



	Experiment title: Local structure and charge distribution in new and aged $U_{1-x}Am_xO_{2\pm\delta}$ fuels for transmutation	Experiment number: CH-3530
Beamline: BM20	Date of experiment: from: 18/02/13 to: 22/02/13	Date of report: 02/04/13
Shifts: 9	Local contact(s): SCHEINOST Andreas / ROSBERG Andre	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): LEBRETON F. ^{1,2*} , MARTIN P. M. ^{3*} , HORLAIT D. ^{1*} , BES R. ^{3*} , BATAILLE M. ^{1*} , DELAHAYE T. ¹ ¹ CEA, DEN, DTEC/SDTC/LEMA - 30207 Bagnols-sur-Cèze, France ² GEMH/ENSCI - 87065 Limoges, France ³ CEA, DEN, DEC/SESC/LLCC - 13108 Saint Paul Lez Durance, France		

1. Introduction

Americium is a minor actinide produced during in-pile irradiation of nuclear fuels which is responsible for a large part of radiotoxicity and heat generation in ultimate nuclear waste. To control and reduce Am inventory, partitioning and transmutation (P&T) in fast reactors was proposed. Over the past few years, P&T research has been mainly focused on transmutation in heterogeneous mode, consisting in the use of uranium-amerium mixed-oxides, i.e., $U_{1-x}Am_xO_{2\pm\delta}$, compounds destined for the periphery of the core. In this context, research is dedicated to both fabrication process development and properties of $U_{1-x}Am_xO_{2\pm\delta}$ fuels. Notably, structural study of such materials performed by XRD (X-ray diffraction) and XAS (X-ray absorption spectroscopy) showed that despite crystallizing in a standard fluorite structure, $U_{1-x}Am_xO_{2\pm\delta}$ compounds exhibit a peculiar charge distribution leading to structural modifications at local range. More precisely, for samples with Am/(U+Am) ratios between 10 and 20 at.%, Am is fully trivalent whatever Am content or oxygen potential of sintering, whereas U is partially oxidized to the pentavalent state [1-4]. In this experiment, two samples with new compositions, namely 7.5% and 50% Am, were studied by XAS.

Considering the high α -activity of ^{241}Am ($1.3 \times 10^{11} \text{ Bq.g}^{-1}$), self-irradiation effects, such as lattice expansion, phase transformation or amorphization, are expected to occur at ambient conditions. For a better understanding and description of these effects in $U_{1-x}Am_xO_{2\pm\delta}$ materials, structural studies are necessary and are currently performed notably by XRD. Considering XAS, first results were obtained for $U_{0.85}Am_{0.15}O_{2\pm\delta}$ through the comparison of two samples, the first one being 20 days old, and the second 220, indicating an increase of the local disorder with the integrated α -dose in these materials [5]. Older samples with 15% and 20% Am were thus studied during this experiment to complete this study.

2. Experimental

2.1. Samples

For this study, two kinds of samples were concerned. The two first are new compositions, with Am/(U+Am) ratios respectively equal to 7.5 and 50 at.%. These new samples were synthesized using the UMACS process, based on the dissociation of the solid solution synthesis and its densification which notably

allows the fabrication of homogeneous and dense fuels [6,7]. Based on XRD results, both samples are monophasic with a fluorite-type structure. Their Am/(U+Am) ratios were also confirmed by TIMS (thermal ionization mass spectrometry) analyses.

The four other samples are aged fuels, three of them with an Am/(U+Am) ratio of 15 at.%, and the last with 20 at.%. They were fabricated in 2009 and 2010, using a process based on a reactive sintering [8]. The ages of the 15% fuels are 1100, 1200 and 1400 days, and that of the 20%, 1450 days.

2.2. Measurement conditions

The XAS measurements were performed in transmissions and fluorescence modes at 15 K using the cryostat of the BM20 beamline. Concerning U, XANES spectra were recorded at U L_{III} edge, whereas EXAFS spectra were acquired at U L_{II} edge up to $k = 13.5 \text{ \AA}^{-1}$, to avoid any contribution of Np edge in the spectrum (^{237}Np being generated through α -decay of ^{241}Am). For Am, XANES/EXAFS spectra were recorded at Am L_{III} edge, up to $k = 18 \text{ \AA}^{-1}$. For two aged samples (a 15% and a 20% Am), tentative measurements were also conducted at Np L_{II} edge, as significant amounts (around 4000 and 5400 ppm respectively for the 15% and 20% Am) of ^{237}Np should be present in those samples. Y, Zr and Mo reference foils were recorded respectively at U L_{III}, Am L_{III} and U L_{II} (and Np L_{II}) edges for energy calibration. For the analysis of XANES spectra, references compounds already available were used. UO_2 , U_4O_9 and U_3O_8 were selected for U^{+IV} , U^{+V} and U^{+VI} , respectively, and AmO_2 and a mixed U-Am oxide, respectively for Am^{+IV} and Am^{+III} .

3. Results and discussion

3.1. New compositions

The XANES spectra of the 7.5% and the 50% Am samples are presented in Figure 1 and compared to those of reference compounds. At Am L_{III} edge, no deviations from the Am^{+III} reference spectrum are noted for both samples, suggesting the presence of only trivalent Am. At U L_{III} edge, a shift from U^{+IV} reference spectrum towards higher energies is noted in both cases, indicating an oxidation of uranium cations. For the 7.5% sample, the spectrum is between those of UO_2 and U_4O_9 whereas for the 50% sample, the XANES spectrum lies between those of U_4O_9 and U_3O_8 .

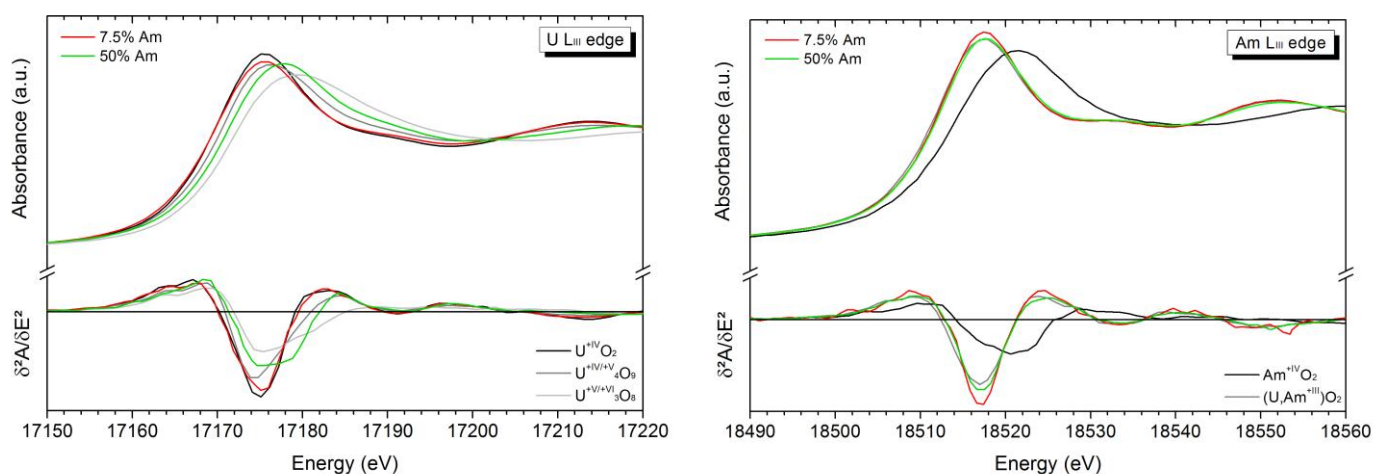


Figure 1. XANES spectra at U and Am L_{III} edges for 7.5% and 50% Am samples compared to those of reference compounds for Am^{+III} , Am^{+IV} , U^{+IV} , $\text{U}^{+IV/+V}$ and $\text{U}^{+V/+VI}$.

The EXAFS spectra and their Fourier transforms, respectively presented in Figure 2 and Figure 3, appear to be quite different between the samples. For the 7.5% Am sample, standard fluorite Fourier transforms

(similar to that obtained for the UO_2 reference compound) are obtained at both edges with two main contributions corresponding to the first U/Am-O and U/Am-U/Am shells. Concerning the 50% Am sample, smaller amplitudes are observed. At both edges, the cationic sub-structure appears to be conserved, as the U/Am-U/Am contributions are well-defined, thus agreeing with XRD results. The oxygen sublattice is however more delicate to describe and seems to be strongly affected by the high Am content and the associated heterogeneous charge repartition. Especially, discrepancies are observed between the two edges for this peak, the oxygen sublattice being presumably more affected around U cations than around Am. As the analyses of these results are still in progress, these observations will thus be further investigated, notably for a better description of the 50% Am sample.

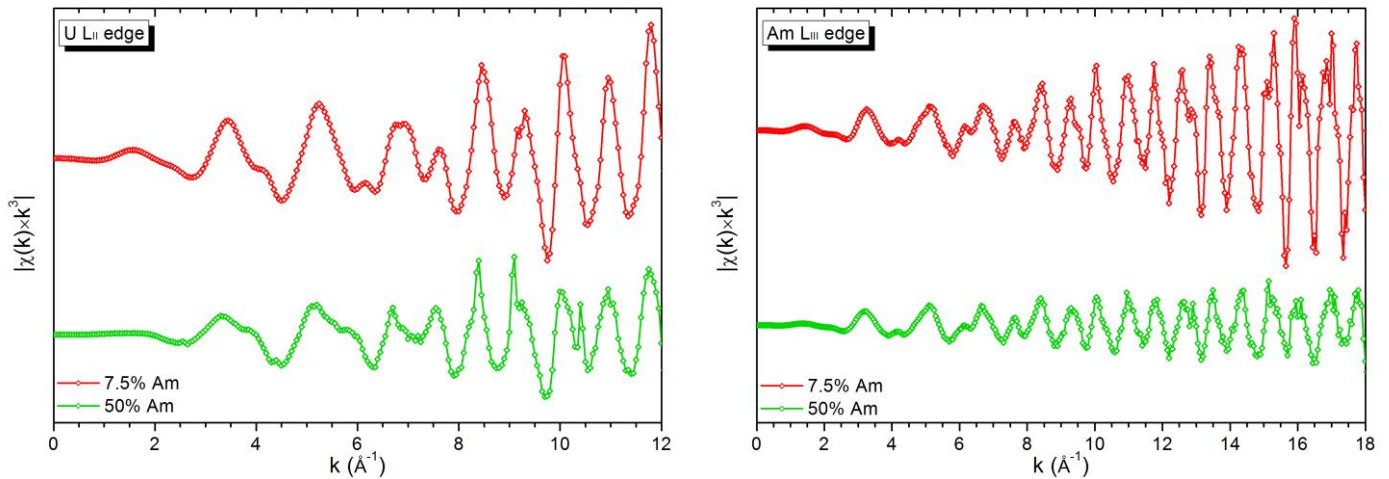


Figure 2. EXAFS spectra at UL_{II} and Am L_{III} edges of 7.5 and 50% Am samples.

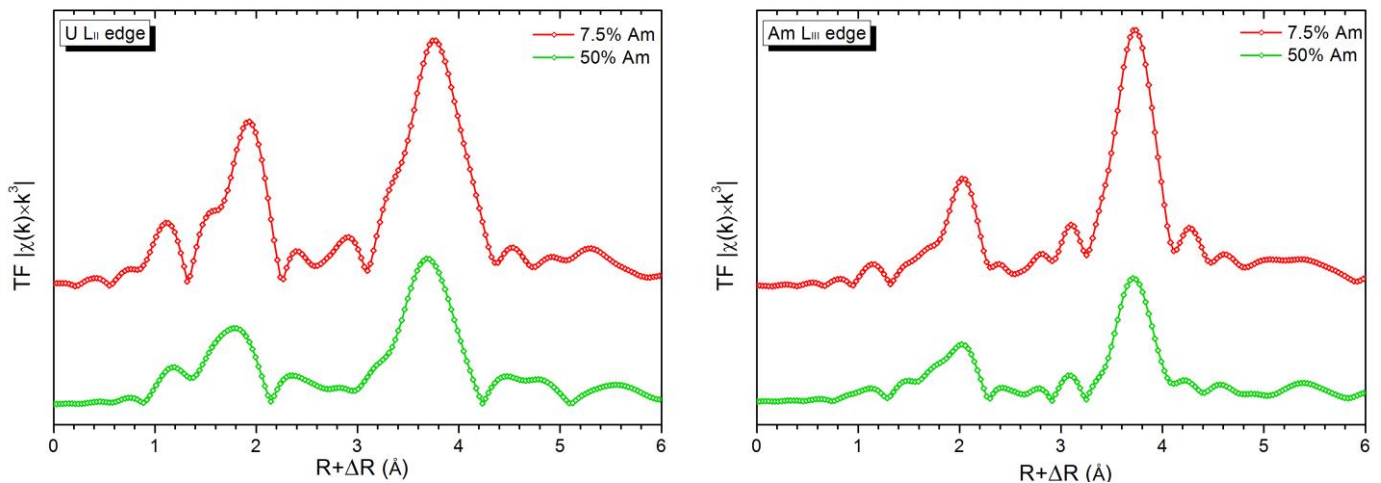


Figure 3. Fourier transforms of EXAFS spectra at UL_{II} and Am L_{III} edges of 7.5 and 50% Am samples.

3.2. Self-irradiation effects

The XANES spectra at U and Am L_{III} edges of the four aged samples are presented in Figure 4 compared to those of reference compounds. All spectra at U L_{III} edge are between those of UO_2 and U_4O_9 reference spectra, confirming the presence of $\text{U}^{+\text{IV/V}}$, whereas those at Am L_{III} indicates the presence of fully trivalent Am. Concerning the measurements at Np L_{II} edge presented in Figure 5, the signal-to-noise ratio is, as expected, lower than at U and Am edges, but the spectra seem to be aligned. Analyses of the XANES spectra are still in progress.

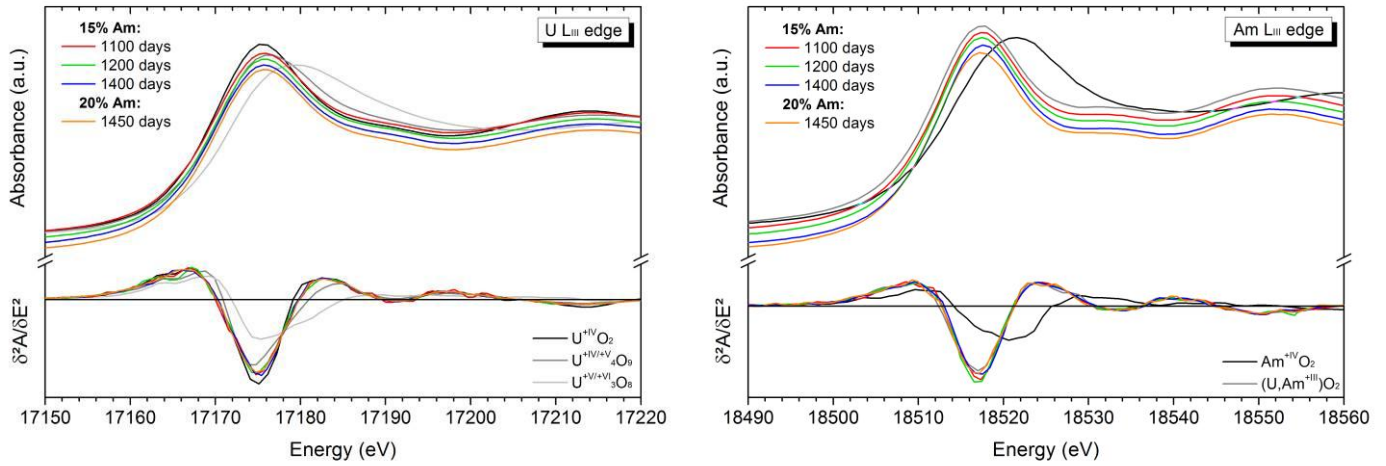


Figure 4. XANES spectra at U and Am L_{III} edges for the aged 15% and 20%Am samples compared to those of reference compounds for Am^{+III} , Am^{+IV} , U^{+IV} , $U^{+IV/+V}$ and $U^{+V/VI}$.

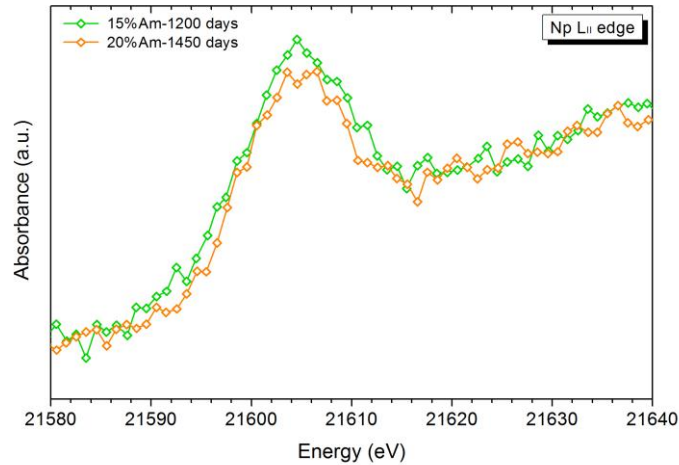


Figure 5. XANES spectra at Np L_{II} edge of a 15% and a 20% Am samples.

EXAFS spectra of these samples and their Fourier transforms are presented in Figure 6 and Figure 7, respectively. Only Fourier transforms corresponding to standard fluorite structure are observed, presenting the two main peaks associated to the first U/Am-O and U/Am-U/Am shells. Their refinement is currently begin performed, and will bring information about the evolution of the structure at local range in these materials.

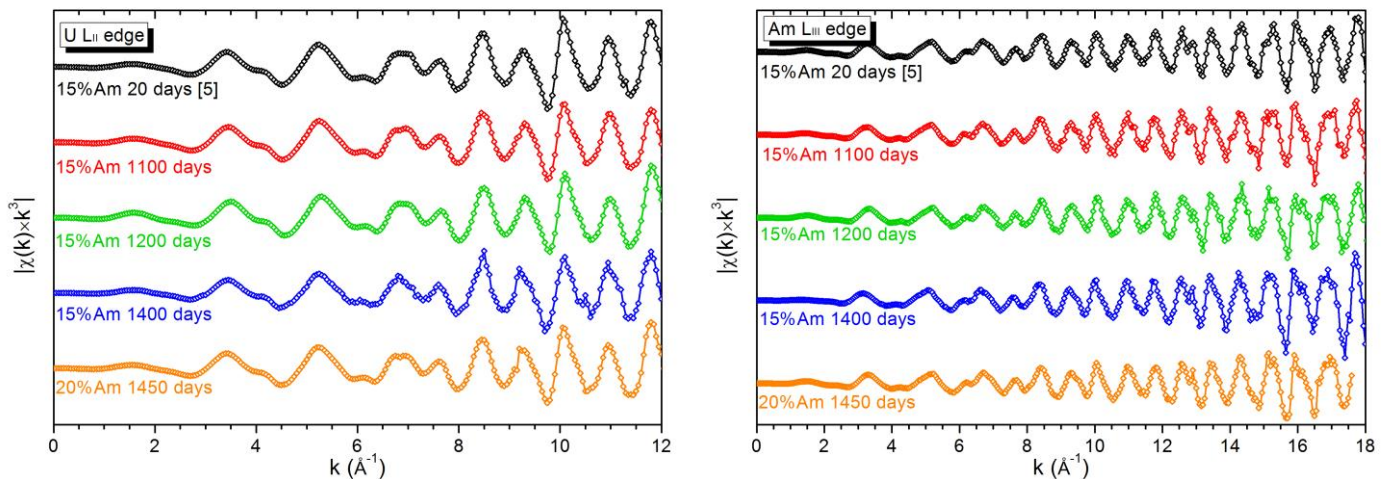


Figure 6. EXAFS spectra at UL_{II} and Am L_{III} edges of the aged 15 and 20% Am samples.

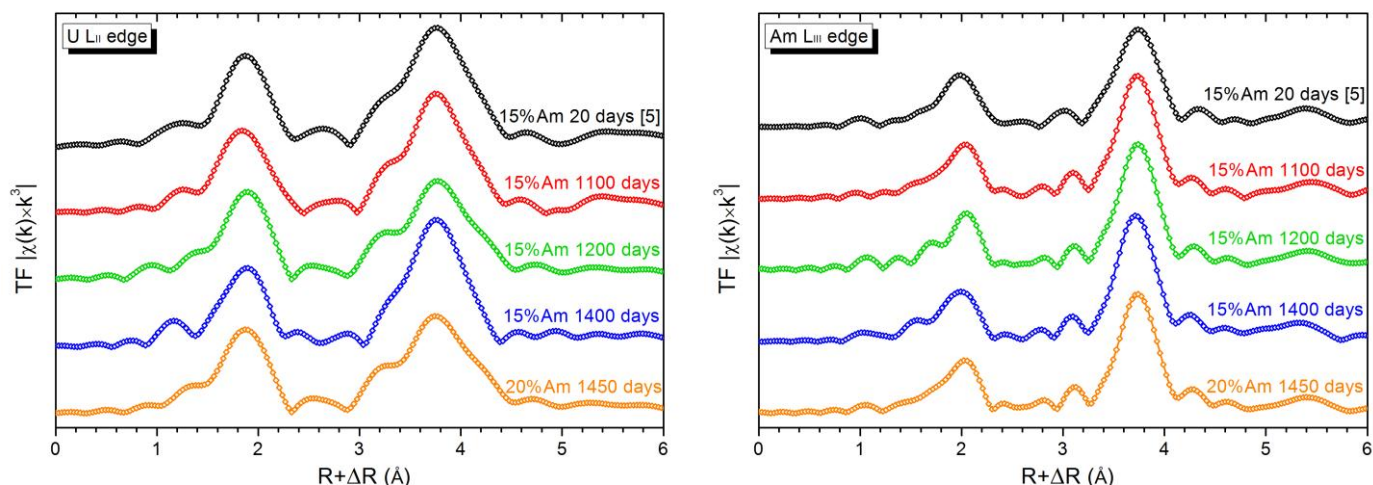


Figure 7. Fourier transforms of EXAFS spectra at UL_{II} and $Am L_{III}$ edges of the aged 15 and 20% Am samples.

4. Conclusions

The reported experiment was dedicated to the study by XAS of several $U_{1-x}Am_xO_{2\pm\delta}$ fuels for transmutation presenting several compositions and ages. The preliminary analyses of obtained results confirmed the presence of fluorite-type structure for all samples, even for high americium content or cumulated α -dose. The spectra analyses are still in progress.

The final results will then be integrated in publications in peer-reviewed journals and/or presentations for international conferences.

5. References

- [1] D. Prieur, P.M. Martin et al., ESRF Report 20-01-705 (2011).
- [2] D. Prieur, P.M. Martin et al., ESRF Report CH-3209 (2011).
- [3] D. Prieur, P.M. Martin et al., *Inorg. Chem.* 50 (2011) 12437-12445.
- [4] D. Prieur, P.M. Martin et al., *J. Nucl. Mater.* 434 (2012) 7-16.
- [5] D. Prieur, P.M. Martin et al., *J. Solid State Chem.* 194 (2012) 206-11.
- [6] T. Delahaye, F. Lebreton et al., *J. Nucl. Mater.* 432 (2012) 305-312.
- [7] F. Lebreton, D. Horlait et al. "Fabrication and characterization of $U_{1-x}Am_xO_{2\pm\delta}$ compounds with high americium contents ($x = 0.3, 0.4$ and 0.5)", accepted in *J. Nucl. Mater.* (2013).
- [8] D. Prieur, A. Jankowiak et al. *J. Nucl. Mater.* 414 (2012) 503-507.