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RETENTION OF NEPTUNIUM IN URANYL ALTERATION PHASES FORMED DURING SPENT FUEL CORROSION

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ABSTRACT

Uranyl oxide hydrate phases are known to form during contact of oxide spent nuclear fuel with water under oxidizing conditions; however, less is known about the fate of fission and neutron capture products during this alteration. We describe, for the first time, evidence that neptunium can become incorporated into the uranyl secondary phase, dehydrated schoepite ($UO_3 \cdot 0.8H_2O$). Based on the long-term durability of natural schoepite, the retention of neptunium in this alteration phase may be significant during spent fuel corrosion in an unsaturated geologic repository.

INTRODUCTION

Owing to its long half-life and alpha activity, Np^{237} is considered to be one of the most important radionuclides to be immobilized in a geologic repository [1]. As both carbonate and hydroxide strongly complex Np ions in solution, it has been presumed that these forms of Np will most likely control the release of Np from a geologic repository [2]. We report evidence that Np may become incorporated into dehydrated schoepite during the corrosion of spent nuclear oxide fuel under some repository-relevant conditions.

Uranium dioxide readily alters to a series of uranyl oxide hydrates and uranyl silicates when exposed to oxidizing conditions in silica-bearing solutions [3]. However, under conditions expected at the proposed geologic repository at Yucca Mountain in Nevada, spent fuel is anticipated to be contacted only with water vapor and/or small amounts of dripping water. As the fuel is exposed to water vapor, a surface corrosion rind may form, consisting of uranyl oxide hydrates and depending on the species present in the groundwater, in the presence of dripping water, uranyl -silicates, -carbonates, and -phosphate may also eventually form [3,4]. A similar paragenesis has been observed at many weathered natural uraninite (UO_2) deposits, such as at Shinkolobwe in the Congo and Peña Blanca in Mexico [4,5].

The behavior of the fission and neutron capture products, during the anticipated corrosion of spent nuclear fuel in an oxidizing environment is important for determining the long-term release rates of radionuclides. Using a unique anion topology approach for comparing the structures of uranyl phases, Burns et al. [6] have predicted mechanisms by which transuranic species could be incorporated into the alteration products of corroded spent fuel. As the U-O bond length (0.18 nm) in the linear species UO_2^{2+} is similar to that of Np-O in NpO_2^+ (0.165-0.181 nm) and when coordinated by O^{2-}, OH^-, or H_2O, the equatorial Np-O bond distances are only about 0.01 nm longer than those found in similarly coordinated uranyl polyhedra, it is reasonable to expect isomorphic substitution of the neptonyl ion in uranyl ion sites [6]. However, owing to valence bonding considerations, the axial oxygens on the linear neptonyl species may require additional valence contributions from interlayer cations or protons in the uranyl phase.

EXPERIMENTAL PROCEDURE

Two types of unsaturated tests are discussed in this paper. The first involves exposing Approved Testing Material (ATM) 103 [7] to water vapor held at 90°C. The ATM103 is a single pin spent nuclear fuel of moderate burn-up (33 MWd/kgM) from the Calvert Cliffs pressurized water reactor, which exhibits low fission gas release (0.25%). Under these conditions the fuel pellets were exposed to a thin film of water. In the other type of tests, termed "high-drip", about 0.75 mL of EJ-13 water is dripped onto the ATM103 fuel package every 3.5 days [8]. The EJ-13 water is a tuff rock-equilibrated groundwater from the J-13 bore-hole near Yucca Mountain. Air is also injected into the test vessel with the water. The waste package design consists of fuel pellets placed on a Zircaloy retainer which has holes to allow the passage of water into a steel collection vessel which is positioned below. The high-drip tests have been in continuous operation for nearly 5 years. Periodically, the collection vessel is removed, and the liquid solution contents analyzed. Another clean collection vessel is then attached to the experimental setup, and the test is continued. The solid samples were taken from the fuel pellets on the Zircaloy retainer. The corrosion products that developed on these spent fuel fragments were examined with optical and scanning electron microscopy (SEM).

Representative particles of the corroded fuel were embedded in an epoxy resin, and thin-sectioned with an ultramicrotome. The resultant 30-50 nm electron-transparent cross-sections of corroded fuel grains were transferred to carbon-coated copper grids and examined in a JEOL 2000 FXII analytical transmission electron microscope (AEM) operated at 200 kV with a LaB$_6$ filament. The AEM is equipped with a Gatan 666 parallel electron energy-loss spectrometer, which has an energy resolution of about 1.6-1.8 eV. The actinide M-edges were obtained by operating the spectrometer in the second-difference mode [9]. This technique removes the channel-to-channel gain variation that occurs with parallel detectors. The method also acts as a frequency filter, enhancing the sharp features such as the "white-lines" on the absorption edges. Hence, peak shape will effect the ability to detect an element. A smooth edge, for instance, will be less visible than a sharp edge. Electron diffraction patterns were taken with a charged coupled device (CCD) camera which permits very low intensity viewing and, therefore, is ideal for electron beam-sensitive materials.

RESULTS

In this section, the results from the analysis of the solid uranium-bearing phases from both the vapor and high-drip rate tests are presented. Before discussing these data, the technique of energy-loss spectroscopy (EELS) and how it pertains to the detection of transuranics will be addressed. In EELS the shape and intensity of an elemental absorption edge depends on that its electron cross-section and chemical state. Hence, the technique can be used to determine the local chemical environment. Compared to X-ray absorption spectroscopy, EELS utilizes much lower energy absorption edges. Edges in the range from 50 eV up to 1900 eV are most commonly investigated; however, in this work, the edges obtained were at an exceptionally high energy-loss range (3500-4500 eV) for a transmission electron microscope. Longer counting times (or integration times) were required, typically 2-5 s, at each energy offset, higher beam intensities, and a large number of continuous acquisitions (typically 20-50). For the second-derivative technique, the derivative is calculated from three spectra taken at slightly different energy offsets (1-6 eV), and then the derivative of these three spectra is calculated. This resulted in a total analysis time of 120-750 s. These conditions necessarily cause immediate amorphization of the uranyl phases but, we believe, not vaporization. Energy-loss analysis with AEM, of course, has much better spatial resolution than x-ray spectroscopic methods.

Low Level Detection of Transuranics

For the detection of fission products and transuranic elements present in spent fuel and its alteration products, EELS has proven to be extremely effective. In Fig. 1, EELS from an uncorroded sample of spent fuel are shown. The major component, uranium, is visible in the two energy-loss ranges presented. In the lower energy range (Fig. 1a), the uranium N$_{4,5}$ edges at 738 eV and 780 eV, along with a number of rare earths, are visible. The transuranic N-edges overlap strongly with the rare earths, and as they are weak features in this energy range, they can not be detected. However, in the high energy-loss range (Fig. 1b), the transuranic M-edges are clearly visible. The sharp absorption edge features in Fig. 1b, correspond to the two electronic transitions, $3d_{3/2} \rightarrow 5f_{5/2}$ (M$_5$) and $3d_{5/2} \rightarrow 5f_{7/2}$ (M$_4$), of the transuranics, that arise from spin-orbit splitting. Owing to the interference with the large number of other elements present in the fuel and in its corrosion products, this high energy-loss range is the only region where the transuranics can be detected with confidence [10]. The higher energy transuranic L- and K- edges are beyond the capabilities of the system.

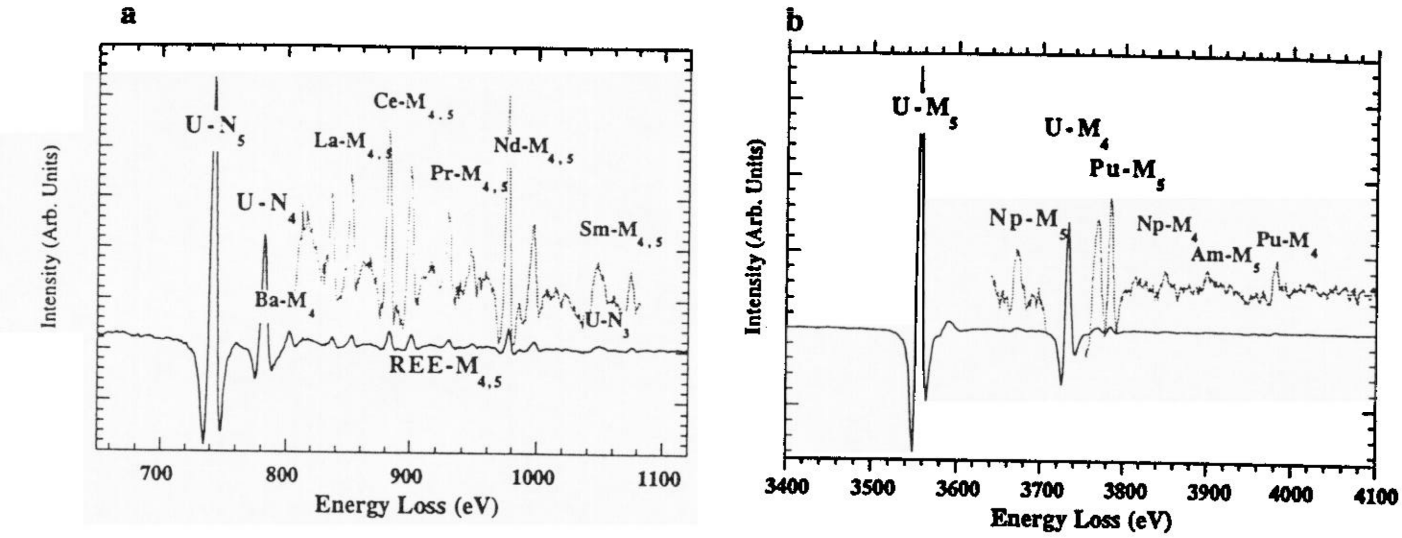

Fig. 1 Second-difference EELS of uncorroded spent fuel. In (a) the rare earth element $M_{4,5}$ edges of La, Ce, Pr, Nd, and Sm are visible. The scale has been expanded 10x so that the rare earths are more clearly visible. In (b) the U-$M_{4,5}$ edges at 3552 eV (M_5) and 3728 eV (M_4), as well as the transuranic 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) have been detected. The scale has been expanded 20x so that the transuranic edges can be seen.

Characterization of Alteration Products from Vapor Phase Tests

Examination of the corroded fuel with SEM demonstrated the presence of characteristic "boat-shaped" crystals of dehydrated schoepite [$(UO_3) \cdot 0.8H_2O$] (see Fig. 2a). The presence of dehydrated schoepite was confirmed with electron diffraction in the AEM. In Fig 2b, a single-crystal pattern of this alteration phase, and Table 1 lists the diffraction spacings obtained from a series of polycrystalline patterns, which support the phase identification.

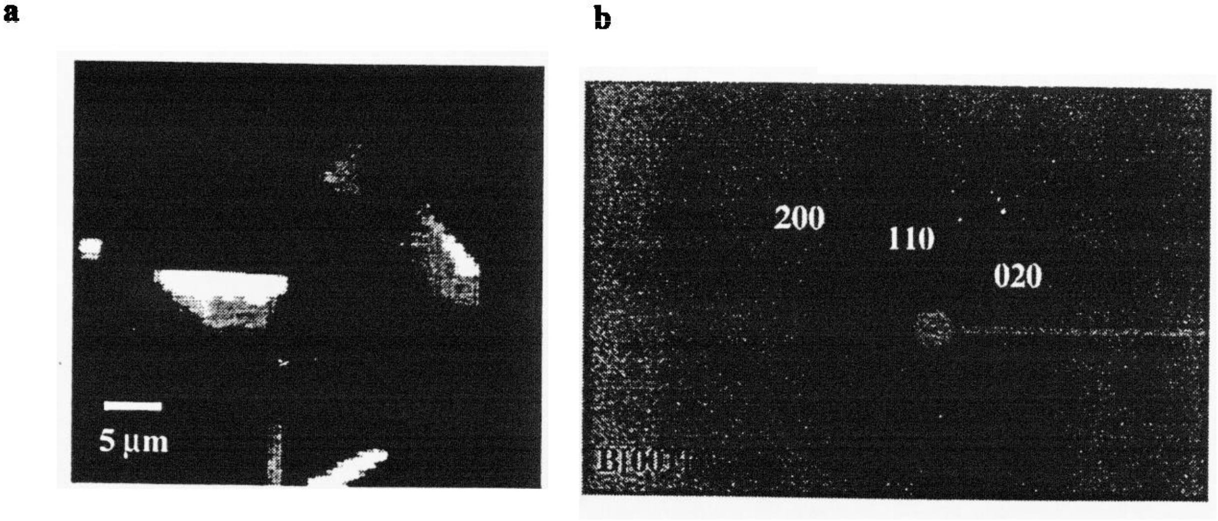

Fig. 2a. The SEM image of the uranyl phase shows the characteristic shaped crystals indicative of dehydrated schoepite. (b) The computer simulations of dehydrated schoepite agreed with the experimentally obtained CCD electron diffraction pattern from the uranyl oxide phase shown above.

Table 1. Measured electron diffraction parameters from the major spent fuel alteration phase in vapor-reacted sample compared to literature x-ray diffraction values of dehydrated schoepite.

d_{obs} (nm)[1] Spent Fuel Alteration Phase	d_{lit} (nm) (*hkl*) Dehydrated Schoepite[2]
0.7023[3]	
0.5316, 0.5206, 0.5242	0.511 (200)
0.3631	
0.3528, 0.3511, 0.3462	0.345 (111), 0.343 (020)
0.2978	
0.2908	0.286 (220)
0.2697	
0.2630	
0.2612	
0.2567, 0.2532	0.249 (311)
	0.214 (002)
0.2189	
0.2045	0.205 (420)
0.1861, 0.1856	0.182 (022)
0.1692	0.171 (222)
0.1471	0.148 (422)

[1] Values are an average of several d-spacings from a number of diffraction patterns. Errors in d-spacings are ±2.5%.

[2] Unit cell parameters are a = 0.686 nm, b = 0.426 nm, and c = 1.020 nm [11].

[3] Reflection only seen in a few patterns. It was lost rapidly during observation.

The only other alteration phase found on the vapor-reacted sample was a Cs-Mo uranyl oxide hydrate. The composition of this phase matched with that previously reported in high-drip tests with ATM106 spent fuel after 0.8 years of reaction, where the ideal composition of this phase was estimated to be $(Cs_{0.90}Ba_{0.55})(UO_2)_5(MoO_2)O_4(OH)_6 \cdot 6H_2O$ [12]. These Cs-Mo uranyl particles were 100-200 nm in length, but no structural information was obtained from them (see Fig. 3).

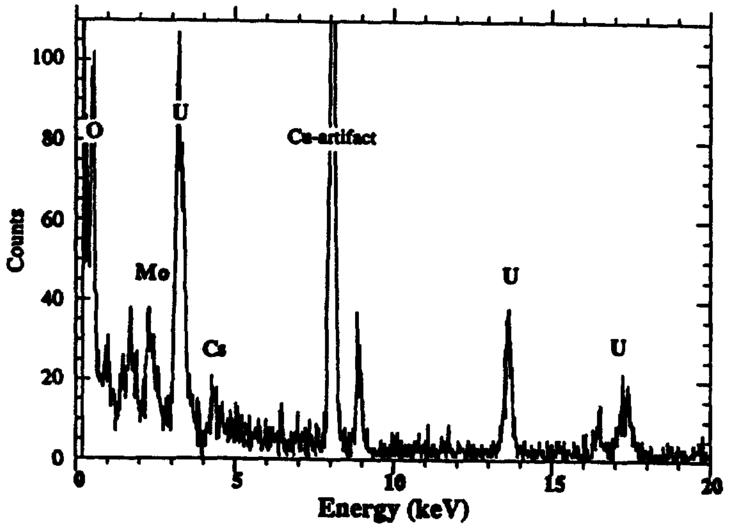

Fig. 3 X-ray energy dispersive spectrum of a Cs-Mo uranyl oxide hydrate. Both the dehydrated schoepite and this Cs-bearing phase were observed on the reacted fuel surfaces.

Energy-Loss Analysis of Dehydrated Schoepite from Vapor Phase Tests

Analysis of the dehydrated schoepite phase with EELS indicated the presence of Np (Fig. 4). Since we examined cross-sections of the corroded fuel grains and alteration products, it is unlikely that the occurrence of Np was due to sorption on the dehydrated schoepite; however, we cannot exclude this mechanism for retention of Np in an alteration phase. Neptunium was observed with EELS in three samples of dehydrated schoepite which were taken from different regions of the corroded fuel pellets.

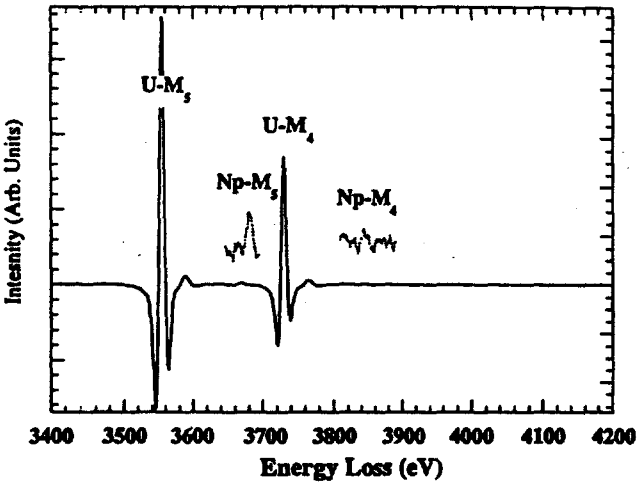

Fig. 4. Electron energy-loss spectrum of dehydrated schoepite showing the presence of Np in the phase. The two intense uranium edges (M$_5$ at 3552 eV and U-M$_4$ at 3728 eV) dominate the spectrum; however, the Np-M$_5$ edge at 3666 eV is clearly visible. The intensity of the Np edges has been increased 20x for easier viewing. The Np-M$_4$ edge at 3850 eV does not appear to be visible above the background.

The U:Np ratio was estimated to be between 1:0.003 and 1:0.006, based on five analyses. In the dehydrated schoepite ($UO_3{\bullet}0.8H_2O$) where Np was detected, this ratio corresponds to one Np atom for every 250 unit cells of $UO_3{\bullet}0.8H_2O$ or about 550 ppm. The U:Np ratio in the ATM103 fuel is 1:0.0005, taken from calculated values reported by Guenther et al. [7] for ATM 103 at 35 MWd/kgM after 15 years. The estimated U:Np ratio in the alteration phase indicates that a large proportion of the Np has entered into the phase. Owing to the scarcity of water under the testing conditions, little, if any, water was able to flow into the steel collection vessel positioned at the bottom of the test apparatus. Under these conditions, it might be expected that the highly soluble elements will become concentrated enough in the thin-film of water to precipitate secondary phases. The absence of Pu and Am in the dehydrated schoepite supports the contention that only Np and U were mobilized during the corrosion process and incorporated into a secondary phase.

Under more dynamic conditions, where flowing water was present, the retention of the Np in alteration phases may not occur. The next section presents similar EELS analysis of uranium-bearing alteration phases formed under relatively high flow conditions.

Electron Energy-Loss Analysis of Uranium Silicate Alteration Phases from High Drip Tests

In the related high-drip tests, the analysis of the corrosion products failed to indicate the presence of Np at the same level observed in the vapor tests. In Fig. 5, the EDS and electron diffraction analysis suggested that this corrosion product was related to β-uranophane (ideally $Ca[(UO_2)(SiO_3OH)]_2{\bullet}5H_2O$). A trace amount of ruthenium was present in the phase and this can also be seen in the energy-loss spectrum (see Fig. 5c). The form of the uranyl alteration phases is dependent on the composition of the fluid in contact with the fuel. In the high-drip tests, the fuel is contacted by silica-saturated EJ-13; hence, uranyl silicates are the dominant alteration products.

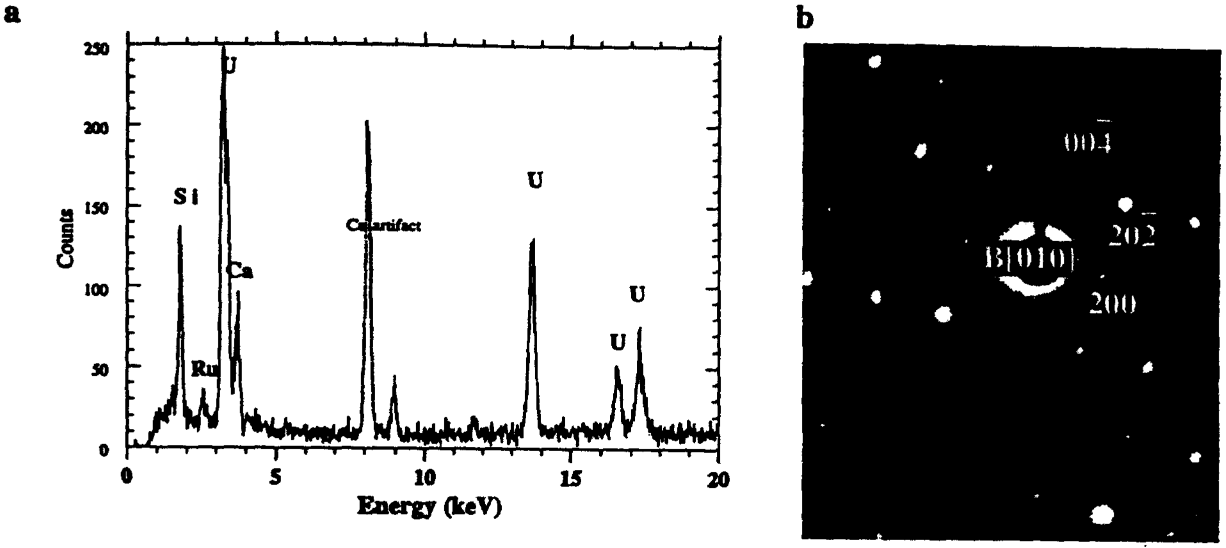

Fig. 5 (a) X-ray energy-dispersive spectrum of an alteration phase from a high drip rate test reacted for 44 months. In (b) an electron diffraction pattern taken along [010] from the uranyl silicate phase is shown. A β-angle of about 93° was obtained from the analysis of the patterns.

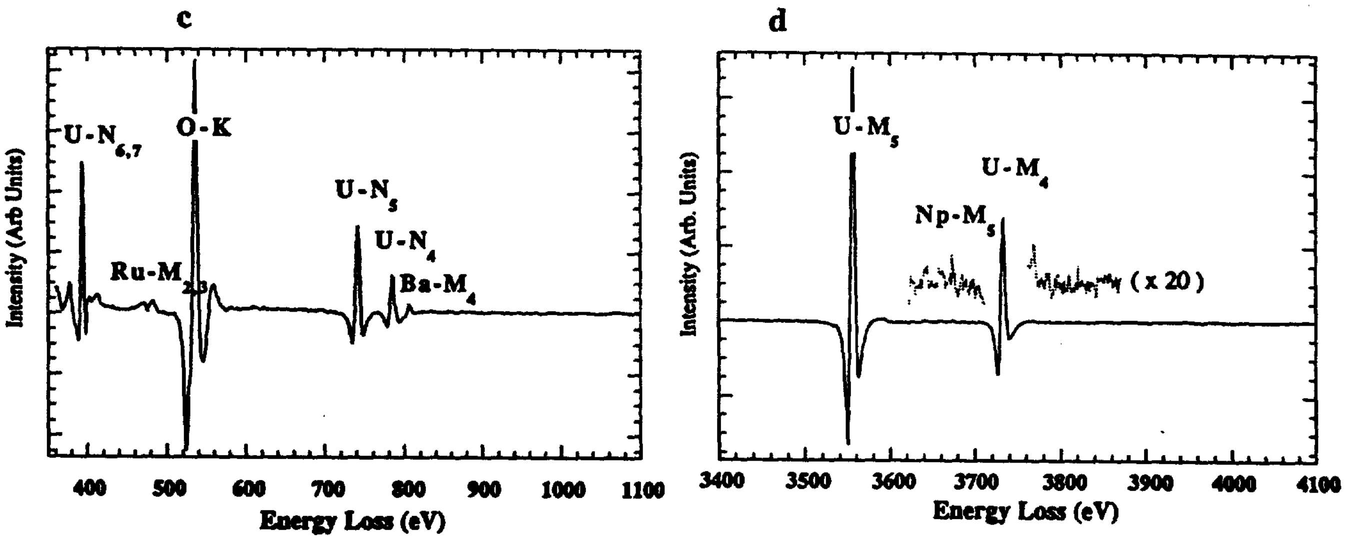

Fig. 5 (c) Electron energy-loss spectrum of uranyl silicate alteration phase from the high-drip test, showing the U-N edges and (d) spectrum showing the high energy-loss M-edges of uranium.

There may be a suggestion of some Np in uranyl silicate phase; however the levels are at, or below, the detection limits for the instrument. The estimated U:Np ratio is not more than 1:0.0005, which corresponds to <50 ppm Np in the phase, which appears to be the detection limit.

DISCUSSION

Substitutions of the type Np^{5+} <-> U^{6+} may occur in all uranyl structures [6]; however, evidence from the majority of solution analyses from waste form testing suggests that Np remains stable as complexes in solution under most common pH-Eh regimes. Nevertheless, within the thin-film of water in contact with the spent nuclear fuel, significant alpha radiolysis will occur, leading to the possible formation of H_2O_2. The altered Eh conditions may result in changes in the Np chemistry which may favor incorporation into the uranyl sheets. These sheets may be easily charge balanced through substitutions of the type O^{2-} <-> OH^-. The most common oxidation state for Np in oxygen-rich waters is Np(V). In the vapor tests, because the pH of the contacting solution is unknown, it may be speculative to describe the form of the Np. However, calculations suggest that in a J-13 Yucca Mountain groundwater above pH 7.5, the dominant species is $NpO_2(CO_3)^-$ and NpO_2^+ below this pH [2]. The pH of the contacting solution in the high drip tests is known to be about 6 [8], suggesting that NpO_2^+ will be the most prominent species.

The incorporation of transuranics into the alteration products of oxide spent fuel corrosion has been predicted on crystal chemical considerations [6]; although, it has seldom been observed. This may be due, in part, to the limitations of instrumental techniques and the difficulty in working with transuranic-bearing samples; however, knowledge of the specific conditions required for substitution of particular radionuclides into alteration phases may lead to development of engineered systems that may retard the migration of these radionuclides.

The observation of Np incorporation into dehydrated schoepite was only possible by examining thin sections of the reacted material with EELS. This technique has excellent detection capabilities and spatial resolution to locate regions where transuranics have been concentrated. Although, the limits of detection for EELS are essentially a function of the analysis time and beam intensity; when using the second-difference method, peak shape is also important. Future improvements in detection limits should be possible with the use of an energy-loss imaging filter which, when operated as a two-dimensional array spectrometer, is much more efficient than the parallel detector used in this study.

CONCLUSIONS

We have demonstrated that the release of Np may be controlled by uranyl alteration phases formed during the corrosion of oxide spent nuclear fuel in an unsaturated environment. Although schoepite is only a transient phase in paragenesis of uraninite, Finch et al. [13] have demonstrated that the schoepite at weathered uraninite deposit at Shinkolobwe has lasted over 250,000 years. Indeed, at the same site the uranyl carbonate, rutherfordine [$UO_2(CO_3)$], exhibited exceptional persistence. This suggests that the retention of Np in dehydrated schoepite during vapor phase corrosion, may not be ephemeral. Consequently, this noteworthy observation of Np in dehydrated schoepite may provide evidence to reduce the impact of Np migration on the present performance assessment calculations for the Yucca Mountain repository.

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