ESRF	**Experiment title:** XAS study of uranium and plutonium local environment in (U,Pu)O$_2$ solid solution	**Experiment number**: **ME-312**
Beamline: BM 20	**Date of experiment**: from: 09 november 2001 to: 13 November 2001	**Date of report**: 28/02/2002
Shifts: 12	**Local contact(s)**: Dr. Andreas BAUER	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* Dr. MARTIN Philippe   Centre de Cadarache
                               DEN/DEC/SESC/LLCC Bat 315
                               13108 Saint Paul Lez Durance Cedex
* Dr. RIPERT Michel   Centre de Cadarache DEN/DEC/SESC/LLCC Bat 315
* Dr. CARLOT Gaëlle   Centre de Cadarache DEN/DEC/SESC/LLCC Bat 315
* Dr. GRANDJEAN Stéphane   CEA/VALRHO, DEN/DRCP/SCPS/LPCA, Bat 399 BP 17171
                               30207 Bagnols sur Cèze Cedex, France
Dr. PETIT Thierry   Centre de Cadarache DEC/SESC/LLCC Bat 315
Dr. BLANC Pierre   CEA/VALRHO, DEN/DRCP/SCPS/LPCA Bat 399.

The plutonium generated in nuclear power reactors can be re-used at least partially through the exploitation of a Mixed OXide (U,Pu)O$_2$ fuel. Industrially, the manufacture of the MOX fuel proceeds in UO$_2$ and PuO$_2$ powders co-crushing, pelletizing and sintering. With this method, a fluorite-type solid solution (U,Pu)O$_2$ is obtained. Currently, rather than a mechanical mixing of pulverulent compounds, a new technique of manufacture for specific needs is under development, based on a co-precipitation of uranium and plutonium (chemical mixture). A better homogeneity of the U and Pu repartition in the solid and at lower temperature is awaited by this wet route. The homogeneity of the final products may represent a significant criterion for an optimized behaviour in power reactors.

During our experiments we analysed samples whose plutonium content was equal to 7, 15, 30 et 50%. The PuO$_2$ reference compound was synthesised following the same chemical procedure. Those samples were analysed by X-ray diffraction. In each case, a face centred cubic structure was observed and the cell parameter deducted obeys the Vegard's law as seen in the following table.

% Pu	a (XRD) (Å)	a (Vegard's law) (Å)	First shell Metal-O (Å)	Second shell Metal-Metal (Å)	Third shell Metal-O (Å)
0	5.47	5.47	2.369	3.868	4.535
7	5.4652	5.4648	2.367	3.864	4.532
15	5.4566	5.4589	2.363	3.858	4.524
30	5.444	5.4478	2.357	3.849	4.514
50	5.434	5.4330	2.353	3.842	4.506
100	5.3976	5.3960	2.337	3.817	4.475

Table 1 : cell parameter a measured by XRD and calculated with Vegard's law, and 3 first coordination shells of metal ion in (U,Pu)O$_2$ solid solution

For each sample, the transmission and fluorescence signals were collected at the uranium (17.126 keV) and plutonium (18.056 keV) L$_{III}$ edges. Energy calibration of the XANES data was achieved using the

references Y foil (17.052 keV) and Zr foil (17.998 keV) positioned after the second ionisation chamber. As observed on these XANES spectra, the position of the white line is, at the uranium edge, the one of the UO_2 and at the plutonium edge, the one of PuO_2. Thus, whatever the plutonium content is, the oxidation state of uranium and plutonium remains equal to +IV.

The evolutions of the Fourier Transform are summarised on the figures 1 and 2. The overall shape of the spectra is almost always the same while the global intensity varies a lot with the plutonium content. Thus, an important decrease of oscillations for the 30 and 15% Pu samples is observed. X-ray diffraction leads to the same result showing a greater disorder than for the PuO_2 and 50 % Pu samples.
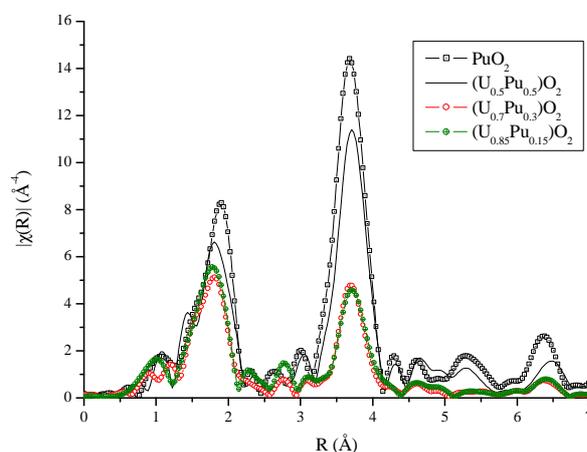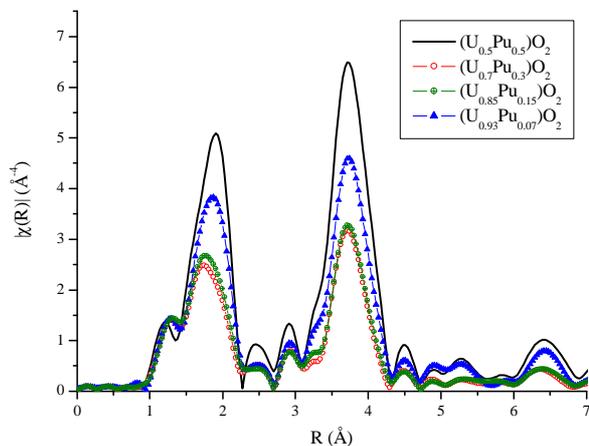
Figure 1 : Fourier Transforms of the uranium L_{III} edge EXAFS (k-range: 2 → 12 Å^{-1}).

Figure 2 : Fourier Transforms of the plutonium L_{III} edge EXAFS (k-range: 2 → 14 Å^{-1}).

At the uranium L_{III} edge, the best fit of the 50% Pu sample leads to the following distances: R_{U-O}=2.352 (5) Å, R_{U-U}=R_{U-Pu}=3.845 (5) Å and R_{U-O}= 4.51 (1) Å. The oxygen neighbours are the same as in UO_2 (8 and 24 for the first and third coordination shells) and the U/(U+Pu) ratio is 0.51. The uranium local environment is clearly the one of an ideal solid solution. The case of plutonium environment is a little more complicated. Indeed, the fitting of the first peak of the Fourier transform of the plutonium L_{III} edge spectra leads to values unsuitable with the fluorite structure. As seen on the figure 2, the shape of this peak (first coordination shell) is no longer gaussian. To fit it, we had to introduce an additional asymmetry term (third cumulant)[1]. Using this method, we finally obtain a shell of 8 oxygen neighbours at a distance of 2.351 (5) Å, which is consistent with the result obtained at the uranium edge. Considering the plutonium-metal shell, we also find an ideal solid solution structure with Pu-Pu and Pu-U distances equal to 3.845 (5) Å. The Pu/(U+Pu) ratio thus obtained is 47%. The results of the analysis at the two edges clearly show that the chemical procedure used to prepare the $(U_{0.5}Pu_{0.5})O_2$ sample is validated.

For the intermediate plutonium concentrations of 15 and 30%, the local environment of uranium and plutonium is highly perturbed as seen in figures 1 and 2. On the opposite to the 50% plutonium sample, a third cumulant has to be introduced in the fitting procedure even at the uranium edge. The results obtained for the first coordination shell consist in 8 oxygen atoms at distances equal to the ones given in table 1. The main difference appears to be a doubling of the Debye-Waller (σ^2_{U-O} (30% Pu) = 0.014 Å^2 instead of σ^2_{U-O} (50% Pu) = 0.0065 Å^2). This is the signature of a higher disordered structure.

It is interesting to note that EXAFS appears to be the lone technique outlining this discrepancy in plutonium and uranium local environment. Some steps of the process via the wet route checked in this study are currently modified considering their potential influence on the mechanisms of formation of ideal solid solutions, particularly with plutonium content lower than 50%. By the way, we ask for a prolongation of this proposal to validate these changes.

[1] Stern, E. A. (1988) *X-ray absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES, chapter 9: amorphous and liquid systems*, edited by D. C. Koningsberger & R. Prins, volume 92 of chemical analysis, New York, John Wiley.