



Experiment title: XAS study of $U_{1-x}Am_xO_{2\pm\delta}$ fuels for transmutation synthesized through innovative processes		Experiment number: CH 3938
Beamline: BM20	Date of experiment: from: 16/11/2013 08:00 to: 19/11/2013 08:00	Date of report: 02/2014
Shifts: 9	Local contact(s): Christoph Hennig	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): F. LEBRETON ^{1,2,*} P.M. MARTIN ^{3,*} , M. CAISSO ^{1,4,*} , D. HORLAIT ¹ , T. DELAHAYE ^{1,*}		
¹ CEA, DEN, DTEC/SDTC/LEMA – 30207 Bagnols-sur-Cèze, France ² GEMH/ENSCI – 87065 Limoges, France ³ CEA, DEN, DEC/SESC/LLC – 13018 Saint-Paul-lez-Durance, France ⁴ IEM, UMR 5635 CNRS-ENSCM-UM2, Université Montpellier 2 – 34095 Montpellier, France		

1. Introduction

Americium isotopes represent a main contribution to the long-term radiotoxicity and heat load of spent nuclear fuel. In order to limit this contribution, americium could be transmuted in fast neutron reactors, notably through the heterogeneous mode, consisting of the use of $U_{1-x}Am_xO_{2\pm\delta}$ compounds destined for the core periphery. In this context, several processes were developed in order to synthesize such compounds, mainly based on powder metallurgy. These processes proved to be reliable at the laboratory scale [1–3], but have a major drawback regarding the high radiotoxicity of americium isotopes, which makes americium-containing powders thus highly contaminant. At an industrial scale, the use of americium-containing powders should therefore be avoided. In this context, new processes are being developed. Two routes are particularly investigated in France, oxalate co-conversion and oxide microspheres. The first one consists of synthesizing mixed uranium-americium oxide powders by co-converting mixed uranium-americium oxalates [4]. The powder then obtained can be used as is for sintering, without the need of any milling step, as was recently demonstrated [5]. The second route, called CRMP (calcined resin microspheres pelletizing) is based on the use of mixed uranium-americium oxide microspheres obtained by heat treatment of ion exchange resins loaded with uranium and americium cations [6,7]. The microspheres obtained can be used for pelletizing and sintering, thus avoiding the use of any americium-bearing powder. The influence of these processes on the structural properties of the uranium-americium mixed oxide compounds obtained remains unknown. This experiment was thus dedicated to a XAS study of compounds obtained at different steps of these processes.

2. Experimental

All mixed uranium-americium oxide samples studied during this experiment present an Am/(U+Am) ratio of 10 at.%. Two were obtained from mixed uranium-americium oxalate. The first one, Sample A, is the oxide obtained after the heat treatment of conversion of the oxalate. The second one, Sample B, is the oxide obtained after sintering of the obtained powder. Samples C, D and E were prepared by the CRMP process. Sample C is composed of oxidized microspheres (obtained after conversion to oxide under air), Sample D, of reduced microspheres the same microspheres reduced during a heat treated under reducing conditions and Sample E is a powdered sample from a sintered pellet prepared from the reduced microspheres. XAS measurements were performed in transmissions and fluorescence modes at 15 K using the cryostat of the BM20 beamline. XANES spectra were recorded at U and Am L_{III} edges, whereas EXAFS spectra were acquired at U L_{II} and Am L_{III} edges. For the analysis of XANES spectra, references compounds already

available were used: U^{+IV}O_2 , $\text{U}^{+IV/+V}_4\text{O}_9$ and $\text{U}^{+V/+VI}_3\text{O}_8$ for uranium oxidation state, and $\text{Am}^{+IV}\text{O}_2$ and a mixed ($\text{U},\text{Am}^{+III}$) oxalate for americium oxidation state.

3. Results

XANES spectra obtained on Samples A and B are presented in Figure 1 and, on Samples C, D and E, in Figure 2. At the Am L_{III} edge, all sample spectra are aligned with that of the (U,Am) oxalate reference compound, indicating the sole presence of Am^{+III} in the sample. At the U L_{III} edge, all sample spectra are, however, shifted towards higher energies compared to the U^{+IV} reference compound. Considering the sintered sample (B and E), their spectra are comprised between those of U^{+IV}O_2 and $\text{U}^{+IV/+V}_4\text{O}_9$, indicating a mixed +IV/+V oxidation state for uranium. For the other samples, spectra indicate the presence of uranium at higher oxidation states. The charge distribution in the uranium-americium samples is thus similar to that previously reported for similar compounds prepared by powder metallurgy processes [8,9]. For the non-sintered samples (A, C and D), EXAFS spectra also seem to indicate a lower level of crystallinity. The ongoing refinement of these spectra will allow more detailed information to be obtained.

4. Conclusion

Uranium-americium mixed-oxide samples synthesized using innovative routes were studied by XAS at the U and Am L_{III} edges. From XANES results, the process has no influence on the charge distribution in these materials. Full analysis of the EXAFS spectra, currently ongoing will allow estimating the influence of these processes based on the use of homogeneous precursors on the local structure, notably on the structural disorder.

5. References

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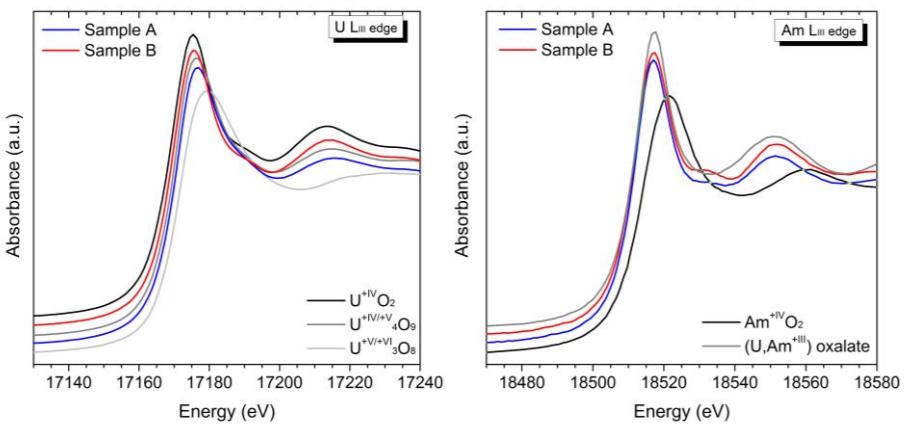


Figure 1. XANES spectra obtained at (left) U L_{III} and (right) Am L_{III} edges on Samples A and B, synthesized from mixed uranium-americium oxalates.

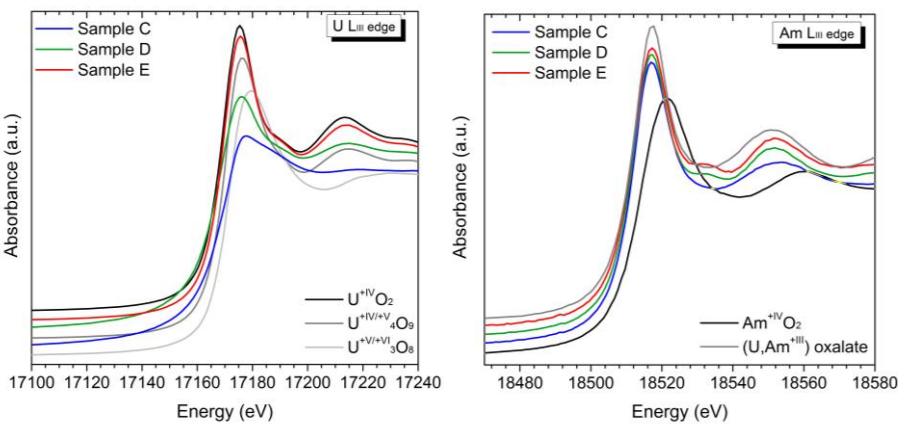


Figure 2. XANES spectra obtained at (left) U L_{III} and (right) Am L_{III} edges on Samples C, D and E, synthesized from ion exchange resin loaded with uranium and americium cations.