X-ray Absorption Spectroscopy of Trace Elements in Spent Nuclear Fuel

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Introduction

Present and future nuclear fuel cycles will rely upon controlling the complex chemistry of trace fission products and transuranium actinides. Knowledge of the chemical states of radionuclides in spent fuel and related materials provides a first line of understanding that may benefit waste disposal, fuel reprocessing, transmutation/recovery, and remediation of sites from weapons-related activities. Few techniques have proven more effective than X-ray absorption spectroscopy (XAS) for determining oxidation states and structural environments of elements in solids. We describe measurements of commercial spent nuclear fuel (CSNF) using XAS to better determine trace element chemistry in this material.

Methods and Materials

To achieve the required spectral resolution, we chose a narrow bandwidth analyzer based on diffractive optics. One such diffractive geometry is the Laue configuration, where x-rays are transmitted through the crystal, rather than reflected from the crystal. To match the diffraction condition across the entire surface of the crystal, the wafer is bent to the form of a logarithmic spiral [1-3]. We have designed several bent-Laue analyzers for the actinide L fluorescence lines with different bandwidths. The narrowest of those was used for the measurements reported here. With a bandwidth of about 75 eV, the tails of the uranium fluorescence peak do not interfere too greatly with the neptunium fluorescence. The bent-Laue analyzer therefore provides a unique capability to perform high-resolution XAS analyses of transuranium actinides and transition metal fission products contained in a U-oxide matrix, an exceedingly difficult undertaking by other XAS techniques [3-5]. Results of our application of this method to the case of neptunium in CSNF and selected CSNF alteration products appears elsewhere [5,6], so we shall restrict ourselves here to the results of our findings on molybdenum in CSNF.

The XAS experiments were performed at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline located at Sector 10 of the Advanced Photon Source (APS). The brightness of the APS facility in the high-energy x-ray regimes makes it ideal for investigating heavy element (e.g., radionuclide) systems.

The x-ray beam from the APS insertion device was directed onto a Si(111) double-crystal monochromator. From there is was focused from 300 x 300 microns to about 10 x 10 microns using Kirkpatrick-Baez (K-B) geometry focusing mirrors. A mirror upstream of the K-B focusing mirrors was used for harmonic rejection. Fluorescence yield was energy-analyzed to reduce spectral overlap between uranium and edges of interest by using a bent-Laue configuration described above. The bent Laue analyzer and detector were placed at a 90 degree angle with respect to the incident beam, so that the elastic and Compton scattered components would be minimized.

A sample consisting of a single grain of CSNF was taken from an Approved Testing Materials (referred to as ATM-103 [6]) fuel fragment. A sample holder, specially designed for triple containment of highly radioactive specimens, was cleaned, test-fitted, and transferred into a glovebox. Further containment was provided by embedding the specimen in polystyrene resin, about 2 mm thick. The specimen was then covered using a pre-cut Kapton film. On a benchtop, the inner containment was placed inside a separate holder providing outer containment, which was, in turn, covered with a second Kapton film, and sealed with an o-ring.

Results

An application of this technique appears in Figure 1, where one can clearly see molybdenum fluorescence spectrum atop a strong uranium spectrum. Incident x-rays with an energy just below the Mo–K absorption edge at 20.0 keV, but above the U–LIII edge at 17.17 keV lead to strong U–Lβ fluorescence as seen in the figure as the spectral trace with symbols. When the energy of the incident x-rays is above the Mo K–edge (solid line trace in Figure 1), the Mo–Kα fluorescence is seen at 17.5 keV, while the rest of the spectrum is unchanged. The molybdenum is present in the fuel at only 0.3 weight percent. It is the ability of the bent Laue analyzer to resolve these weak features in the presence of a strong background that makes the XAS analysis of trace elements in CSNF possible.

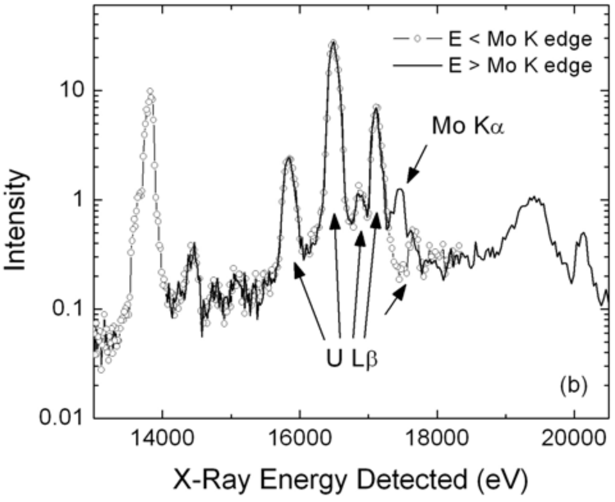

Figure 1. Bent-Laue analyzer detection of fluorescence yield above and below the Mo K-edge in CSNF [6].

By scanning the incident x-ray energy while integrating the total area in the molybdenum fluorescence peak, one obtains an XAS edge spectrum as shown in Figure 2. Interestingly, the near-edge structure could not be fitted using a linear combination of reference spectra obtained from Mo metal, MoO_2 and MoO_3. This may be owing to the presence of a large fraction of the Mo as metallic Mo in the hexagonal close-packed “epsilon ruthenium” phase rather than having the body-centered cubic coordination of pure molybdenum metal [7, 8]. Details of the near-edge XAS can be extremely sensitive to site symmetry, as is likely manifest in this case.

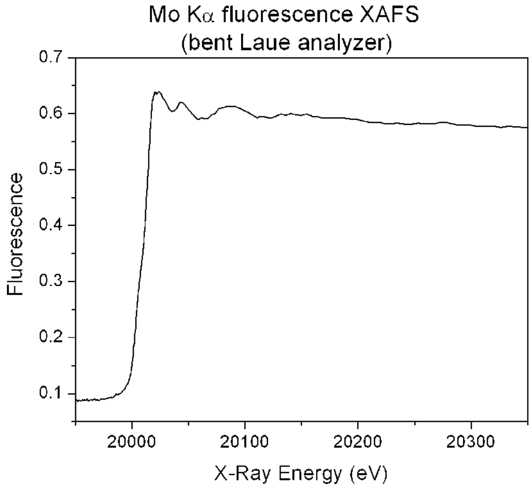

Figure 2. Molybdenum K-edge spectrum from CSNF, using Bent-Laue analyzer detection.

Next, we can extract information about atomic coordination of the Mo atoms within the CSNF by careful analysis of the extended fine structure (XAFS) contained within the absorption edge spectrum [9]. The Fourier transform modulus of the fine structure, which results in a pseudo-radial distribution function of molybdenum, is shown in Figure 3. Note that the first coordination shells of both oxide (Mo–O) and metallic (Mo–Mo) molybdenum are observed. The apparent peak positions are shifted from the corresponding bond lengths by a phase shift [9]. These bond lengths are too close to each other to arise from the same phase, and thus indicate a mixture of metallic and oxidized molybdenum. The phase-corrected bond lengths (scattering paths) are found to be Mo–O [R = 2.14(5) Å] and Mo–metal [R = 2.61(4) Å], in good agreement with oxide and metallic phases of molybdenum. The presence of metallic Mo has been described previously [7,8], but the extent to which the Mo is oxidized in CSNF has not been known, although it is expected to depend on the oxygen potential in the fuel [8].

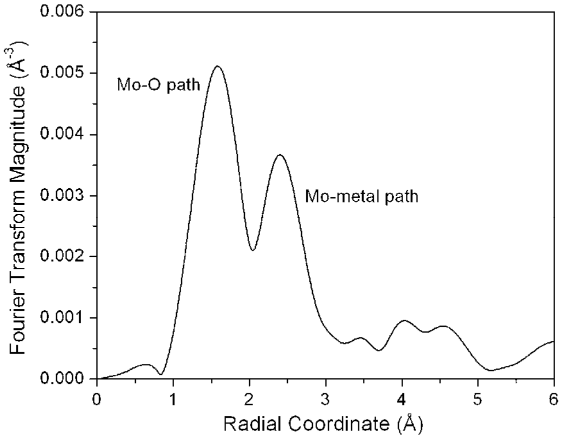

Figure 3. Fourier transform modulus (pseudo-radial distribution function) of the XAFS signal contained in the absorption edge of figure 2.

Discussion

Recent advances in available synchrotron x-ray sources and a sophisticated detection scheme based upon the bent-Laue analyzer have allowed detailed x-ray spectral information to be obtained from trace elements in a challenging specimen (CSNF). Direct observations of oxidation state, coordination, and even site symmetry have been reported for molybdenum CSNF. Additional results for neptunium and plutonium have been obtained and are reported elsewhere.

References

[1] Z. Zhong, D. Chapman, B. Bunker, G. Bunker, R. Fischetti, and C. Segre, *J. Synchrotron Rad.* 6, 212-214 (1999).

[2] C. Karanfil, Z. Zhong, L. D. Chapman, R. Fischetti, G. B. Bunker, C. U. Segre, and B. A. Bunker, CP521 *Synchrotron Radiation Instrumentation: Eleventh U.S. National Conference*, P. Pianetta et al., eds., 178-182 (2000).

[3] A. J. Kropf, R. J. Finch, J. A. Fortner, And S. Aase, C. Karanfil, C. U. Segre, J. Terry, G. Bunker, and L. D. Chapman, to appear in *Review of Scientific Instruments.*

[4] J. A. Fortner, R. J. Finch, A. J. Kropf, and J. C. Cunnane, *Proceedings of the International Conference on High-Level Waste Management*, Las Vegas, NV March 30-April 4, 2003; J. A. Fortner, R. J. Finch, A. J. Kropf, and J. C. Cunnane, submitted to *Nuclear Technology*.

[5] A. J. Kropf, J. A. Fortner, R. J. Finch, J. C. Cunnane, and C. Karanfil, *Proceedings of XAFS XII: The 12th International Conference on X-ray Absorption Fine-Structure Spectroscopy* , Malmö, Sweden, June 22-27, 2003, to appear in *Physica Scripta.*

[6] Guenther et al., “Characterization of Spent Fuel Approved Testing Material – ATM-103”, PNL-5109-103, Pacific Northwest Laboratory, Richland, WA (1988).

[7] L. E. Thomas and R. J. Guenther, *Mater. Res. Soc. Symp. Proc. Vol.* 127, 293 (1989).

[8] H. Kleykamp, J. O. Paschoal, R. Pejsa, and F. Thommler, *J. Nucl. Mater.* 130, 426 (1985).

[9] E. A. Stern, "Theory of EXAFS," in *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, edited by D. C. Koningsberger and R. Prins, (Wiley-Interscience, New York, 1988).

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