Crystal Chemistry of Radionuclides in Spent Nuclear Fuel and Its Alteration Products

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Introduction

Spent uranium oxide nuclear fuel hosts a variety of trace impurities, forged by nuclear fission, neutron capture, and radioactive decay. In the high-temperature, high-radiation field environment of a reactor (and, to a lesser degree, during subsequent storage) these trace elements are either incorporated into the fluorite structure of the uranium dioxide (e.g., neptunium, plutonium) or exsolved into separate phases (e.g., technetium, molybdenum, and ruthenium). We use synchrotron x-ray absorption spectroscopy and microscopy to reveal the local environment and chemistry of neptunium, plutonium, technetium, and molybdenum within spent uranium oxide nuclear fuel.

Obtaining useful x-ray spectroscopic information requires that the background from the matrix uranium be substantially decreased, which we achieve using a bent-Laue diffractive optics energy analyzer with a bandwidth of about 75 eV.

Challenges

- What is the crystal chemistry of fission products and transuranics incorporated into commercial spent nuclear fuel (CSNF)?
- What happens to neptunium, plutonium, technetium as CSNF corrodes? Are they:
  - Sequestered into stable uranium(VI) phases?
  - Re-precipitated as pure oxide (e.g., NpO_2 or Np_2O_5)?
  - Released to groundwater?
  - Likely to stay put?
- Uranium oxide in a waste repository is expected to behave analogously to natural uranium deposits . . . however, man-made elements (Np, Tc, Pu, etc.) have few natural analogs.

Our goals are to:

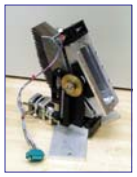
- Enhance the understanding of fundamental mechanisms of radionuclide release.
- Determine the kinetics of fuel corrosion.
- Quantify radionuclide release as fuel corrodes.
- Understand the formation of secondary alteration phases, sorption of radionuclides onto the surfaces of near-field materials, and the formation and mobility of colloids.

Fundamental Processes:

- Initial conditions + thermodynamics + kinetics.
- Coupling of processes: electrochemical, mass transport.

Argonne's Approach

Few techniques have proven more effective at determining oxidation states and structural environments of elements in inhomogeneous solids than x-ray absorption spectroscopy (XAS). Using a novel "bent-Laue analyzer" detection scheme based on diffractive optics, we have obtained detailed XAS information from Mo, and Tc in specimens of CSNF. The bent-Laue analyzer provides unprecedented rejection of the intense uranium fluorescence background, yielding spectral information from elements present at concentrations on the order of 1 part in 10,000.



Several XAS measurements from CSNF were performed at the Materials Research Collaborative Access Team (MR-CAT) insertion device beamline located at Sector 10 of the Advanced Photon Source (APS), a third-generation x-ray synchrotron source located at Argonne National Laboratory. The brightness of the APS facility in the high-energy x-ray regimes makes it ideal for investigating radionuclide-containing specimens, which have relatively high-energy absorption edges, and which must be carefully encapsulated for radiological safety.

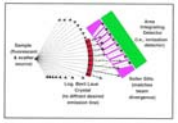
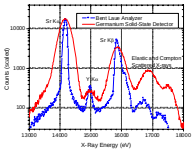
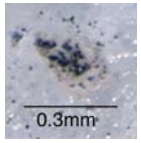
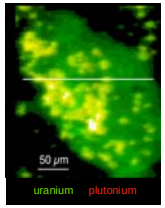


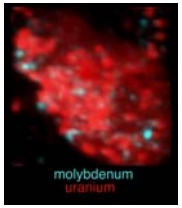
FIG. 1. A sketch of the "logarithmic bent Laue analyzer" concept.

A fundamental difficulty in detecting and measuring the x-ray absorption spectra of trace elements in a uranium matrix is that the fluorescence is generally not well separated in energy from the numerous uranium L-β lines. Solid-state detectors cannot resolve these energies at sufficient count rates. Measuring useful spectroscopic information requires that the background from the matrix uranium be substantially decreased. To achieve the required spectral resolution, we chose a bent-Laue analyzer with a bandwidth of about 75 eV, so that the tails of the uranium fluorescence peak were well separated from the other peaks.



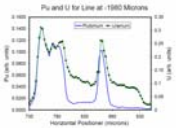


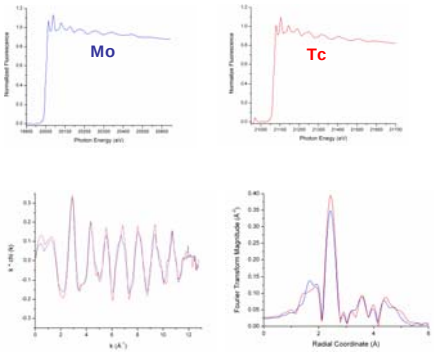




X-ray Microscopy

A sample of fuel grains and alteration products **(far left)** was taken from a fuel fragment that had undergone 10 years of corrosion testing at elevated temperature (90°C) under slowly dripping groundwater. Element-specific x-ray fluorescence maps showed that plutonium was always found to coexist with uranium (**left, center**), while molybdenum was often present as separate exsolved particles (**near left**). A line scan **(right)** illustrates how uranium may be more mobile than the plutonium, which did not substantially coprecipitate into the uranyl alteration phases.



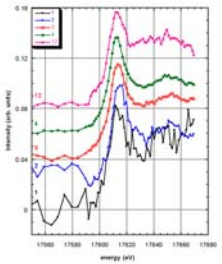


X-ray Absorption Spectroscopy

By analyzing XAS data from a particular absorption edge, we can determine the local environment of a specific atomic species. Photoelectron scattering from neighboring atoms creates a subtle modulation of the absorption above the edge energy known as extended fine structure. Careful analysis of the extended fine structure (EXAFS) contained within the absorption edge spectrum yields detailed information about the absorbing element, including distances to near neighbors, types and numbers of neighboring atoms, and details of the radial distribution function. The energy of the absorption threshold and near-edge absorption features also can be used to obtain information about the charge state of the central atom and the site symmetry.

At upper left are normalized XAS from molybdenum (blue) and technetium (red) K-edges. At lower left are the absorption fine structure, and its Fourier transform, which illustrate the nearly identical coordination environments of these elements in the exsolved particles. The structure is consistent with a metallic epsilon-ruthenium phase, which has surprisingly resisted corrosion for more than 10 years.

At right are a series of XAS from the neptunium L_{III}-edge at selected points across the specimen. Increased noise levels reflect regions of lower concentration. Like plutonium, neptunium is not found to substantially coprecipitate into uranyl alteration phases. The spectra from the most intense regions are indicative of Np(IV), at concentrations of only one part in 2000.



Conclusions

We find the plutonium and neptunium in spent fuel are tetravalent, with each having a local environment consistent with solid solution in the uranium dioxide matrix. The majority of molybdenum and technetium were found to exist together and to have identical local environments, consistent with metallic epsilon-ruthenium. These findings hold even for some fuel particles that have been partially oxidized by aqueous corrosion at 90ºC in air. Current data for the standard reduction potentials of the redox couples NpO_2^+/Np^{4+} and UO_2^{2+}/U^{4+} suggest that the UO_2^{2+}/U^{4+} couple may keep the corrosion potential below that required to oxidize Np(IV) to Np(V) as long as U(IV) predominates (that is, until most of the U(IV) has been oxidized).

These data, for the first time, have allowed direct observation of oxidation state, coordination environment, and site symmetry of fission product elements in CSNF. These data demonstrate XAS as a definitive method for establishing chemical incorporation of trace elements into uranium-dominated crystals in a quantitative manner. In addition to near-term applications that will allow a better understanding of radionuclide release from corroding waste in the Yucca Mountain Repository, this advance is expected to find applications in understanding fission product behavior in advanced fuel cycles (e.g., fission product behavior in nuclear fuels operating at high temperatures). In-situ measurements of trace elements in CSNF and its alteration phases have been made possible by the bent-Laue analyzer.

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