



Experiment title:

HERFD-XAFS analyses on SIMFUEL samples submitted to annealing treatments in conditions representative of those of severe accident

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30-02-113

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BM30B

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Report:

The objective of the project is to determine Fission Products (FPs) behavior in conditions representative of a Severe Accident (SA) of a nuclear PWR reactor. This will help improving the actual understanding on their 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 Ba speciation. Four SIMFUEL samples were treated in different conditions representative of a severe accident. They were composed of a UO₂ matrix doped with 12 oxides as FP surrogates (**Table 1**). The first sample (T₀) was left as-sintered and the three others were heated up to 300, 1200 and 1700°C under pure Ar.

Table 1: SIMFUEL composition (concentration in at%)

Sample composition (at.%)											
Ba	Ce	Cs	La	Mo	Sr	Y	Zr	Rh	Pd	Ru	Nd
0.26	0.61	0.35	0.20	0.61	0.13	0.06	0.60	0.03	0.42	0.64	0.91

The mechanism proposed in the literature for its release under oxidizing conditions indicates that it is initially present in the fuel as BaO. Between 1100 and 1500°C, Ba is normally found in an oxide phase with a perovskite structure described as (Ba, Cs, Sr)(Mo, Zr, U, RE)O₃ [1]. BaMoO₄ is also present at these temperatures. Above 1500°C BaZrO₃ disappears and all the Ba is found as BaMoO₄ [2].

Previous studies led on SIMFUEL samples by mean of XAS [3] showed that the initial state sample (sample T₀) contained Ba under the oxidized form +II. Moreover, in this sample, Zr oxidation state and environment is characteristic of a perovskite structure.

Thermodynamic estimations using the FACTSAGE software coupled with the SGPS database predict the existence of BaMoO₄ in the three thermally treated samples. Studies at Mo K-edge on the samples O1200°C and O1700°C showed that part of the Mo is actually present under the oxidation states +VI [4]. Moreover, as shown on **Figure 1**, Ba precipitates with Zr in the T₀ sample and with Mo in the sample heated up to 1700°C.

High Energy Resolution Fluorescence Detection (HERFD) XANES have thus been performed at Ba L₃ edge using a He bag. The Crystal Analyzer Spectrometer (CAS) was constituted of five Ge(400) crystals with a Bragg angle of 79° and the fluorescence signal was recorded with a VORTEX Si detector.

This experiment had many interests. First, it helped probing a diluted element in a crystalline UO₂ matrix. Then, it allowed separating the contributions of the different emitting elements (notably Cs and La) to the fluorescence. Finally, as the energy resolution is better than that of a Solid State Detector, it will enable a better interpretation of the XANES signal [5,6].

To illustrate this point, spectra obtained both in fluorescence (using the CAS) and in transmission mode (using Si diodes) on a BaZrO₃ reference sample are plotted on **Figure 2** (left). The narrower and more intense white line and the better resolved peaks from 5255 to 5280 eV prove that the resolution achieved with the CAS is far better.

The XANES spectra obtained for T₀ and O1700°C samples are plotted on **Figure 2** (right). E₀ of every sample is similar confirming that Ba is in oxidation state +II as expected for an alkaline earth element (**Table 2**). An evolution of Ba is clearly visible between both samples. The shape of the T₀ spectra is close to, but broader than the BaZrO₃ spectrum one. Concerning the O1700°C spectrum, it is similar to but more intense than the BaMoO₄ one.

Unhappily, one of the reference sample expected (BaMoO₃) had been synthesized but was not stable enough to be used for the experiment. Its XANES spectrum will be calculated thanks to FDMNES and compared to the samples spectra. More time will thus be needed for the experimentalists to fully exploit the data. Yet, more beam time is needed on FAME to complete the results obtained.

- First, EXAFS spectra should be collected. Indeed, those recorded in this experiment are poor quality spectra. Performing EXAFS on these samples is of high interest because it may bring direct experimental evidence on the nature of the neighbors of Ba and on the structure in which it is involved.
- Then, EXAFS spectra are required at the K-edge of Mo (20 keV). This would bring complementary information to support the existence of BaMoO₄ in the O1200 and O1700 samples. Time was requested in the proposal 30-02 113 to carry out this experiment but not enough time was left to get the spectra. The future proposal could also include measurements at the K-edge of Zr (17.998 keV) as far as it seems to precipitate with Ba in samples T0 and O300.
- Finally, beam time will also be requested to perform μ-XAFS (XANES and EXAFS) directly on the precipitates containing Ba on ID21 (**Figure 1**). These analyses will enable to better characterize these precipitates by avoiding averaging the signal on the whole sample and will also limit the absorption of the U-bearing matrix.

[1] H. Kleykamp, *J. Nucl. Mater.* 131 (1985) 221–246

[2] E. Geiger, *PhD thesis*, Université Paris-Saclay (2016) Available

[3] E. Geiger et al. *J. Nucl. Mater.* 471 (2016) 25–33

[4] E. Geiger et al. *J. Phys. Conf. Ser.* 712 (2016) 012098

[5] I. Llorens et al. *Rev. Sci. Instrum.* 83 (2012) 063104

[6] J.-L. Hazemann et al. *J. Synchrotron Radiat.* 16 (2008) 283–292

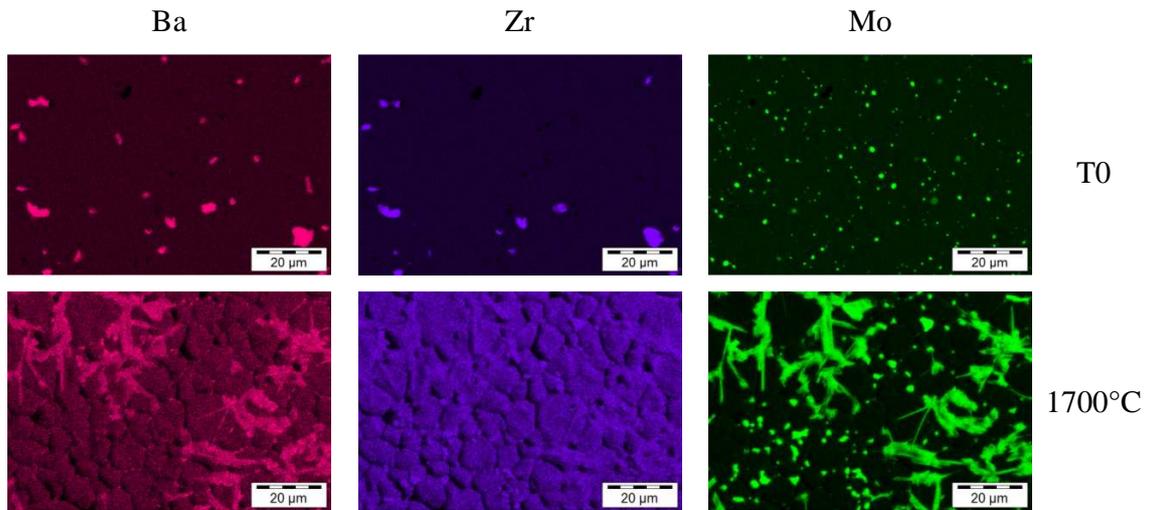


Figure 1: Ba (left hand side), Zr (middle) and Mo (right hand side) X-ray maps collected on samples T_0 (top) and $O1700^\circ\text{C}$ (bottom)

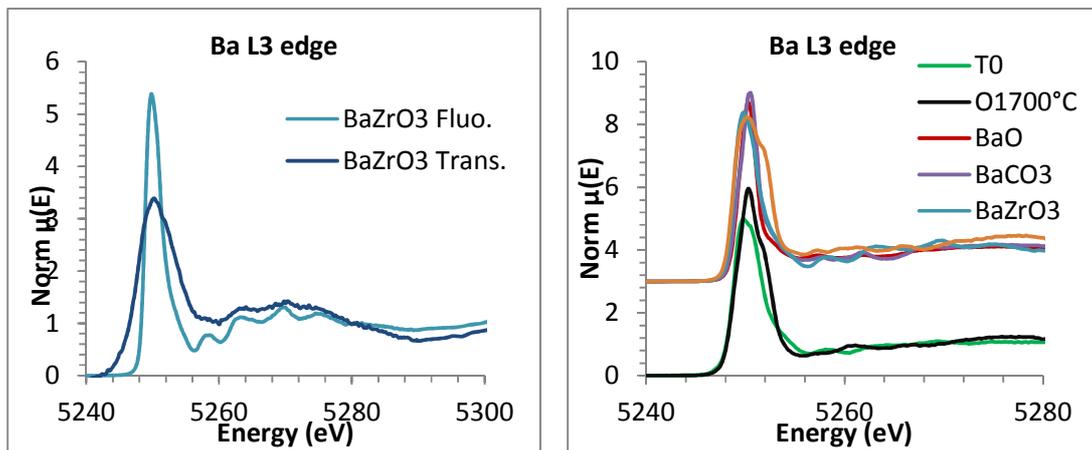


Figure 2: HERFD XANES spectra collected at Ba L3 edge on a reference sample containing 1wt% of BaZrO_3 diluted in BN (left hand side) and on samples T_0 , $O1700^\circ\text{C}$ and several reference samples (right hand side)

Table 2: E_0 and white line position of samples T_0 and $O1700^\circ\text{C}$ XANES spectra

Spectrum	$E_0 (\pm 0.25\text{eV})$	White line ($\pm 0.25\text{eV}$)
T_0	5248.85	5249.81
$O1700^\circ\text{C}$	5248.75	5250.32
BaO	5249.41	5250.29
BaCO_3	5249.01	5250.45
BaZrO_3	5248.84	5249.81
BaMoO_4	5248.60	5250.12