III} near edge spectrum from a borosilicate glass with 10 mass% Pu oxide (Ox and Rd represent oxidized and reduced glasses, respectively)**

The local structural environments of U in the silicate glasses have also being studied with XAFS. Figure 2 shows U L_{III} x-ray absorption spectra of the SL glasses with various concentrations of U and melted under two different conditions. Glasses doped with 10 to 40 mass% UO_3, excluding glasses prepared under reducing conditions, yielded remarkably similar spectra, except for the systematic increase in white line intensity with U content. The oxidation state of U in the oxidized SL glasses more closely resembles that of U_3O_8 than UO_2. In contrast, the overall line shape, energy position, and presence of the actinyl signature indicate that U in the SL-U40AR glass is nearly all tetravalent and in the SL-U40R glass that a significant fraction is tetravalent. Furthermore, the extended XAFS clearly identifies the U(IV) in the reduced glasses from U-U scattering as UO_2. The estimated average valence of U in the oxidized glasses is five compared with a value about four in the reduced glasses.

The solubility and distributions of Gd and Cs in yttria-stabilized zirconia single crystal and polycrystalline zirconolite are being studied with ion beam implantation. Direct observation of the

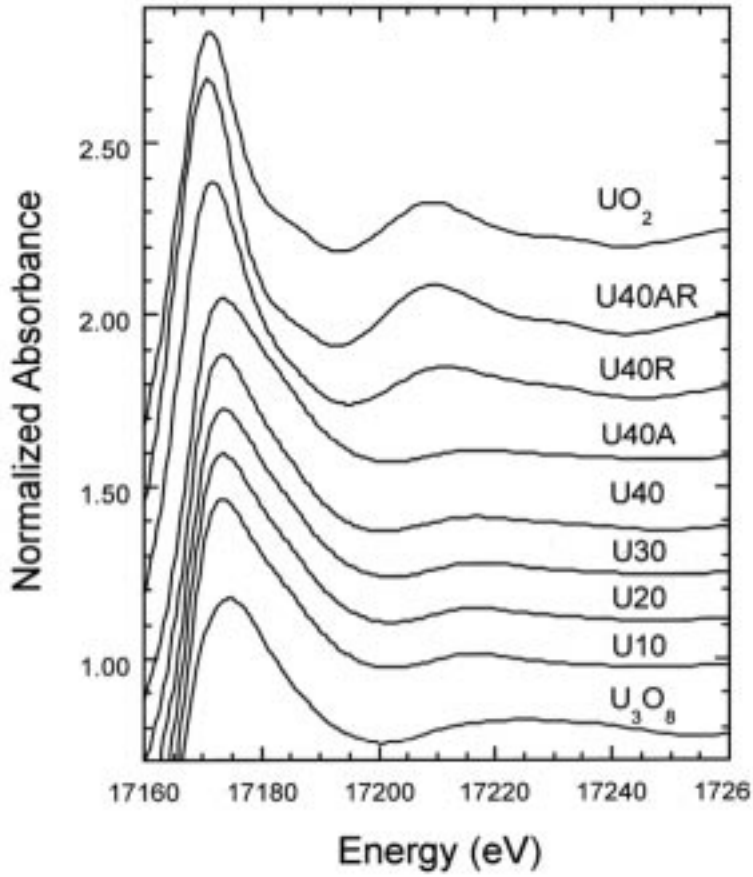

Figure 2. **Normalized U L_{III} near edge spectra from soda-lime glasses with various concentrations of U (U10-40: U concentrations in the SL glasses, R: reduced SL glasses, A: the SL glass with high Na_2O content)**

dynamic microstructure change during ion implantation was made using in-situ transmission electron microscopy. Amorphization of zirconolite was observed at room temperature after a dose of < $3x10^{14}$ ions/cm^2 of Cs^+. After $5x10^{16}$ ions/cm^2, ~5 nm precipitates were observed. With the implantation of an additional $5x10^{16}$ ions/cm^2 of Cs^+ at 500°C above the critical amorphization temperature of zirconolite; the amorphous zirconolite crystallized from the undamaged deeper region. The precipitates grew slowly in size to ~20-30 nm and their density increased to ~10^{15}/cm^3.

Planned Activities

The XAFS study for Pu and U in silicate and borosilicate glasses is on-going. The results obtained from the above studies will assist in the elucidation of the structural roles of Pu and U in the glass, which are critical for a better understanding of their solubility limits in the glasses. Studies of glass compositional and structural effects on the solubility limits of U, Pu, and rear earth neutron absorbers and U/Pu redox chemistry in crystalline waste forms have been initiated. These studies are projected to be completed within about two and one-half years.