EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** XAS study of self-irradiation effects on the local structure of $(U,Pu)O_2$ MOx nuclear fuels	**Experiment number**: MA-5456
Beamline: BM20 - ROBL	**Date of experiment**: from: 15/11/2023 to: 21/11/2023 from: 03/02/2023 to: 07/02/2023	**Date of report**: 25/07/2023
Shifts: 12	**Local contact(s)**: Damien Prieur, André Rossberg	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

After discussion with the beamline staff, we decided to change the project of this proposal from the "study of self-irradiation effects on the local structure of $(U,Pu)O_2$ MOx nuclear fuels" to the study of the oxidation effects on the simulated high burnup MOx nuclear fuel.

Innovative mixed oxide (MOx) $(U,Pu)O_{2-x}$ fuels for both thermal and fast neutron reactors are currently studiedto developp a more sustainable nuclear fuel cycle. In order to improve and ensure its safety, it is necessary to have a deep understanding of the properties of the $(U,Pu)O_{2-x}$ fuel at every stage of its life even in accidental scenarios. In this project, we aimed at investigating the behaviour of spent MOx fuel under heavily oxidizing condition typical of accidents during interim storage.

Due to fission, for each actinide cation (U, Pu, …) consumed, two lighter nuclei are formed, called Fission Products (FP). Most of these elements have largely different chemical behaviour with respect to U or Pu, thus they change significantly both the thermo-physical and microstructural properties of the pristine fuel during its lifetime [1]. In order to overcome the limitations associated with the irradiated fuel radiotoxicity, model materials called "SIMfuel" have been developed. SIMfuels are manufactured with the same process used for fresh fuel but the material is doped with stable isotopes of radioactive fission products. SIMfuels have therefore reduced radiotoxicity, and allow to study separately the effects of selected FPs. Traditionally SIMfuel is fabricated without Pu [2,3], thus its applicability to real irradiated MOx fuel is therefore limited. Contrary to uranium, plutonium can be present in a reduced state (Pu^{3+}) which has a strong impact on both local oxygen stoichiometry and local redox equilibrium. The study of Pu-bearing SIMfuel (or SIMMOx) is thus critical for the understanding of the MOx fuel behaviour in accidental conditions

For this study, we employ SIMMOx doped with 11 non-radioactive isotopes of fission products. Those are divided into three categories based on their behaviour in irradiated fuel, namely: FPs soluble in the oxide matrix, FPs found in metallic precipitates, and Ba, which has been correlated to the formation of a wide range of oxide precipitates. To our knowledge, this is the first study on SIMMOx with this large variety of FPs. Samples from all compositions have been annealed at specific temperatures and atmospheres (oxygen potential) corresponding to nominal and accidental conditions.
Three batches of SIMMOx samples have been fabricated at CEA Marcoule with the following compositions (called S, M, and B) given in Table 1 below (g/g %). A fresh MOx with same (Pu+Am)/(U+Pu+Am) of the SIMMOx samples has been synthesized (REF), in order to have un undoped reference for our study.

Table 1 Mass concentration (g/g%) of each element in the threecompositions studied. The difference from 100% represents the oxygen content.

	Ba	Ce	La	Mo	Nd	Pd	Rh	Ru	Sr	Y	Zr	U	Pu	Am
REF	-	-	-	-	-	-	-	-	-	-	-	65.1	22.4	0.46
S	-	0.88	0.43	-	2.10	-	-	-	0.11	0.11	1.00	61.1	21.0	0.42
M	-	0.84	0.44	1.45	1.96	0.8	0.34	1.49	0.12	0.10	1.18	58.6	20.2	0.40
B	0.86	0.83	0.43	1.44	1.94	0.79	0.34	1.47	0.12	0.10	1.17	58.1	20.0	0.40

On each batch, an oxidizing treatement has been performed under flowing air, for a duration of 110 hours, and a temperature of 583 K.
On a previous experiment (MA 5032), the as-synthesize samples were studied, and part of the results are available in [4]. In this experiment we analized samples from each of the four composition (REF, S, M, and B) after the oxidation treatment. The sample naming scheme is straightforward, we wil use the name of the composition (REF, S, M, or B) and if the sample has been oxidized, “OX” is added ath the end. For example, sample “M” has a composition M and has not been oxidized, while sample “M-OX” has composition M and has been oxidized (-OX).

For each sample, fluorescence and transmission signal have been collected for UL_{III}, PuL_{III}, PuL_{II}, AmL_{III}, YK, ZrK, MoK, RuK, RhK, PdK, and SrK edges.

First, we collected XANES spectra at the U, Pu and Am L_{III} edge in order to assess the effect of the oxidation treatement on the oxidation state. The EXAFS signal has also been collected at the U L_{III} and Pu L_{II}–edge to investigate the effect on the local atomic environment. An example of UL_{III} edge XANES and EXAFS spectra is shown in **Erreur ! Source du renvoi introuvable.**.

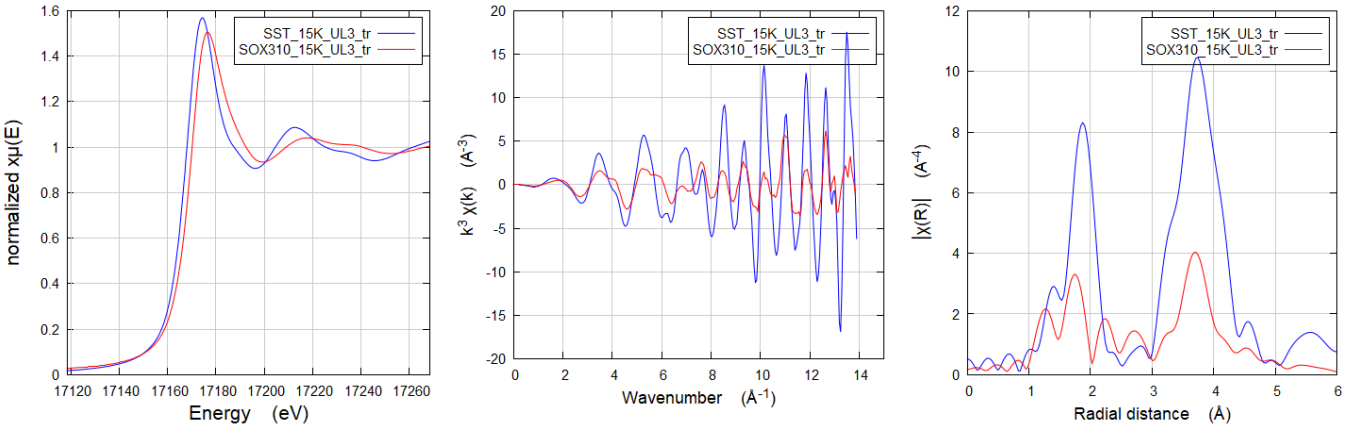

Figure.1 UL_{III} XANES and EXAFS spectra of samples S (blue) and S-OX (red).

We notice a significant shift in the absorption edge towards higher energies, whhich suggests that U is oxidizing. Furthermore, from the EXAFS analysis, we can notice a strong reduction in the oscillation intensities, which seems consistent with what observed in [5] for oxidized $(U,Am)O_2$ systems. This could be the effect of the restructuring of the anionic sublattice due to the oxidation of the actinides.
This interpretation is supported also by the evolution observed at the Sr K-edge presented in Figure 2.

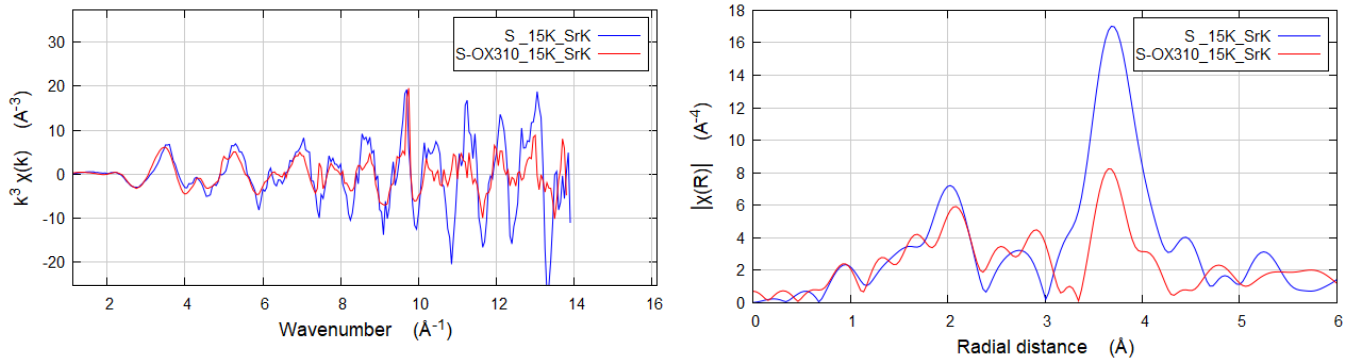

Figure 2 EXAFS signal (left) and its Fourier Transform (right) of samples S (blue) and S-OX (red), collected at Sr K-edge.

As shown, the intensity of the oscillation is decreased also for Sr, confirming that the local order around the cations is reduced following oxidation. These results strongly suggest that the cations local environment shifts from a highly ordered 8-coordinated fluorite-type, to an environment characterised by higher disorder. The properties of this new environment are still under investigation.

Similar results can be observed for Pu and Am, and for the other compositions. Notably, we found that Am is always mainly in 3+ state, even after oxidation treatment. This suggests that Am is always found in its 3+ state in nuclear fuel, even in accidental conditions.
Nevertheless, the treatment of the data is still ongoing.

As for the analysis of the FP, the XANES of th Mo K-edge and of Ru K-edge is presented in Figure 3.

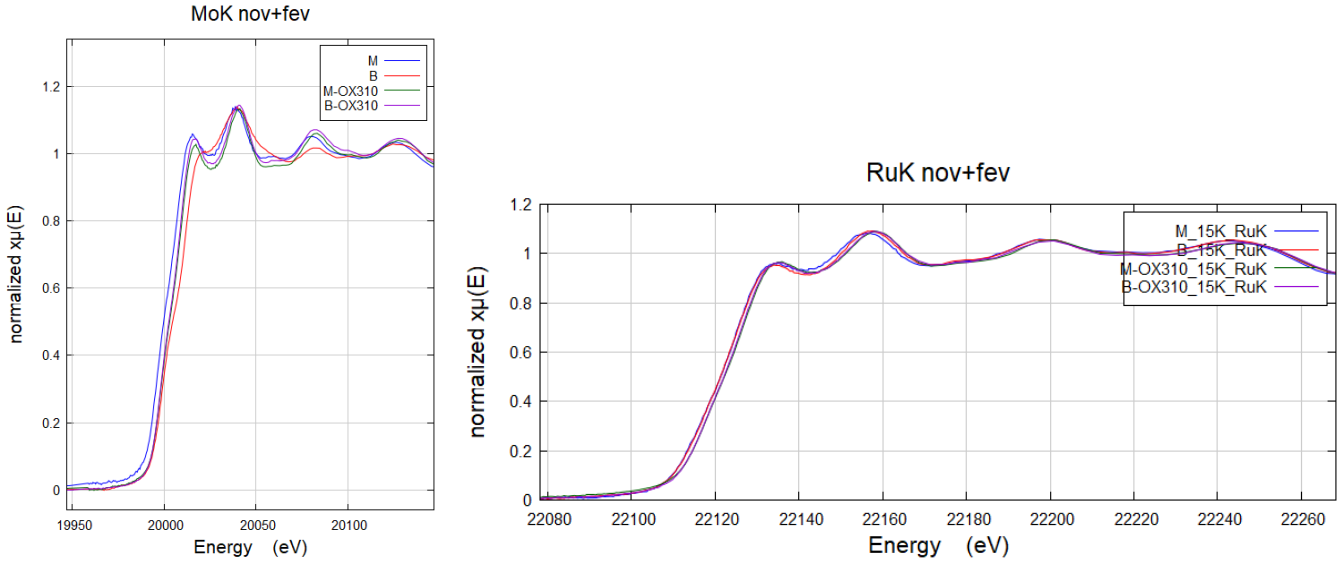

Figure 3 XANES collected at the Mo K-edge (left) and Ru K-edge (right) of the composition M and B before and after thermal treatment.

We can notice a strong evolution of the molybdenum speciation between batch M and B, and between as-synthesized and oxidized samples. On the other hand, the evolution of Ru speciation seems very small or negligible.

The analysis and interpretation of the data on the other FPs is still ongoing, and the results are being coupled with several laboratory and synchrotron techniques such as EPMA, Raman microscopy, and Synchrotron Powder XRD.
The experiment A20-1857 (March 2023) investigated through HERFD-XANES some of the crucial element of our samples, such as Ba and Ce, supplying complementary information to this present experiment.

The complete set of the data will be published by the second quarter of 2024.

[1] Y. Guerin. Compr. Nucl. Mater., 2012.
[2] E. Geiger et Al., J. Nucl. Mater., 2016.
[3] C. Le Gall, PhD thesis, Grenoble Alpes, 2018.
[4] R. Caprani et Al., J. Nucl. Mater., 2023.
[5] E. Epifano, PhD thesis, 2017.