ESRF	**Experiment title:** XAS investigation of (U,Am)O2 and (U,Pu)O2 solid solutions obtained by oxalic co-precipitation	**Experiment number**: CH- 2738
Beamline: BM20	**Date of experiment**: from: 15 may 2009 to: 19 may 2009	**Date of report**:
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Report:

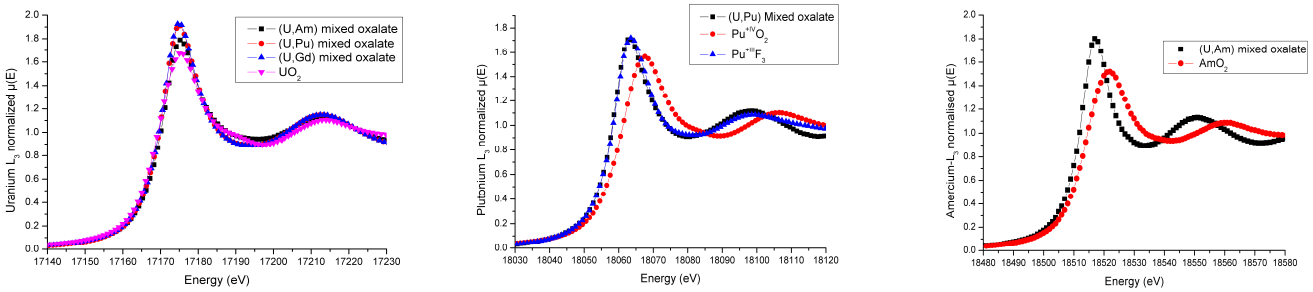
Innovative fuel cycles are currently studied within the framework of the fourth generation (GEN-IV) nuclear reactors development. The two main objectives of these fuel cycles are an efficient use of energetic resources by recycling together the major and valuable actinides such as uranium and plutonium, and a drastic decrease of the radiotoxicity of the ultimate wastes by partitioning and transmutating the minor ones such as americium, curium or neptunium. Indeed, the challenge is to be able to incorporate a large amount (up to ~20 at.%) of highly radioactive minor actinide into the mixed (U,Pu) nuclear fuel. Moreover, only a fluorite type solid solution, as in case of pure $(U,Pu)O_2$, has to be obtained for the final product.

Rather than a mechanical mixing of pulverulent compounds, as in the actual MOX manufacturing process, innovative synthesis methods based on co-precipitation are currently developed [1]. In particular, the oxalic co-precipitation of U(IV) and Pu(III) followed by the thermal conversion of the co-precipitate into oxide, was recently optimized in the CEA Atalante facility at Marcoule. Characterization on mixed U(IV)-An/Ln(III) oxalate structures [2] indicated that a solid solution with the generic formula $M_{2+x}U^{IV}_{2-x}An^{III}_{x}(C_2O_4)_5.nH_2O$ (M = monocharged cation) can be expected. The originality of this mixed oxalate is based on a mixed crystallographic site which can accept either a tetravalent actinide or a trivalent one. Monovalent cations equilibrate the charge in the structure depending on the molar ratio of An(III) to An(IV). Thermal conversion of the co-precipitates should lead to an ideal $(U,An)O_2$ fluorite-type solid solution. As demonstrated in a previous study [3], it must be noted that EXAFS appears to be the lone technique that could outline a discrepancy in cation local environments.

For this experiment we focused on one concentration: 10%. The following systems were characterized: $(U_{0.9}Pu_{0.1})$, $(U_{0.9}Am_{0.1})$, $(U_{0.9}Gd_{0.1})$ and $(U_{0.9}Ce_{0.1})$ and for each systems mixed oxalate and mixed oxide samples were analysed. XAS spectra for both cations were collected at 30K using He-cryostat. Energy calibrations were accomplished using Y foil (17 038 eV) or Mo foil (20 000 eV) positioned after the second ionization chamber. EXAFS curve fitting was performed in k^3 for R values in the range 1.5–4.4 Å for both edges. Phases and amplitudes for the interatomic scattering paths were calculated with the code FEFF8.40.

The XANES collected on mixed oxalates are compared with reference compounds in Figure 1. Conclusions are clear concerning oxidations states: for all samples uranium cation is +IV while americium and plutonium cations are +III. Thus, as in the case of U(IV)-Ln(III) mixed oxalate the trivalent state for americium and plutonium is now demonstrated.

Results of EXAFS fit performed on $(U_{0.9},Pu_{0.1})$ and $(U_{0.9},Am_{0.1})$ samples are summarized in Tables 1 and 2. The crystallographic structure of U(IV)-An/Ln(III) oxalates indicates that each cation is surrounded by 5 oxalate ligands (C_2O_4).



(a) Uranium L_3 *(b) Plutonium L_3* *(c) Americium L_3*

Figure 1: XANES spectra collected on mixed oxalate samples

	N	DW(Å^2)	R (Å)
U-O	10.7(5)	0.006	2.46(1)
U-C	9.2(5)	0.004	3.28(1)
U-O	10(1)	0.004	4.56(2)

(a) Uranium L_3

	N	DW(Å^2)	R (Å)
Pu-O	10.5(5)	0.007	2.53(1)
Pu-C	10.0(5)	0.004	3.32(1)
Pu-O	10.5(5)	0.004	4.60(2)

(b) Plutonium L_2

Table 1: Fit results on ($U_{0.9}$,$Pu_{0.1}$) mixed oxalate sample

	N	DW(Å^2)	R (Å)
U-O	9.4(5)	0.006	2.45(1)
U-C	9.9(5)	0.007	3.28(1)
U-O	10(1)	0.016	4.50(2)

(a) Uranium L_3

	N	DW(Å^2)	R (Å)
Am-O	10.4(5)	0.007	2.50(1)
Am-C	9.0(5)	0.007	3.32(1)
Am-O	10(1)	0.004	4.54(2)

(b) Americium L_3

Table 2: Fit results on ($U_{0.9}$,$Am_{0.1}$) mixed oxalate sample

As observed in Tables 1 and 2, coordination numbers for the three shells corresponding to the C_2O_4 ligands are equal to ~10 for each cation. These results confirm the presence of 5 oxalate ions around U(IV), Pu(III) and Am(III) cations in the mixed ($U_{0.9}Pu_{0.1}$) and ($U_{0.9}Am_{0.1}$) oxalates. For a same compound, the only significant differences observed between the two actinides are distances which are systematically shorter around uranium than around Pu or Am. These differences can be explained by the difference of ionic radii between U+IV and trivalent Pu and Am, but values are unknown for such cations coordinated with 10 atoms. To check this assumption, we can compared mean distances calculated from XRD cell parameters using atoms positions determined for U-Ln(III) [2] with which measured with EXAFS.

	U(Pu)-O	U(Pu)-C	U(Pu)-O
XRD (Å)	2.48	3.29	4.53
EXAFS (Å)	2.47 (2)	3.29 (2)	4.56 (4)

(a) ($U_{0.9}$,$Pu_{0.1}$) mixed oxalate

	U(Am)-O	U(Am)-C	U(Am)-O
XRD (Å)	2.46	3.29	4.52
EXAFS (Å)	2.46 (2)	3.29 (2)	4.50 (4)

(b) ($U_{0.9}$,$Am_{0.1}$) mixed oxalate

Table 3: Mean distances calculated from XRD results and measured by EXAFS

As shown in Table 3, a very good agreement can be observed between XRD and EXAFS. Thus, **by combining conventional XRD and XAS characterizations we have demonstrated that results obtained on U(IV)-Ln(III) (synthesis of an ideal solid solution) can be extended to ($U^{+IV}_{0.9}Pu^{+III}_{0.1}$) and ($U^{+IV}_{0.9}Am^{+III}_{0.1}$) systems.**

Concerning ($U_{0.9}Pu_{0.1}$)O_2 and ($U_{0.9}Am_{0.1}$)O_2 samples, due to experimental difficulties during the calcination step both mixed oxide samples are hyperstoichiometric with a massive oxidation of uranium IV to VI. As in the case of plutonium sample, the validity of the process was already shown with previous experiment [4], the demonstration remains to be performed with (U,Am)O_2. Moreover, unexpectedly the conditions was not sufficient to oxidize Am^{+III} ions to Am^{+IV} even with a large amount oxygen content in the furnace atmosphere. Thus, new experiments are needed to explore (U,Am)O_2 system in function of calcination conditions and americium concentration and a new proposal on this subject will be deposited at the ESRF.

References

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