Radionuclide Association with Alteration Phases

Source term release and transport phenomena

Presented to:
DOE-CEA Technical Exchange Meeting

Presented by:
Jeffrey A. Fortner
Argonne National Laboratory

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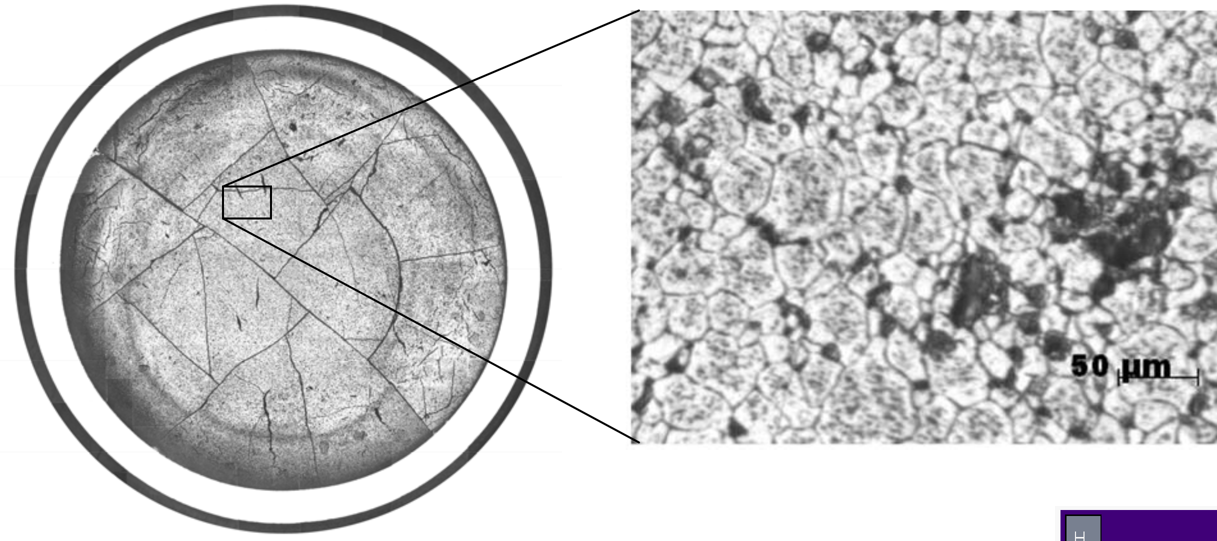
Objectives

- **What is known about solid-state chemistry of trace radionuclides in a uranium-dominated system?**
- **Will sequestration of radionuclides reduce dissolved concentrations in the environment?**
- **Can one predict, from initial conditions of spent fuel in a repository, the retention of these radionuclides into alteration phases?**

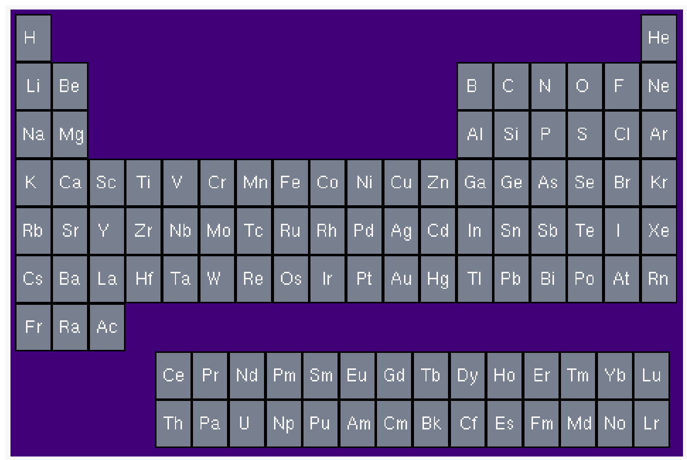
Structure of Spent Nuclear Fuel (SNF)

Mix of grains, grain boundaries, fission gas, and “gap” regions



Images courtesy
Hanchung Tsai,
Argonne National Lab

$$SNF = UO_2 \ (\sim 98\%) + \sim 2\%$$



Radionuclides in Fuel Alteration Phases

- **Uranium oxide fuel 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.**
  - **What happens to the neptunium, plutonium, technetium as spent nuclear fuel corrodes?**
    - **Can laboratory measurements predict behavior over geologic scales of time and distance?**

Alteration Phase Paragenesis

Time →

	Vapor	Low	High
Na, Ca uranyl silicates		(X)	**X**
Soddyite (U-rich silicate)		**X**	(X)
Uranyl oxy-hydroxides	**X**	**X**	(X)

Water infiltration rate →

Argonne Unsaturated Tests of Spent Nuclear Fuel produced mineral replacement mirroring observations in natural uranium deposits

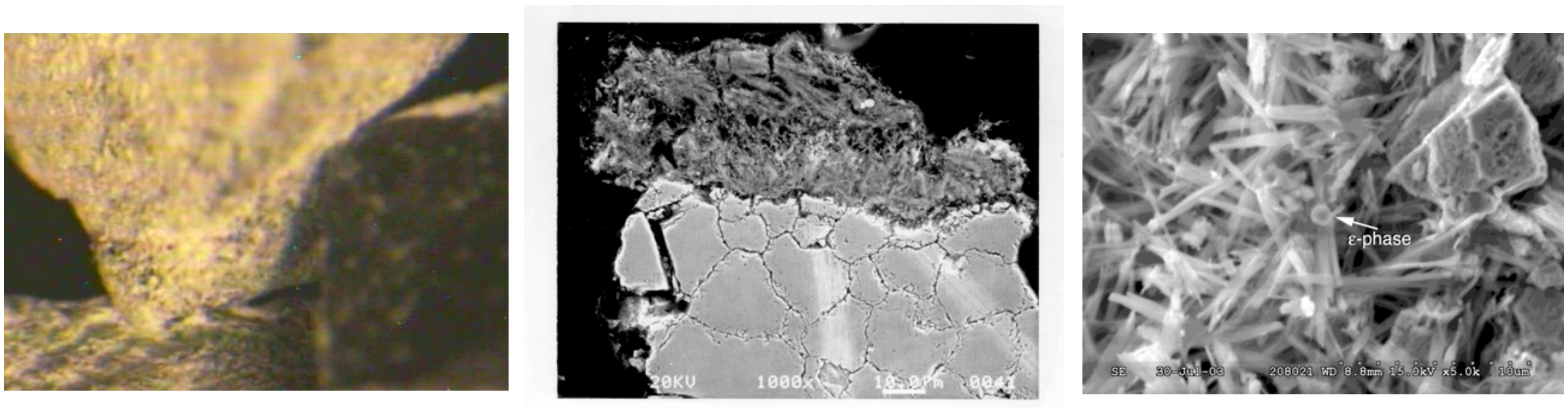
After Finch *et al.*, 1999

Np Sequestration:Background

- **Burns *et al.* (1997) noted similar crystal chemistry of neptunyl [Np(V)O_2^{+}] and uranyl [U(VI)O_2^{+2}] ions and hypothesized Np sequestration into U minerals.**
- **Burns *et al.* (2004) demonstrated Np incorporation into *Na-compreignacite* ($Na_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$) and *uranophane* ($Ca(UO_2)_2(SiO_3OH)_2(H_2O)_5$) - but *not meta-schoepite* ($UO_3 \cdot 2H_2O$) or β-$(UO_2)(OH)_2$.**
- **Buck *et al.* (2004) demonstrated Np incorporation for *studtite* $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$ and *uranophane*.**
- **Douglas *et al.* (2005) added Np to *Na-boltwoodite* $(Na(UO_2)(SiO_3OH) \cdot 1.5(H_2O)_5)$.**
- **Finch and Kropf (2004) documented Np substitution into α-U_3O_8 up to $Np_{0.33}U_{2.67}O_8$.**
  - ***Role of charge balancing***

Other evidence for Np in alteration phases

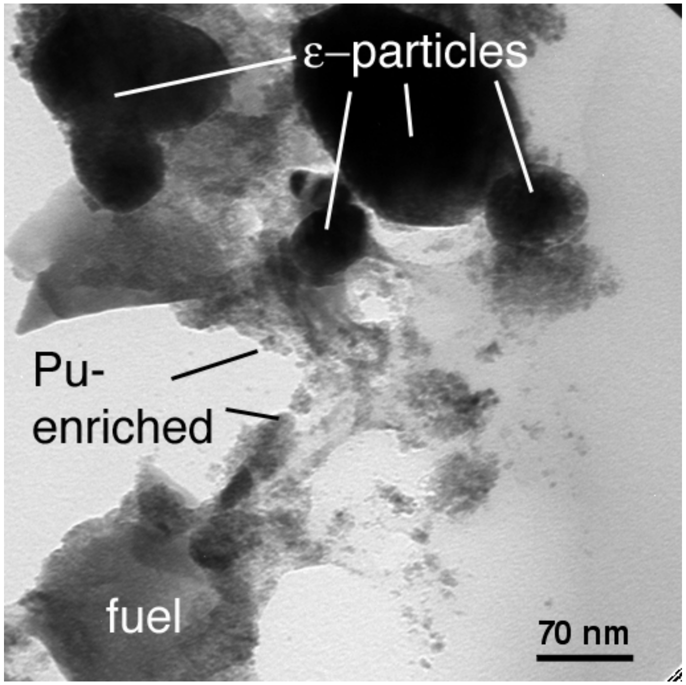
- **Argonne unsaturated tests on oxide spent fuel released Np ~ congruently with U (which formed copious alteration phases)**

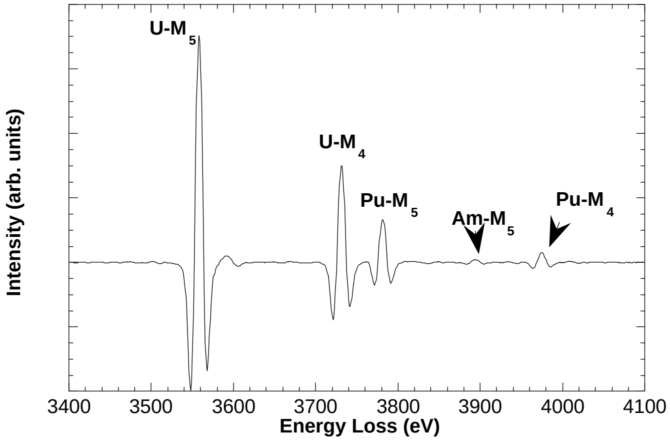


Light and electron micrographs of corroded SNF

Pu enrichment in rind on corroded SNF

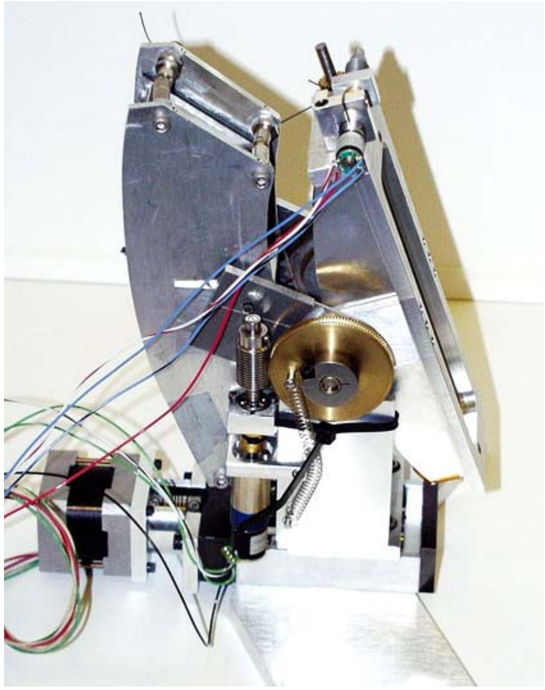
- **Less-soluble Pu, Am, lanthanides, Zr, etc. retained in rind on fuel surface**
- **Described in detail by Buck *et al*., 2004**
- **Note surviving 5-metal ε-particles**





Trace element x-ray fluorescence spectroscopy at the Advanced Photon Source

The Bent Laue X-ray Energy Analyzer



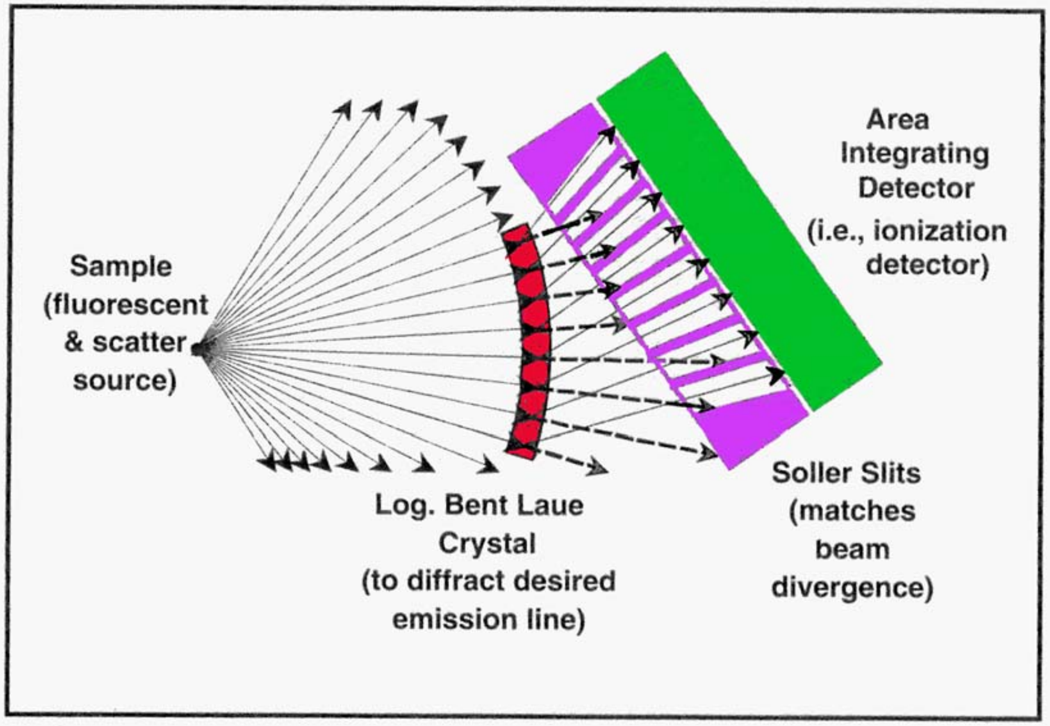
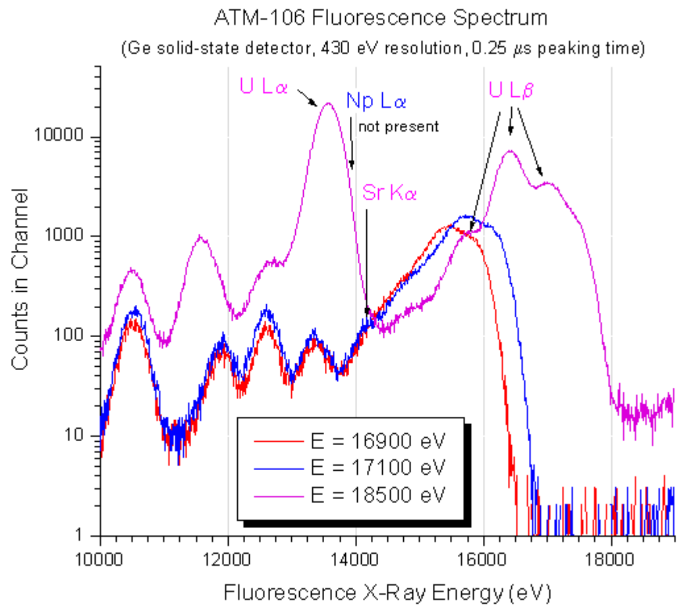
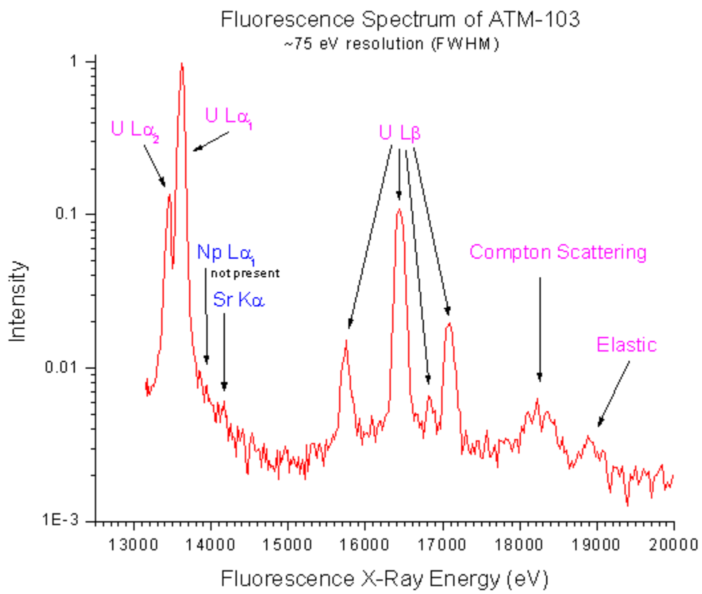


FIG. 1. A sketch of the "logarithmic bent Laue analyzer" concept.

Karanfil, L. D. Chapman, G. B. Bunker, Z. Zhong, R. Fischetti, C. U. Segre, and B. A. Bunker, 2001

Altered CSNF:
Bent Laue Analyzer XRF





Fluorescence spectra from a fuel uranyl alteration phase using a conventional solid-state detector.

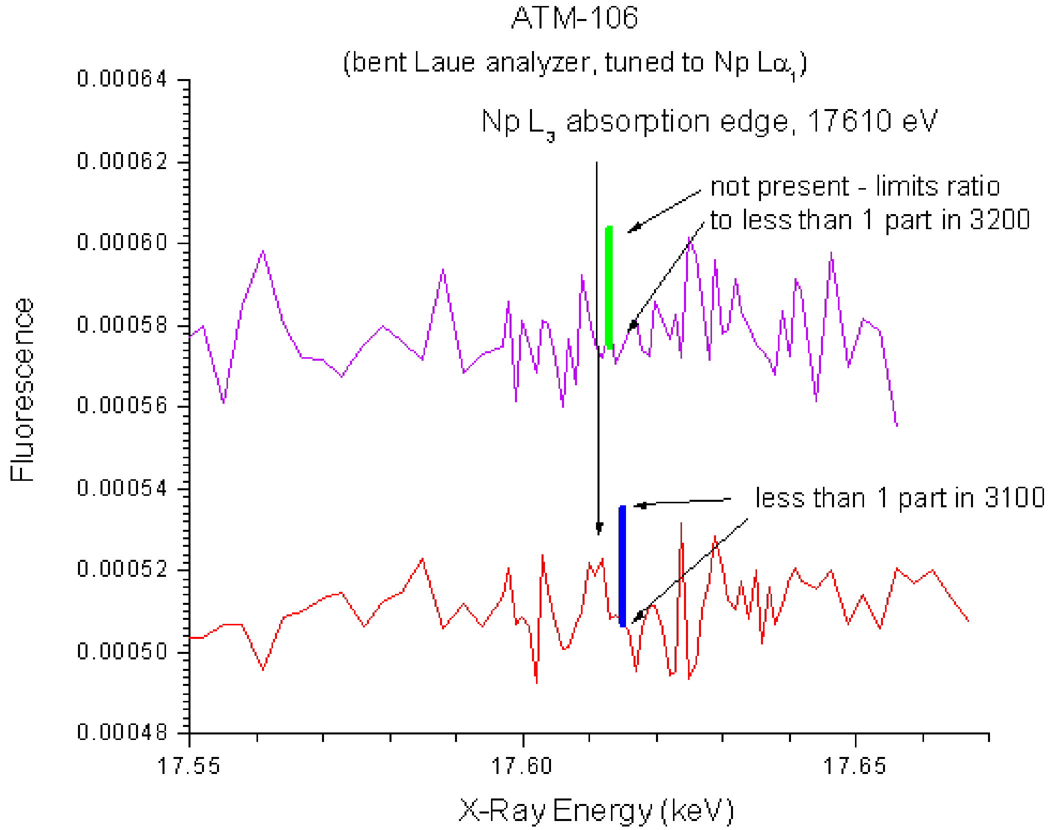
Note the large background at the Np fluorescence energy (13.945 keV) owing to the presence of copious uranium.

Fluorescence spectrum from a fuel uranyl alteration phase using the bent Laue analyzer.

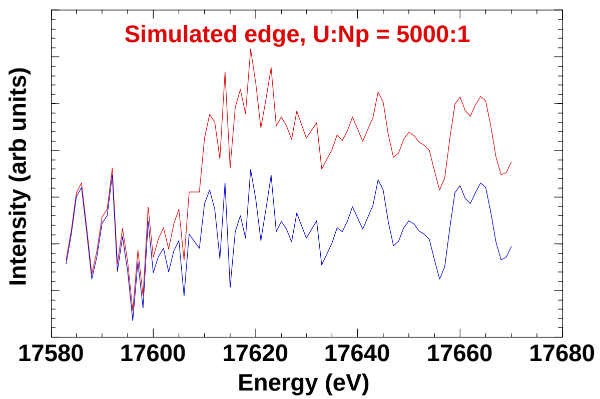
Note the greatly improved resolution and background rejection at the Np-L_3 energy.

Upper limits on Np into Schoepite

Vapor-reacted fuel alteration phases

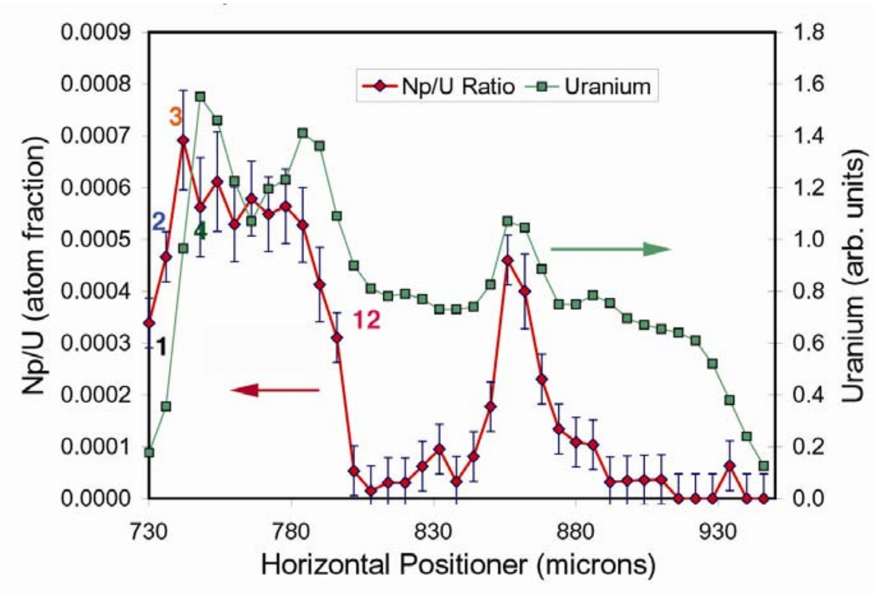


- Peak-to-peak error bars represent 1 part neptunium in 3000 parts uranium.
- Detailed analyses indicate that neptunium is present at less than 1 part in 5000.



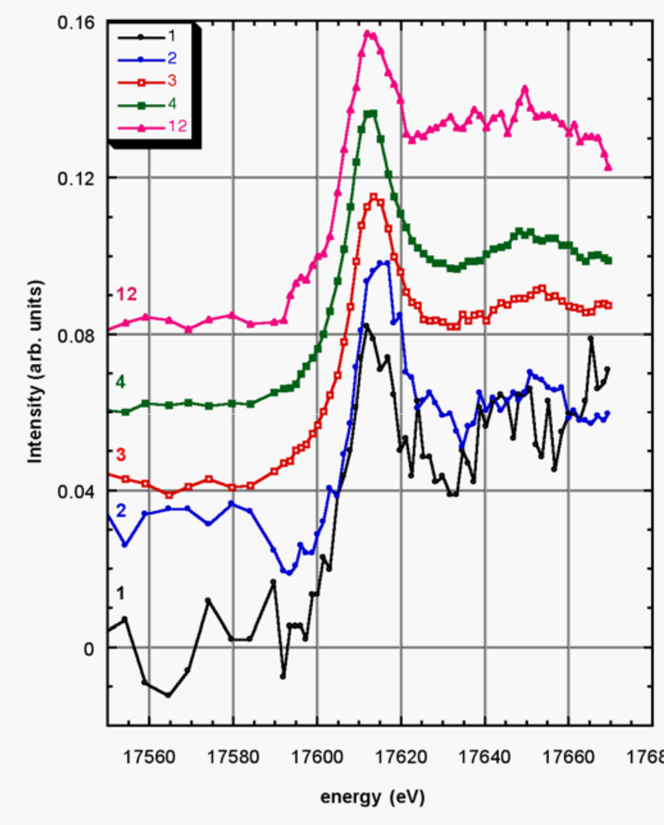
Np in corroded CSNFwith alteration products

Np/U fluorescence line scans



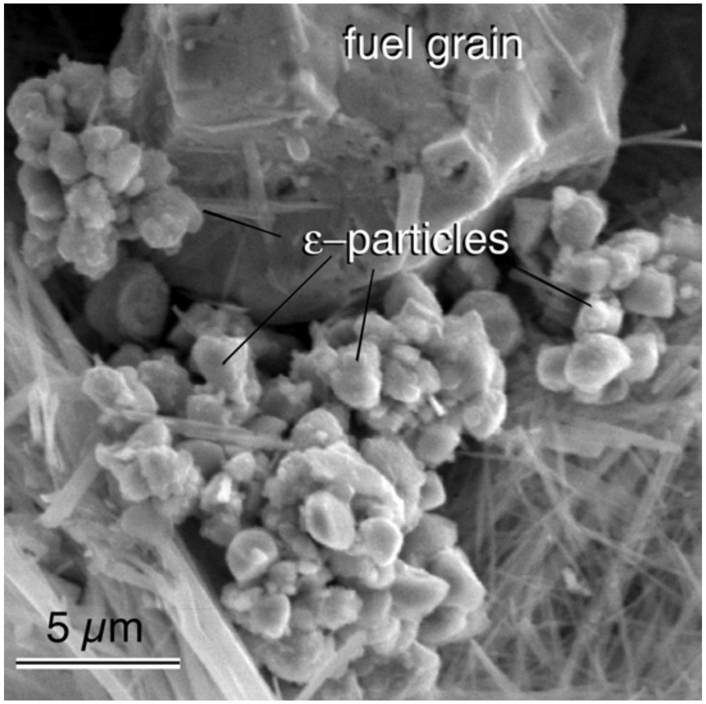
(sodium/silicate) groundwater-reacted fuel with alteration phases. Still, very little (*but not zero*!) Np in altered region

Np XANES



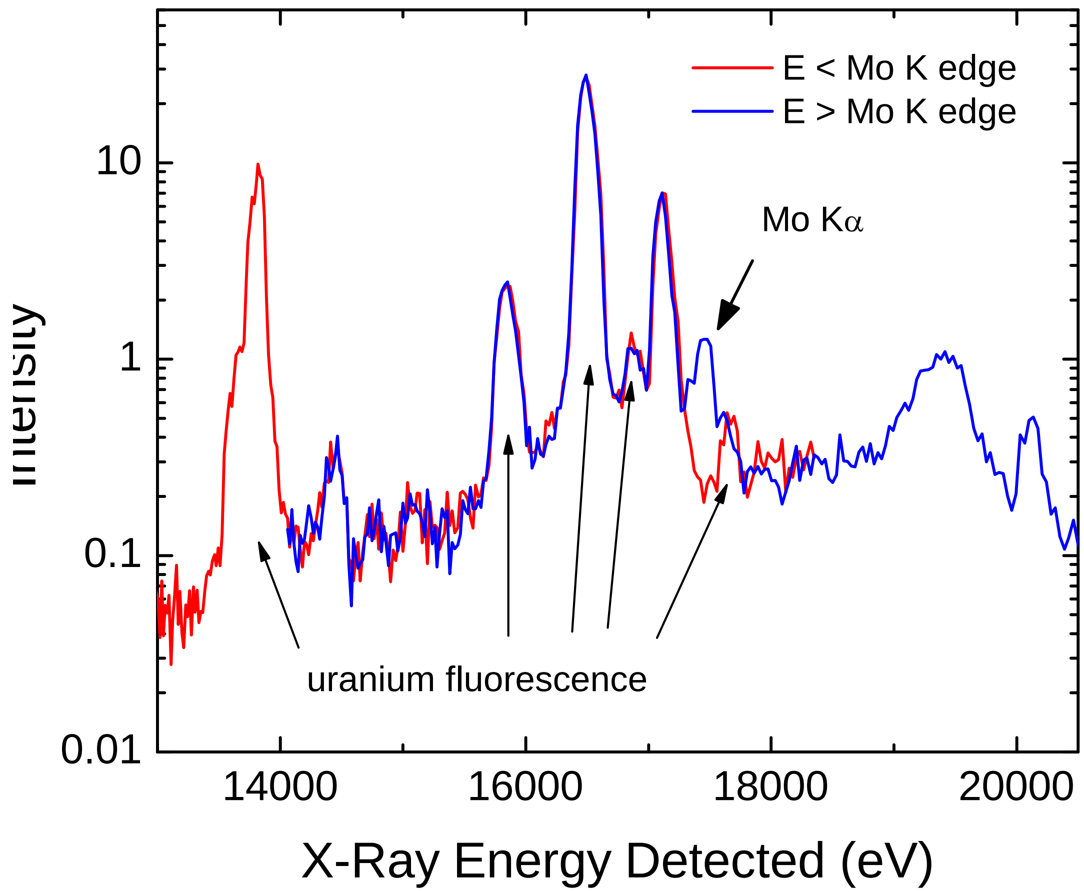
Are ε-phase particles corroding?

Tc-bearing metal alloy particles

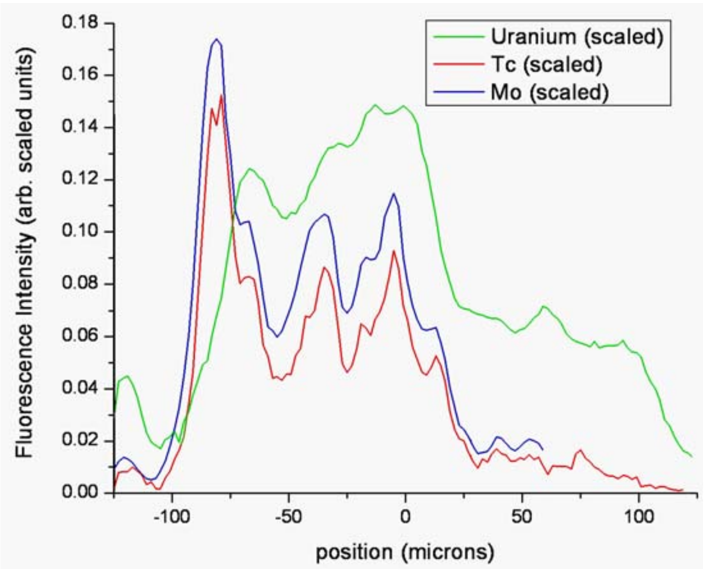


Scanning electron micrograph showing Mo- and Tc-rich ε-particles concentrated on the surface of a corroded UO_2 fuel grain, with acicular uranium (VI) silicates nearby. The ε-particles have persisted 9 years of exposure to dripping groundwater, 90°C, 100% RH

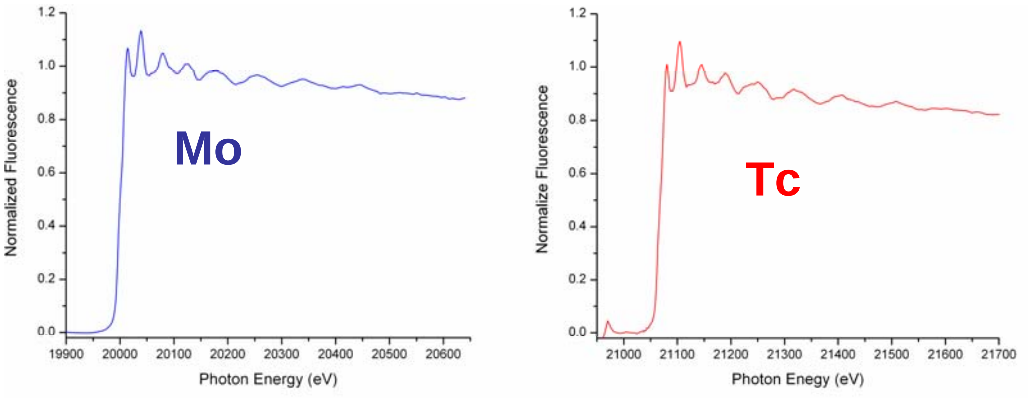
Mo fluorescence



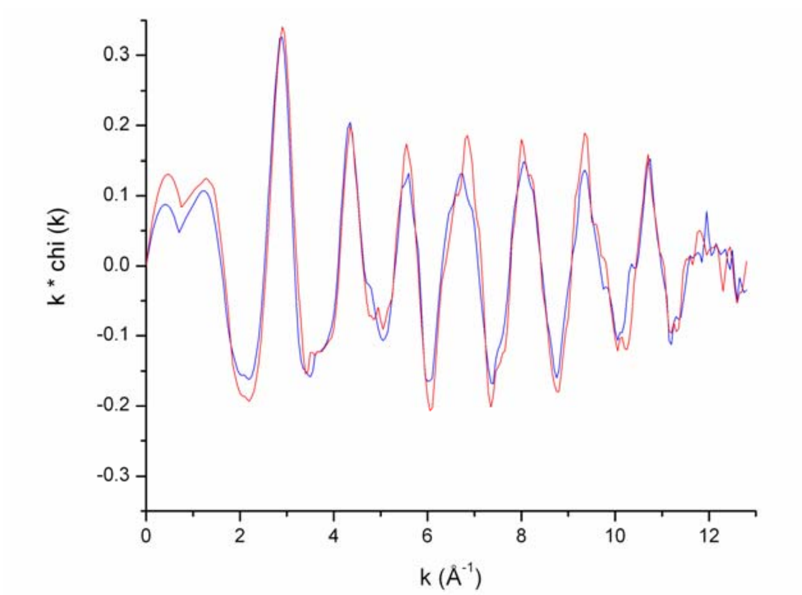
- CSNF with energy above and below the Mo Kedge
- Five U Lβ lines visible
- Mo Kα fortuitously between uranium lines

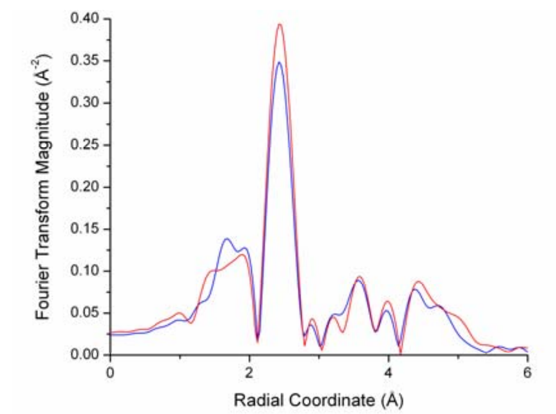


Mo and Tc EXAFS



Spectra from a concentrated region show metallic alloy persisting despite corrosion of CSNF.





Fine structure analysis : Mo and Tc

Observations

- **Np will likely be incorporated into uranyl alteration phases- *however*, Np(IV) in fuel may be stable at the CSNF corrosion potential.**
  - **Delayed onset of U/Np phase formation.**
  - **NpO_2 may be an estimator of dissolved concentration.**
- **Tc in metallic phases may likewise be slow to oxidize while fuel is intact.**
- **Pu and other sparingly soluble elements likely to form distinct phases.**

Acknowledgements

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