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CORRODED SPENT NUCLEAR FUEL EXAMINED WITH EELS

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DISCLAIMER

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Direct disposal of spent nuclear fuel (SNF) into the proposed unsaturated geologic repository at Yucca Mountain, NV is being studied at several laboratories, including Argonne National Laboratory [1]. Corrosion tests with SNF are being conducted to understand the long-term behavior of SNF under conditions designed to simulate the unsaturated conditions at the site. The SNF used in this study was the Approved Testing Material (ATM)-106 with a burn-up of 43 MW•d/kg U [2]. A sample of ATM-106 fuel was exposed to dripping simulated groundwater for 271 days; after this time the experiment was terminated and the material removed for further study. Details of the testing methodology have been given by Finn et al. [1].

Previous attempts to study SNF with TEM have used ion milled samples [3], in this study we prepared the samples by ultramicrotomy which reduced the radiological hazard substantially. Particles of the reacted SNF were carefully removed from the surface with the aid of an optical microscope and diamond scribe and then embedded in a Medcast epoxy block. The selection of suitably sized particles (<5 μm in diameter) and correct orientation was critical to producing usable ultramicrotomed thin sections of SNF for TEM (see Fig. 1a). We have successfully produced TEM thin sections which can be used for detailed EELS. Analyses were performed on a JEOL 2000FXII/ Gatan 666 PEELS with a LaB_6 filament. The energy resolution was 1.6-1.8 eV.

Figure 1b shows the reacted fuel and an attached alteration phase. The objective of the TEM investigations has been to determine the nature of SNF corrosion through the identification of alteration phases and determination of the distribution of neutron capture and fission products. The alteration phase was identified by electron diffraction, x-ray energy dispersive spectroscopy, and EELS as a layered cesium molybdenum uranyl oxide hydrate, structurally related to phases of the becquerelite group uranium minerals. These uranyl oxide hydrate alteration phases will control the solubility of uranium and, hence, determine the long-term durability of the solid SNF waste form.

The large number of elements in SNF can make TEM/EDS analysis a challenge. As well as removing channel-to-channel gain variation in parallel detectors, the second-difference EELS technique serves as a frequency filter that selectively enhances the high frequency features, such as the $M_{4,5}$ absorption edges ("white lines") of rare earth elements (REE) and transuranics (TRU). In Figure 2, second-difference EELS of REE within the corroded particle of SNF is shown. The technique allows detection of REE that are present at < 20 ppm. In Figure 2a, the TRU M_4 and M_5 edges, which correspond to $3d_{3/2} \rightarrow 5f_{5/2}$ and $3d_{5/2} \rightarrow 5f_{7/2}$ transitions, respectively, have been used to detect low levels of TRU in the SNF. Overlap of TRU $N_{4,5}$ edges with the more intense REE $M_{4,5}$ edges effectively excludes this lower energy region from being used. An extremely high intensity, coupled with relatively long integration times (5-20 s) and repetitive runs, can allow detection of individual TRU elements, Np, Pu, and Am (see Fig. 2b). The calculated concentrations of TRU elements in ATM-106 SNF are 2590 ppm Pu and 115 ppm Am [2].

With ultramicrotomed TEM samples, we have been able to study a very hazardous material. The sections prepared were of such quality that highly detailed EELS analysis was possible allowing for the detection of low levels of transuranics in the reacted fuel. This work will assist in gaining an improved understanding of the corrosion mechanism of spent fuel in an aqueous environment [4].

References

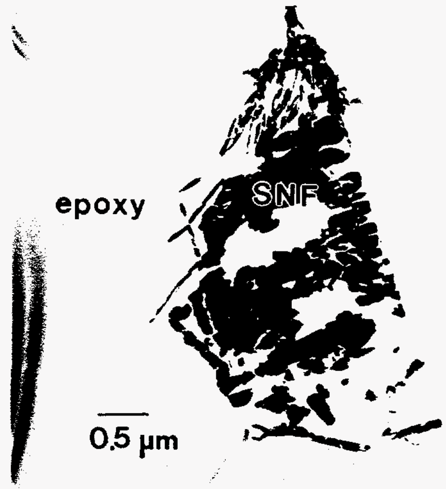
[1] P. A. Finn et al., *Radiochimica Acta*, 66/67 (1994) 189

[2] R. J. Guenther et al., Characterization of Spent Fuel Approved Testing Material-ATM-106, *Pacific Northwest Laboratory Report*, PNL-5109-106 (1988)

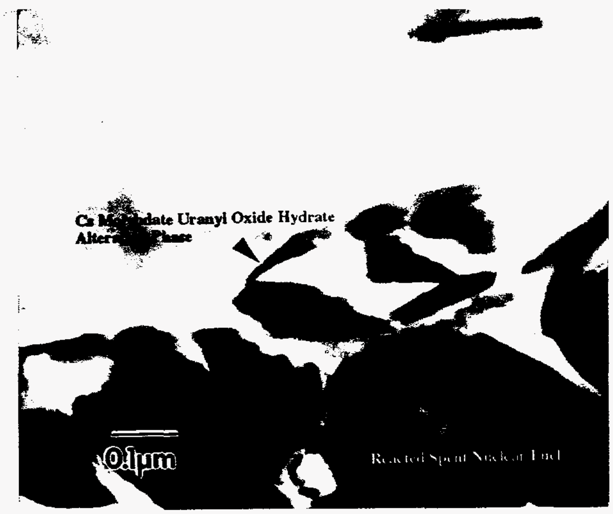
[3] L. E. Thomas et al., *J. Nucl. Mater.*, 166 (1989) 243

[4] Spent fuel tests performed by P. A. Finn, D. J. Wronkiewicz, J. W. Emery, and J. C. Hoh. Work supported by the U.S. Department of Energy under contract W-31-109-ENG-38.

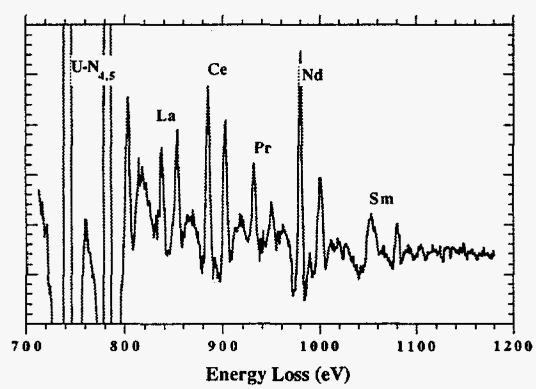
1a



1b



2a



2b

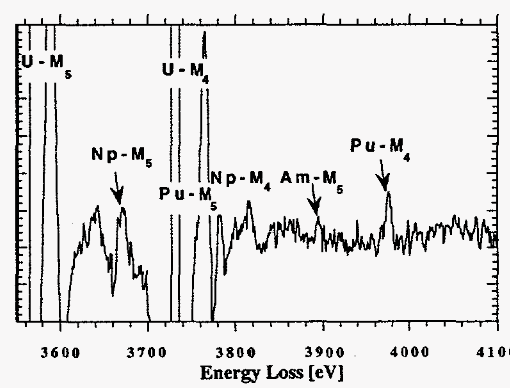


Fig. 1 (**a**) Low Magnification Image of Thin Sectioned SNF and (**b**) Image of Reacted SNF and attached Cs Mo Uranyl Oxide Alteration Phase.

Fig. 2 Second-Difference EELS of SNF Showing REE $M_{4,5}$ edges of La, Ce, Pr, Nd, and Sm. The major component of SNF, uranium, is visible in the two energy loss ranges analyzed. In (**a**) $N_{4,5}$ edges of U at 738 eV and 780 eV along with a number of REE and in (**b**) $M_{4,5}$ edges of U at M_5 = 3552 eV, M_4 = 3728 eV, along with the TRU elements, Np (M_5 = 3666 eV and M_4 = 3850 eV, Pu (M_5 = 3778 eV, M_4 = 3973 eV), and Am (M_5 = 3887 eV, M_4 = 4092 eV).