![ESRF logo] **ESRF**	**Experiment title:** Fission Products behavior in conditions reproducing Severe Accidents: the Cs speciation and its interaction with Mo, into UO$_2$ SIMFUELS synthesized via Spark Plasma Sintering	**Experiment number**: 16-01-808
Beamline: BM16	**Date of experiment**: from: 24/11/2021 to: 06/12/2021	**Date of report**: ~~17~~30/0~~4~~5/2022
Shifts: 18	**Local contact(s)**: Jean-Louis Hazemann	*Received at ESRF:*
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Objective

The objective of the project was to determine Fission Products (FPs) behavior in conditions representative of a Severe Accident (SA) of a nuclear LWR reactor. This will help improving the actual understanding on the FPs release mechanisms and confirming or not the hypothesis on which some codes for SA scenario predictions are based. Within this frame, the goal of this experiment was to study caesium speciation. Four SIMFUEL samples were thermally treated to simulate intermediate steps of a SA scenario. Three temperatures were used for the thermal treatments, that are 750°C, 900°C, 1200°C (T$_0$, T$_1$, and T$_2$, respectively) and the $\Delta G(O_2)$ ranged between -450 kJ/mol to -350 kJ/mol. All the samples were composed of a UO$_2$ matrix doped with different Cs-compounds, as reported in **Table 1**~~Table 1~~.

The aim of the analysis was to conclude on the Cs local structure and in particular the effects of the thermodynamic conditions and the presence of Mo. Indeed, according to the model of the fission products release, an interaction between Cs and Mo could occur in the steps of a SA, but this was never experimentally observed in the Light Water Reactors (in contrast to fast neutrons reactors, where Cs$_2$MoO$_4$ is well known).

Materials and Methods

High Energy Resolution Fluorescence Detection (HERFD) XANES have thus been performed at Cs L2 edge (5359 eV). The FAME-UHD beamline is equipped with a 14-crystals CAS (crystal analyser spectrometer) made of two horizontal arrays with seven Si 400 crystals each. The configuration determines a Bragg's angle of 81.38°. The beam had a rectangular size of 300 μm x 200 μm (width x height), but the samples were oriented at 45° with the respect of the longitudinal direction. In addition, the setup is completed by the helium box, which contains the crystals and most of volume between the sample and the detector. Thanks to an adjustable window made of Kapton, the photons can travel for most of their path inside helium, reducing the absorption in air to the minimum.

UO_2 pellets with Cs-compounds (wt% concentration)	750°C (T$_0$) $\Delta \overline{G}$(O2) (kJ/mol)	900°C (T$_1$) $\Delta \overline{G}$(O2) (kJ/mol)	1200°C (T$_2$) $\Delta \overline{G}$(O2) (kJ/mol)
(CU samples) 5% Cs_2UO_4	-442 -386	-443	-439
(CU$_2$ sample) 5% $Cs_2U_2O_7$	-	-	-437
(CM samples) 5% Cs_2MoO_4	-372	-450	-446
(CU$_2$M samples) 2% $Cs_2U_2O_7$ + 2% MoO_2	-395	-442 -373	-436

The samples were kept into small resin blocks obtained by cutting the larger resin matrix used for polishing. Figs. 1 (a-b) report the resin block in light green, containing the polished sample, in black. Fig.1-c shows the sample holder used for XANES (in this case the block-sample is wrapped into a 8 μm Kapton foil).

The data analysis was performed in Larch, an evolved program of the more known Athena software.
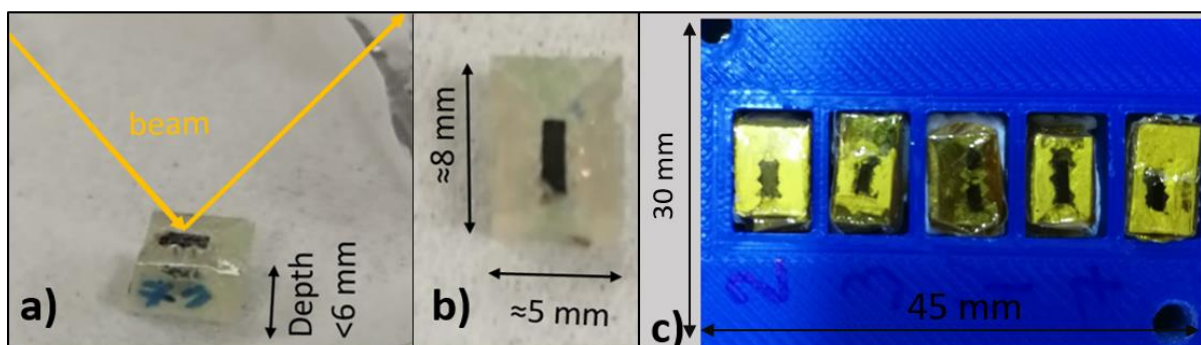
Figure 1 (a-c). Resin block containing the pellet with top polished surface (a-b). Sample holder for XANES experiment (c)

Results

The first analysis concerned the references samples, i.e. those pellets made of pure Cs-compound diluted into a BN matrix. For this experiment three references were available: Cs_2UO_4, $Cs_2U_2O_7$, and Cs_2MoO_4.

Figure 2 (a-b) reports the reference spectra: a small difference between Cs_2UO_4 and $Cs_2U_2O_7$ can be noticed, whereas a more specific features result from Cs_2MoO_4 spectrum which shows a much lower white line intensity and different oscillations after the edge.

This type of result is absolutely new because such differences were never noticed in previous analyses at Cs L_2/L_3 edges. A more detailed analysis of the local structure showed that Cs in Cs_2MoO_4 has a higher number of O neighbors and with a more dispersed distribution of the Cs-O bond, in comparison with the Cs_2UO_4 and $Cs_2U_2O_7$ structures. A direct comparison is shown in
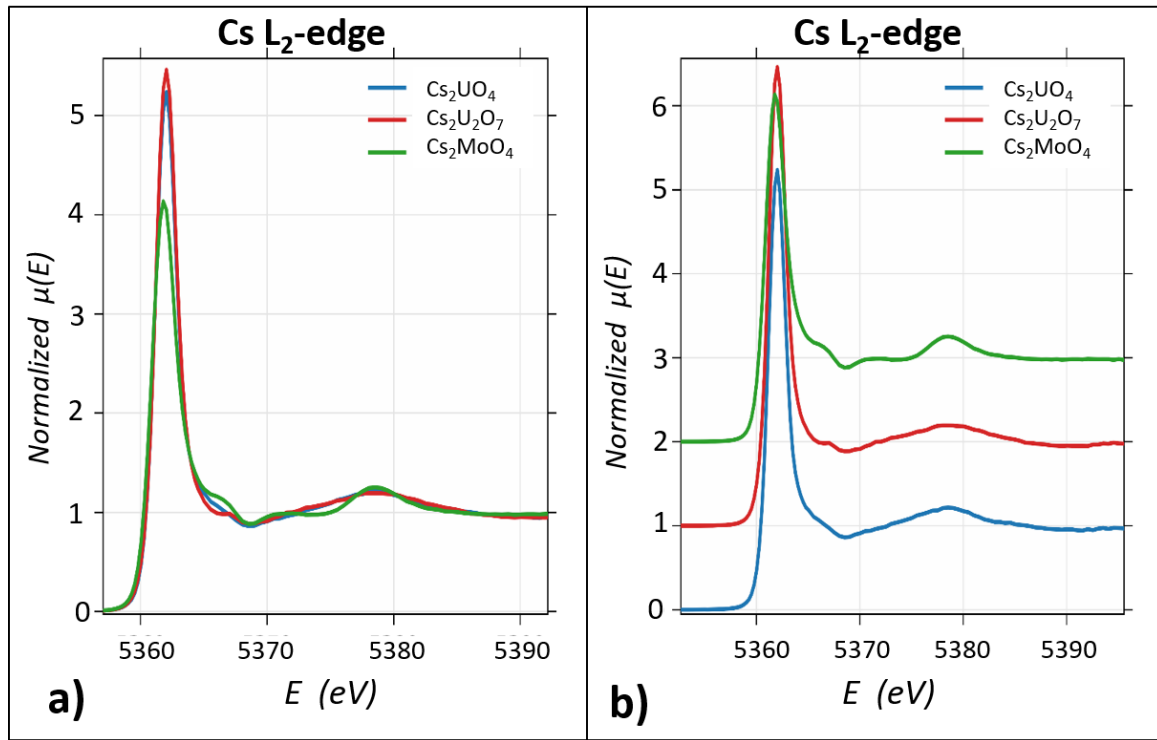

Figure 2 (a-b). Comparison of superimposed references spectra (a) and displaced spectra (b)

Figure 3 below, where Cs_2MoO_4 and $Cs_2U_2O_7$ structures are compared.
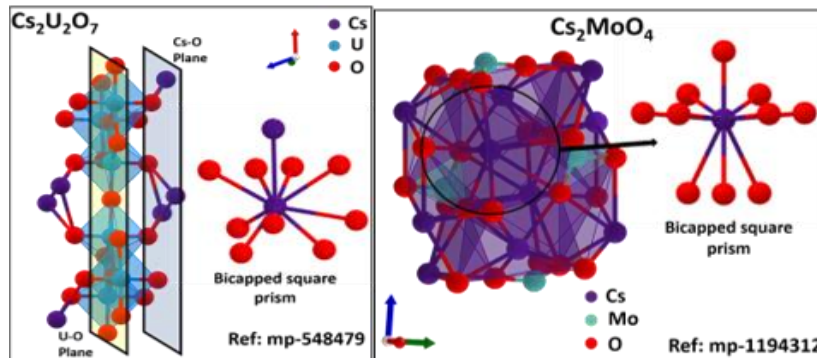

Figure 3. Left: $Cs_2U_2O_7$ structure (9 O neighbors). Right: Cs_2MoO_4 structure (10 O neighbors).

Based on these features it was possible to differentiate the Cs_2MoO_4 structure in the real SIMFUEL samples. Nevertheless the pure Cs_2MoO_4 compound spectrum was never obtained because the present Cs_2MoO_4 interacted with the UO_2 matrix decomposing partially with the following formation of a Cs-uranate type structure. The linear combination (LC) fitting was then applied to determine the percentage of contribution of both the references (pure compounds) structures to the real SIMFUEL samples.

As general observation the concentration of Cs did not result homogeneous in the samples, as it was observed by the varying number of counts with the position. An example of the spatial scan

of one pellet is given in Figure 4: the SEM-EDX image on the bottom confirms the inhomogeneous Cs presence, noticed also with the XAS analysis.
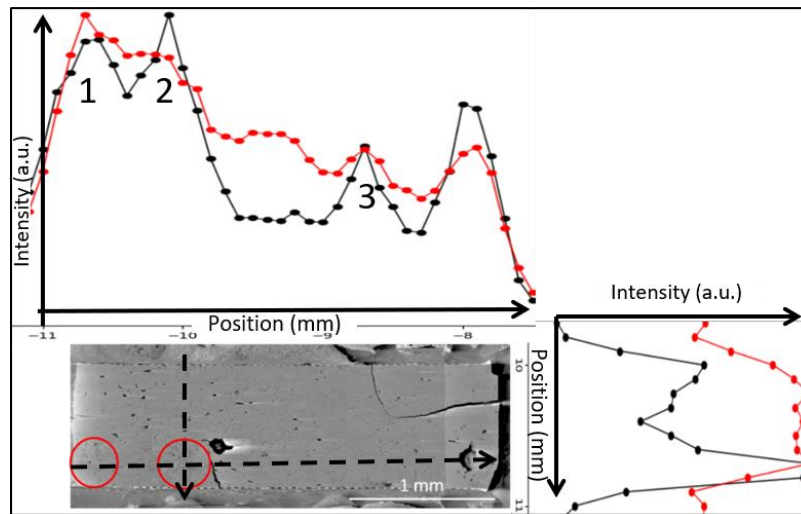

Figure 4. **Example of inhomogeneous Cs concentration where the red line indicates the fluorescence signal coming from the UO_2 matrix, while the black curve refers to Cs signal. The different peaks in black indicate a higher Cs concentration.**

Figures 5-8 show the results of the different SIMFUEL samples for each composition in comparison with the reference spectra. Cs_2O spectra was calculated with the FDMNES code.

For some samples more than one spectrum is collected for each condition, because of the different Cs concentration, which sometimes lead to evident differences of the resulting spectrum.
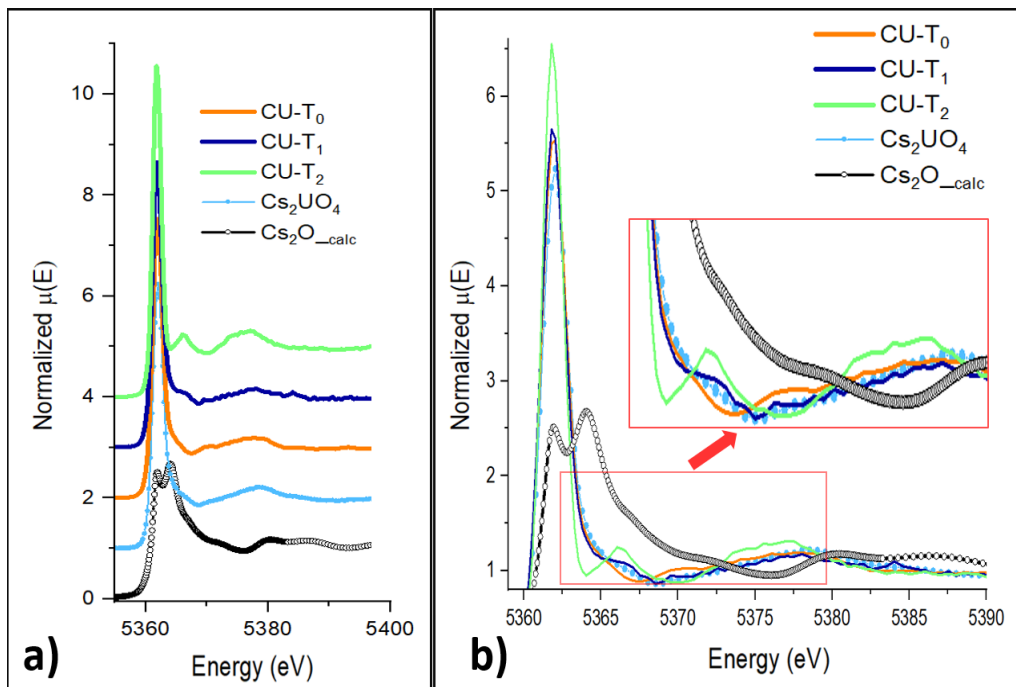

Figure 5. Samples CU (5 wt% Cs_2UO_4) compared with the Cs_2UO_4 reference and the calculated theoretical spectrum of Cs_2O
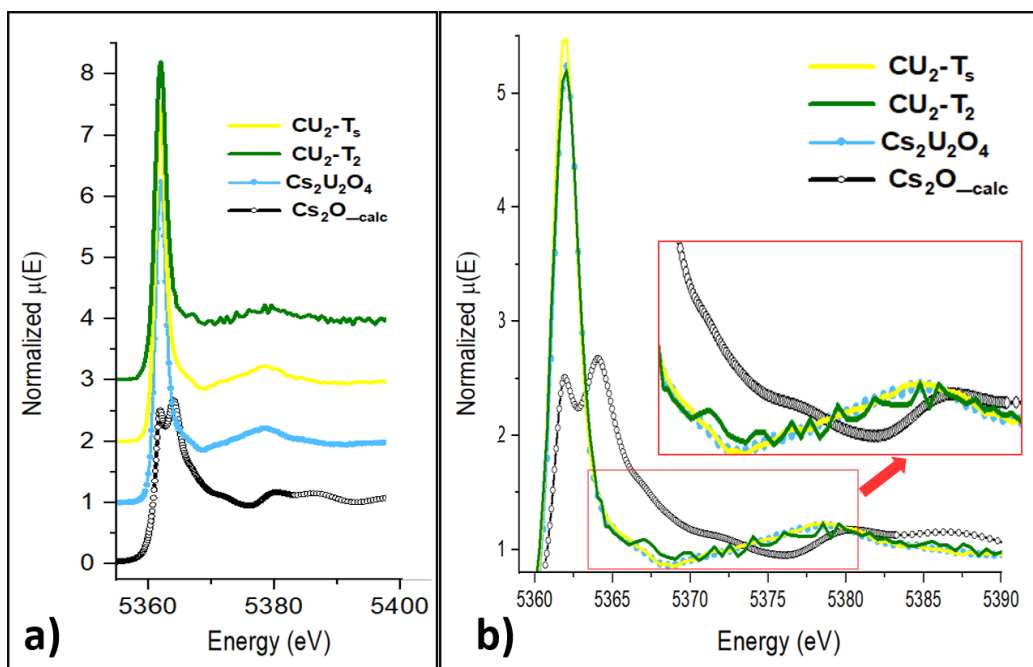
Figure 6. Samples CU₂ (5 wt% Cs₂U₂O₇) compared with the Cs₂UO₄ reference and the calculated theoretical spectrum of Cs₂O
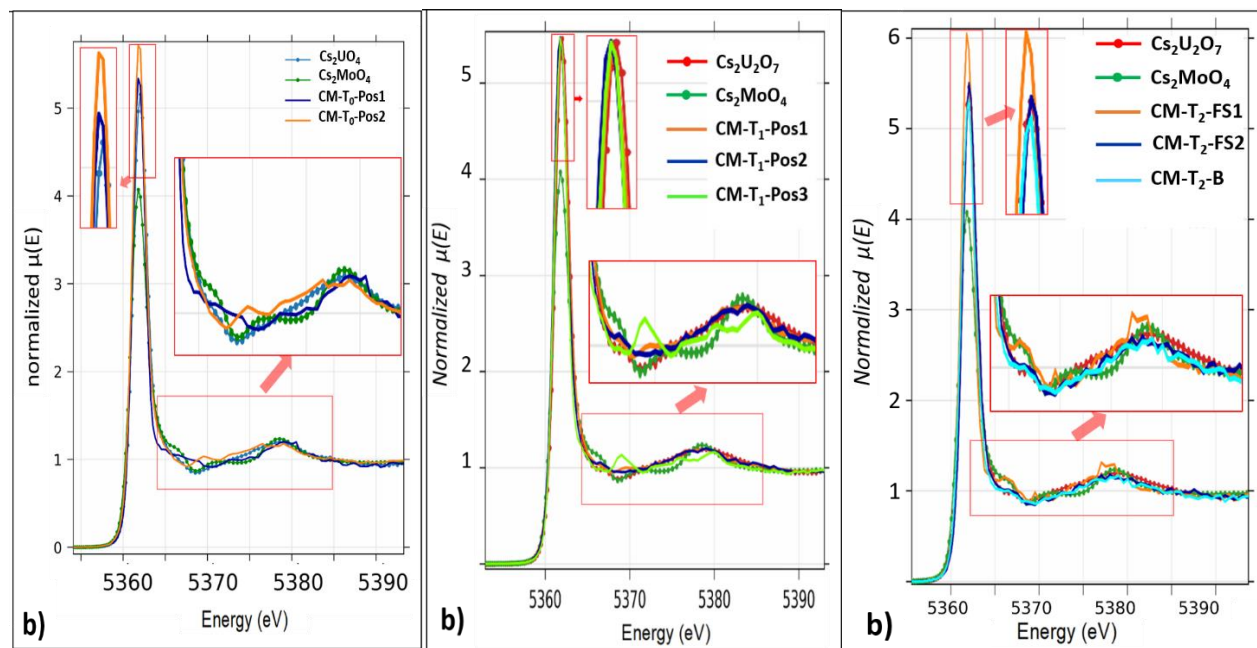
Figure 7. Samples CM (5 wt% Cs₂MoO₄) compared with the Cs₂UO₄ and Cs₂MoO₄ references
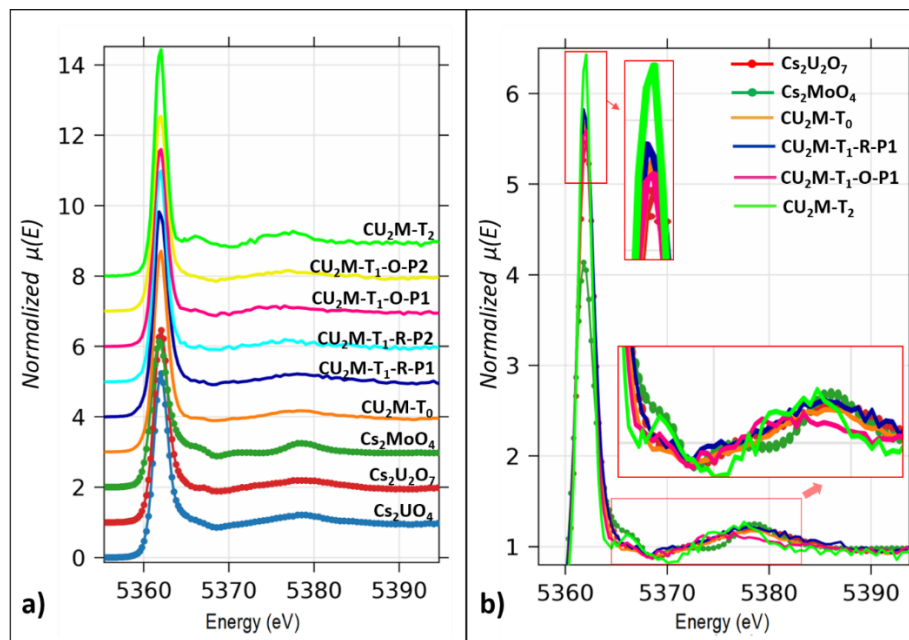
Figure 8. Samples CU₂M (2% Cs₂U₂O₇ + 2% MoO₂) compared with the Cs₂UO₄ /Cs₂U₂O₇ and Cs₂MoO₄ references

FINAL CONCLUSIONS

- The Cs_2MoO_4 reference shows important differences compared with the Cs-uranate references. The high number of counts (>8000 cts at 5.4 keV) ensures that these differences are real;
- Often the Cs is found concentrated to the edges of the pellet, suggesting a migration during the thermal treatments;
- Sometimes within the same sample, two positions show important differences in their spectra. Normally a correlation can be noticed between number of counts and spectrum (similar number of cts have similar spectra);
- The $UO_2+Cs_2MoO_4$ (CM) samples (750-900-1200) do not show pure Cs_2MoO_4 characteristics, especially the intensity. However the LC fitting allows to determine a contribution of Cs_2MoO_4 spectrum between 16% to 49% compared with Cs_2UO_4 reference. The thermal treatment must have influenced the Cs environment causing a decomposition and interaction with the UO_2 matrix.
- For T_2 (1200 °C) the deepest change from the reference can be noticed, demonstrating the effect of temperature on the Cs environment: the spectra tend to have a much higher white line intensity and a different oscillation, independently on the initial presence of Mo. This suggests that at 1200°C either another unknown Cs-uranate or Cs-oxide structure is formed;
- By adding Mo K edge analyses it would be possible to have more reliable conclusions.