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:** Speciation and microstructure effect of fission products in uranium plutonium mixed oxide fuel	**Experiment number**: MA-5032
Beamline: BM20	**Date of experiment**: from: 03/11/2021 to: 09/11/2021	**Date of report**: 04/03/2021
Shifts: 18	**Local contact(s)**: Damien Prieur	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

R. Caprani[1,2,3]*, P. Martin[1]*, J. Martinez[1]*, S. Orlat[1]*, JR Sevilla[1]*

[1]CEA Marcoule – DES/ISEC/DMRC, Univ Montpellier, BP 17171, F-30207 Bagnols-sur-Cèze, France

[2]Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, P.O. Box 10119, 01314 Dresden, Germany

[3]University of Montpellier, Department of Chemistry ESCB, 226-234 Av. du Professeur Emile Jeanbrau, 34090 Montpellier, France

Report:

Innovative mixed oxide (MOX) (U,Pu)O2-x fuels for both thermal and fast neutron reactors are currently studied within the framework of the development of a more sustainable nuclear fuel cycle. In order to improve and ensure the safety of a power plant, it is necessary to have a deep understanding of the properties of the (U,Pu)O2-x fuel at every stage of its life inside the reactor. 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. The presence of Pu inside the matrix has been proven to have deep consequences on the chemical, physical, and microstructural properties of the material. 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 to the understanding of the MOx fuel behaviour during irradiation.

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.
Two batches of SIMfuel samples have been fabricated at CEA Marcoule with the following compositions (called S and M) given in Table 1 below (g/g %).

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

	Ba	Ce	La	Mo	Nd	Pd	Rh	Ru	Sr	Y	Zr	U	Pu	Am
S	-	0.88	0.43	-	2.1	-	-	-	0.11	0.11	1.00	61.1	20.99	0.43
M	-	0.84	0.44	1.45	1.96	0.8	0.34	1.49	0.12	0.10	1.18	58.63	20.24	0.41

On each batch, different thermal treatments were applied in order to simulate different temperatures (1100 – 1700 °C) and oxygen potential conditions (from -6 to -500 kJ/mol), corresponding to different nominal and accidental conditions such as Loss Of Coolant Accident (LOCA).
The name and characteristics of the thermal treatments is shown in Table 2.

Table 2 Parameters and goals of the implemented thermal treatments.

Thermal treatment name	Temperature (° C)	Duration (hours)	Oxygen potential (kJ/mol)	Goal of the treatment
ST	1700	4	-383	Investigating th effect of O/M=2.00
RE	1100	24	-534	Investigating th effect of O/M=1.98
OX	200	168	-6	Simulating cladding failure in geological repository
AC	1100	4	-354	Simulating start of oxidizing phase in Loss Of Coolant Accidents (LOCA) scenarios

The total number of samples was then 8, having two different compostion to which four thermal treatments were applied. Moreover, some reference samples have been added in order to help in the data interpretation, bringing the total number of studied samples to 13. The sample naming scheme is strightforward: *composition name* + *annealing name*, e.g. the sample M-ST corresponds to the sample with composition M to which conditions ST have been applied.

For each sample, fluorescence and transmission signal have been collected for all elements in the material. The studied edges are UL_{III}, PuL_{III}, AmL_{III}, YK, ZrK, MoK, RuK, RhK, PdK, and SrK. A problem of vacuum in the synchrotron ring caused the loss of about 10 shifts over the total of 18 assigned. This issue forced us to collect only XANES signal, and post-pone the EXAFS collection to future experiments. Finally, the quality of the collected signal on the sample M-OX is insufficient to perform any analysis. This is probably due to a previously undetected problem encountered during the XAS sample fabrication.

First, we collected XANES spectra at the U, Pu and Am L_{III} edge in order to determine the O/M ratio of these species as consequence of different annealing conditions (temperature and oxygen potential). Example of XANES signals collected is shown in Figure 1 (UL_{III} edge). With XANES data we were able to obtain the average oxidation state of each actinide (U, Pu, Am) in the samples, and then compute the O/M ratio, resumed in Table 3.

Table 3 Average O/M of U, Pu, Am, and total for each sample.

Sample	O/U	O/Pu	O/Am	O/M
S-ST	2.038	1.942	1.500	2.011(5)
S-RE	2.003	1.926	1.500	1.981(5)
S-OX	2.443	1.944	1.500	2.311(5)
S-AC	2.058	1.946	1.500	2.027(5)
M-ST	2.061	1.991	1.504	2.040(5)
M-RE	2.012	1.932	1.500	1.989 (5)
M-AC	2.052	1.949	1.500	2.023 (5)

As shown from the results, Am is always found in +3 state, regardless of fabrication temperature and oxygen potential. This is suggesting that Am is always found in its +3 state in nuclear fuel, in all the range of parameters studied.
Furthermore, for all samples the ratios O/U and O/Pu are always >2 and <2 respectively, showing the presence of both U(V) and Pu(III). This particular phenomenon is still under investigation, but our data strongly suggest the presence of U(V) even in regime of hypostoichiometry (O/M<2), and the presence of Pu(III) even in hyperstoichiometry (O/M>2).

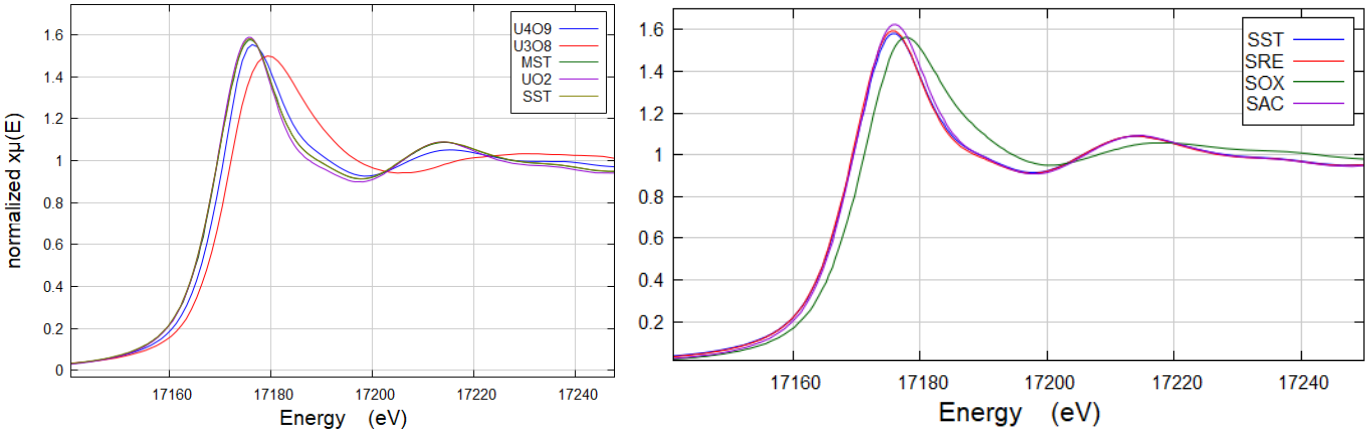

Figure 1 XANES UL_{III} spectra of selected samples and references.On the left a comparison between the samples S-ST and M-ST with the main U compounds of interest. On the right, the effect of the thermal treatments on the samples of composition S is shown.

Lastly, the XANES signal has been collected at the K-edges of Mo, Ru, Rh, Pd, Sr, Zr, and Y. Thermodynamical modelling shows that Pd, Ru, and Rh should always be in their metallic state, forming intermetallic alloys [3]. This is confirmed by the data for all the samples containing them (M-ST, M-RE, M-AC)
The other dopants exhibit peculiar behaviour, due to their rich chemistry. The data concerning these elements are still being treated.
Future experiments for the acquisition of the EXAFS signal will help the interpretation of the XANES dat collected during this experience.

Collection of the EXAFS signal is scheduled to take place at the BM20-ROBL between the 12th and the 19th of April 2022.

[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.