EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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:** Speciation and microstructure effect of fission products in uranium plutonium mixed oxide fuel under strong oxidation conditions	**Experiment number**: A20-1857
Beamline: BM20 - ROBL	**Date of experiment**: from: 01/03/2023 to: 06/03/2023	**Date of report**: 28/07/2023
Shifts: 15	**Local contact(s)**: Kristina Kvashnina, Elena Bazarkina, Damien Prieur	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

This work is the follow up of exepriments MA-5032 and MA-5456.

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.

In this experiment we analized samples from each of the four composition (REF, S, M, and B) before, and after the oxidation treatment. The total number of samples is therefore 8. The samples 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 <u>not</u> been oxidized, while sample “M-OX” has composition M and has been oxidized (-OX).

For each sample, the XANES has been collected in HERFD mode for the following edges: UM$_{\mathrm{IV}}$, PuM$_{\mathrm{IV}}$, BaL$_{\mathrm{III}}$, CeL$_{\mathrm{III}}$, LaL$_{\mathrm{III}}$, and NdL$_{\mathrm{III}}$ edges. The analysis of AmM$_{\mathrm{IV,V}}$ edge has not been possible due to its low concentration in the samples.

The data of the U M$_{\mathrm{IV}}$-edge XANES is presented in Figure 1. It is clear that the oxidation state of uranium changes drastically with the oxidizing treatment. The shape of the spectrum for sample S is consistent with a majority of U(IV) and a small fraction of U(V). On the other hand, after oxidizing treatment (sample S-OX), almost all uranium atoms seems to be U(V).

No significant evolution is observed in plutonium spectra, which are consistent with 100% of Pu(IV).

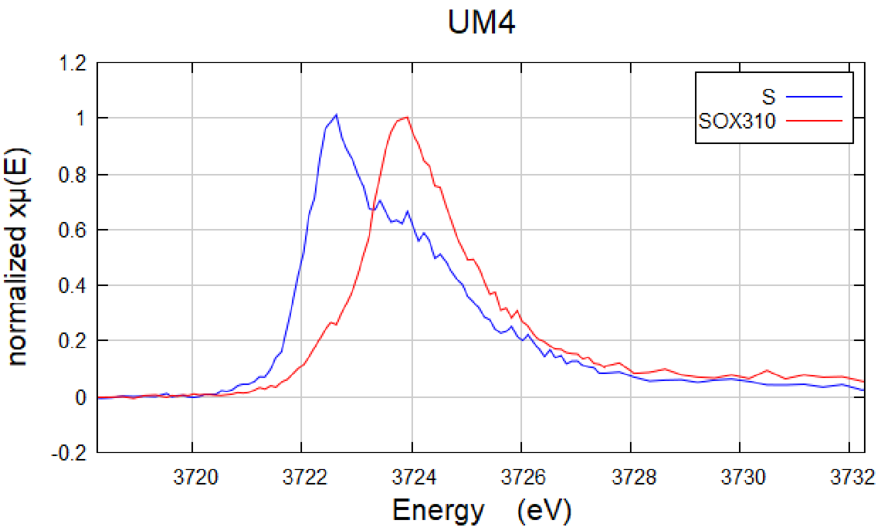

Figure 1 HERFD-XANES collected at the U M$_{\mathrm{IV}}$-edge for samples S (blue) and SOX310 (red).

Figure 2 presents the HERFD-XANES spectra collected at Ba L$_3$-edge and Ce L$_3$-edge. For each edge, the signals before (blue) and after (red) oxidation are compared. Some experimentally acquired spectra of reference compounds are also plotted alongside the samples spectra.

We can observe that Ba speciation remains unchanged after the oxidizing treatment, and can be consistent with a perovskite-type compound.

Before oxidation, Ce looks as a mixture of Ce(III) and Ce(IV), as expected for this kind of samples. After oxidation, Ce speciation changes drastically, revealing a possible de-splitting of the two distinct feature highlighted by the CeO$_2$ reference.

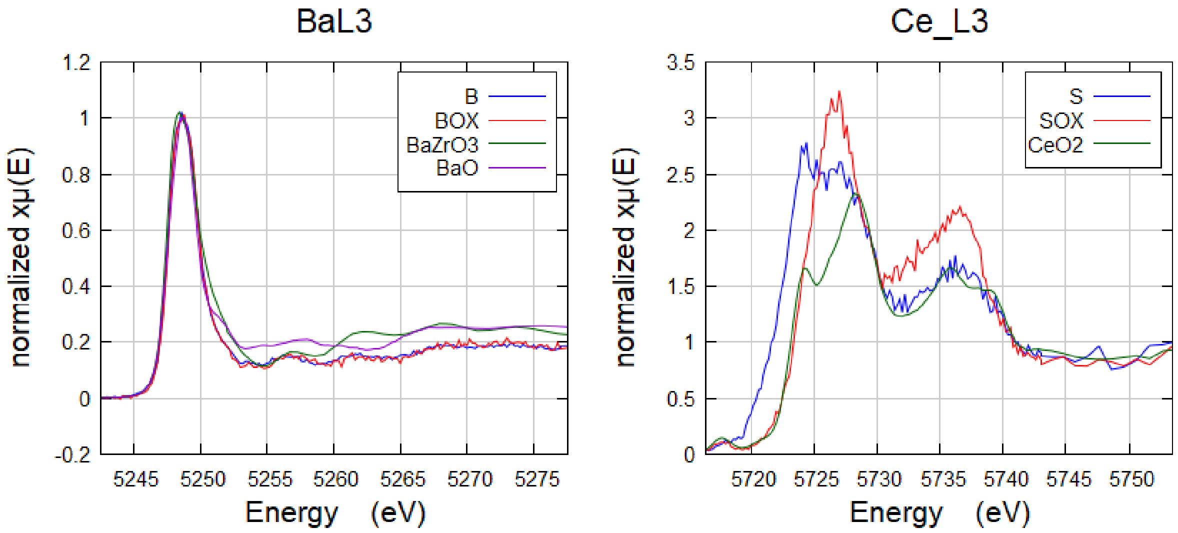

Figure 2 XANES spectra collected at the Ba L$_3$-edge (left) and at the Ce L$_3$-edge (right). For each edge, the signals before (blue) and after (red) oxidation are compared. Some experimentally acquired spectra of reference compounds are also plotted.

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 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.