



	Experiment title: Study of americium and plutonium chemistry in MOX fuel oxide	Experiment number: CH 2967
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Report:

Innovative Mixed OXide (MOX) (U,Pu)O_{2-x} fuels for sodium fast neutron reactors (SFR's) systems are currently studied within the framework of the fourth generation (GEN-IV) nuclear reactor systems. GEN-IV's main purpose is to use energetic resources more efficiently by recycling valuable actinides such as uranium and plutonium. SFRs will also be able to burn long-lived minor actinides (MA) such as Am, Np and Cm recovered from used fuel leading to a drastic decrease in their potential radiotoxicity and the heat load for the final disposal. Among MA, americium is of main concern. Two options are considered: (a) homogeneously adding americium to the fuel in small amount (homogeneous mode) or (b) introducing it in higher concentration into fertile blankets (heterogeneous mode) [1]. Regarding the first option, MOX fuel incorporating up to 6% AmO₂ is a promising candidate [2].

Because they significantly affect the sintering properties as well as irradiation performances, the oxygen potential and the oxygen to metal (O/M) ratio are important factors to be considered when designing oxide fuels. Therefore, a thorough knowledge of the correlation between oxygen potential and O/M ratio is essential. To determine this relationship, an experimental determination of U, Pu and Am oxidation states as a function O/M in MOX fuel is needed.

The aim of this experiment was to follow the chemistry of uranium, plutonium and americium, and in particular their oxidation states, in (U, Pu, Am)O_{2-x} samples sintered under different oxygen potentials.

To this purpose, MOX samples with the following composition (U_{0.750}Pu_{0.246}Am_{0.004})O_{2-x}, were manufactured at the LEFCA facility at CEA Cadarache (France) using the COCA process (COBroyé CADarache). This involved direct co-milling of the oxides and leads to a homogeneous plutonium distribution [3]. Three sets of samples were manufactured and sintered at 1750°C for 4 hours. Moisty conditions are given in table 1 as well as calculated oxygen potential (μO₂).

Sintering conditions	μO ₂ (kJ.mol ⁻¹)
Ar 95% + H ₂ 5% + 200 ppm H ₂ O	-446
Ar 95% + H ₂ 5% + 90 ppm H ₂ O	-467
Ar 95% + H ₂ 5%	-506

Table 1 : sintering condition (O₂ impurity is taken equal to 20 ppm).

XANES spectra collected for U, Pu and Am cations are compared

with reference compounds in Figure 1. As expected the oxidation state of uranium cations remains equal to +IV for the 3 compositions. Americium-L_{II} XANES also shows no variation up to the highest oxygen potential of -446 kJ.mol⁻¹, *i.e.* is always trivalent. A different behaviour is observed for plutonium with a slight shift of both white line maxima and first inflexion point of Pu-L_{III} XANES to a lower energy as a function of μO₂. Thus, a reduction of Pu^{+IV} to Pu^{+III} is clearly evidenced.

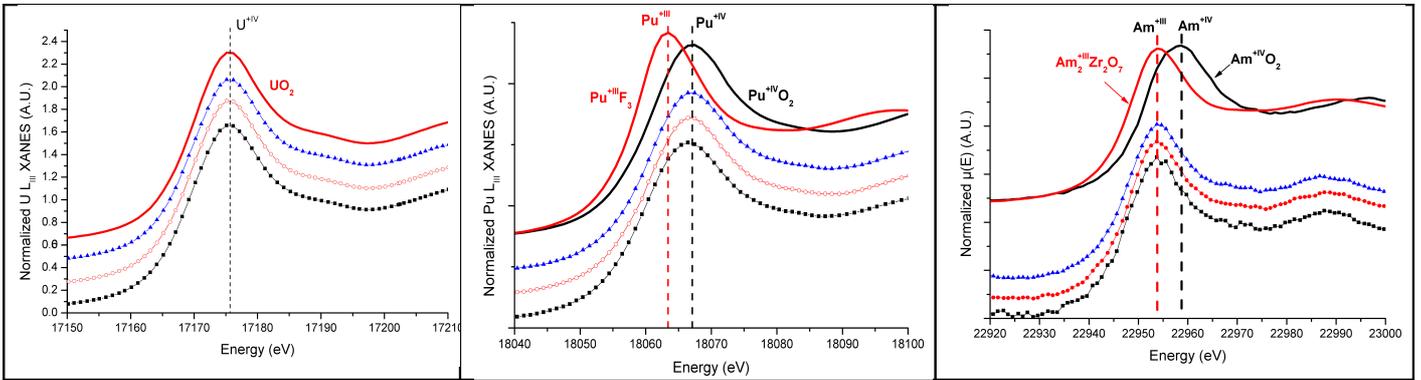


Figure 1: XANES spectra of MOX samples sintered with μO_2 equal to -446 kJ.mol^{-1} (\blacktriangle), -467 kJ.mol^{-1} (\circ) and -506 kJ.mol^{-1} (\blacksquare) compared with reference compounds (full lines).

By fitting XANES spectra collected on MOX samples with a linear combination of reference compounds relative concentrations of the Pu^{+III} and Pu^{+IV} could be determined. For Pu^{+IV} we used spectrum collected on PuO_2 and for Pu^{+III} we tested the fit using the spectra collected on PuF_3 or ($\text{U}^{+IV}, \text{Pu}^{+III}$) mixed oxalate [4]. In both cases, we obtained the same values. Based on these results, the O/M ratio for the three sintering conditions have been calculated. Results are given in Table 2.

μO_2 (kJ.mol^{-1})	Pu cation repartition (%)		O/M
	Pu^{+IV}	Pu^{+III}	
-506	0.80	0.20	1.973
-467	0.88	0.12	1.984
-446	0.92	0.08	1.989

Table 2: Plutonium cations percentage and calculated O/M ratio.

Local environment around uranium and plutonium are compared in Figure 2. It reflects the XANES evolution: The lack of modification as a function of O/M observed around U ions is in agreement with the fixed U^{+IV} valency observed in XANES spectra. Whereas, slight modifications are present around Pu cations especially the intensity loss of coordination shells which indicates an increase disorder. This last observation is consistent with the Pu^{+III} occurrence in the fluorine structure.

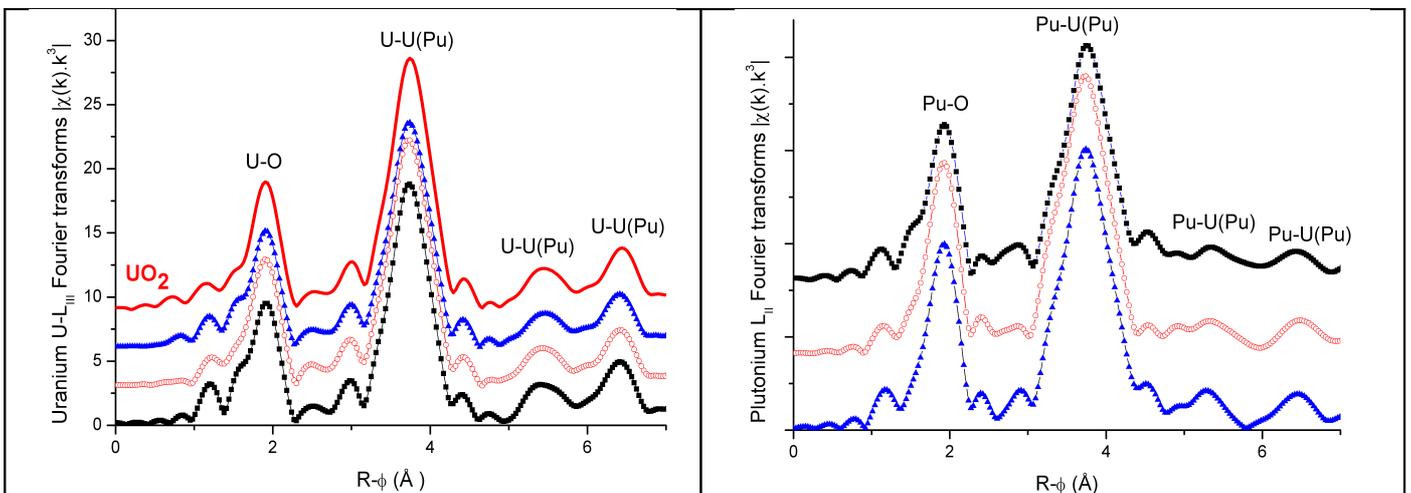


Figure 2: Fourier transforms of EXAFS spectra of MOX samples sintered with μO_2 equal to -446 kJ.mol^{-1} (\blacktriangle), -467 kJ.mol^{-1} (\circ) and -506 kJ.mol^{-1} (\blacksquare) compared with reference compounds (full lines).

Our results show that for substoichiometric $(\text{U}_{0.750}\text{Pu}_{0.246}\text{Am}_{0.004})\text{O}_{2-x}$ samples, americium reduction occurs more readily than plutonium reduction. Americium cations are fully reduced to Am^{+III} before any reduction of plutonium cations is observed. Moreover, uranium cations remain tetravalent. To our knowledge, it is the first time that experimental information on such a topic is reported. Thermochemical calculations to validate the model suggested by these results are in progress. The next step will be the study of MOX samples doped with a higher concentration of americium ($\sim 5\%$).

References

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- [2] T. Wakabayashi *et al.*, Nucl. Technol. 118, (1997) 14.
- [3] Y. Guerin *et al.*, in: ANS International Topical Meeting on LWR Fuel Performance, Park City, UT, USA, ANS, La Grange Park, IL, 2000, p. 706.
- [4] P. Martin *et al.*, ESRF experimental Report CH-2738 (2009).