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An innovative Method to study Volatile Fission Products speciation in nuclear fuels under Severe Accident Conditions

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Abstract

The development of realistic models for fission products behavior during a severe accident requires experimental data on fission products speciation into the fuel (as irradiated and during the transient) together with thermodynamic predictions. Due to the limitations in terms of experiments and characterization techniques available to study fission products speciation in nuclear irradiated fuels, simulant materials (SIMFUEL manufactured thanks to conventional process) are often used. However, these materials do not allow the study of volatile fission products because they are totally released during the sintering stage. In the case of SIMFUEL with implanted fission products surrogates, the chemical state and the corresponding evolution of the phases during the thermal sequence are not entirely representative of the real case. An innovative method to study volatile fission products speciation in SIMFUEL samples has thus been developed. Spark plasma sintering was used to synthesize dense SIMFUEL samples containing cesium in collaboration with the JRC-Karlsruhe within the frame of the GENTLE program. Thermodynamic calculations made using the TAF-ID v.6 associated with the FACTSage software enabled to determine the conditions in which to perform thermal treatments. In-temperature XAS experiments in conditions representative of a severe accident are developed in collaboration with FAME-UHD beamline at the ESRF (Grenoble, France). Additional thermal treatments will also be performed to enable further characterizations (ceramography, SEM-EDX...).

Keywords: Severe accident, Fission products, volatile, Cesium, SPS, in-situ XAS

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Introduction

During irradiation cycles of nuclear fuel in a reactor, Fission Products (FP) are created and retained in the fuel, modifying its microstructure and properties (thermal conductivity, creep behavior...). In case the three containment barriers would fail, as it might be the case during a Severe Accident (SA), FP can be released from the fuel into the environment. Their chemical nature and the quantities released (source term) at these stages strongly depend on the scenario and the accidental conditions involved (temperature, type of fuel, burn-up, oxygen potential...). A deep understanding of FP release mechanisms out of the fuel is thus essential to get a realistic estimation of the source term and to be able to better predict the consequences of the accident.

Therefore, many research programs on irradiated fuels have started worldwide, leading to a better understanding of FP behavior during temperature transients under a controlled atmosphere. A classification of FP according to their volatility has also been proposed largely thanks to the HEVA/VERCORS programs, launched by the CEA in 1989 [1]:

- Volatile (Xe, Kr, I, Cs, Sb, Te, Cd, Rb, Ag);
- Semi-volatile (Mo, Rh, Ba, Pd, Tc);
- Low-volatile (Ru, Ce, Sr, Y, Eu, Nb, La);
- Non-volatile (Zr, Nd, Pr).

To go further, getting experimental data on FP speciation and confronting them to thermodynamics predictions are necessary. Complementary to irradiated fuels studies, the use of SIMFUEL makes it possible to investigate FP speciation by means of powerful techniques such as X-ray absorption spectroscopy [2]–[4]. A model based on experimental observations performed on irradiated fuels, SIMFUEL and thermodynamic calculations has thus been proposed to explain the released fractions during a VERCORS-like sequence [3], [5]–[8]. According to this model, reactions between FP and other structural materials take place at different temperatures, strongly influenced by the oxygen partial pressure.

Among the volatile FP, Cs is of great interest for it has a high fission yield and might present a huge radiological impact on the environment and on population on the long term. It is also able to interact with other FP and change their release kinetic. Indeed, it can react with Mo and U to form cesium molybdates or uranates and can also be found in oxide precipitates along with Ba and Zr [5], [9], [10]. However, some major uncertainties still remain notably concerning Cs behavior. Indeed, the conventional way to synthesize SIMFUEL does not allow volatile FPs to remain in the UO₂ matrix as they are released during the sintering process (1650°C, 4h). In the case of implantation processes, the evolution of the phases during the thermal sequence is not representatively reproduced [8], [11], [12].

Recently, SPS was successfully used to synthesize dense UO₂ pellets containing CsI [13]. The objective of the present work is to investigate the possibility of studying Cs behavior inside more representative samples towards irradiated fuels. To this end, an innovative approach which will be described in this paper has been developed and lies on:

- The syntheses of SIMFUEL samples containing Cs, Mo, Ba and Zr through SPS at the Joint European Commission (JRC) Karlsruhe, Germany;
- Thermodynamic calculation for dimensioning the thermal treatments;
- In temperature X-ray Absorption Spectroscopy performed under controlled atmosphere on FAME-UHD beamline at the European Synchrotron Radiation Facility (ESRF);
- Additional thermal treatments performed into a dedicated furnace in the same conditions in order to verify that post-tests observations are consistent with FP states at high temperatures.

1. Experimental

1.1. Materials

In order to study Cs behavior in SA-like conditions, five batches of samples containing FP surrogates under different chemical forms have been prepared (**Table 1**). The ratios between each FP are representative of a pressurized water reactor fuel with a burn-up of 76 GWd.t_{HM}⁻¹. Only the results obtained on batch n°4 will be detailed.

Table 1: Composition of the different batches synthesized (concentrations in wt%)

Batch	UO ₂	Cs ₂ MoO ₄	Cs ₂ UO ₄	BaZrO ₃	BaMoO ₄	MoO ₃
1	99.1	0.9				
2	98.4	0.9		0.7		
3	99.8		1.2			
4	98.1		1.2		0.7	
5	98.5		1.2			0.3

Commercial depleted UO₂ was first pre-reduced at 800°C during 4h under Ar + 6.5% H₂ in order to avoid a stoichiometry gradient to appear in the pellet after sintering (**Figure 1**) [14]. The lattice parameter was determined through XRD on a Rigaken MiniFlux 600 device and the final O/M was calculated according to equation (1) [15]. It was reduced from 2.16 to 2.01.

$$a = 5.4705 - 0.132x \quad (1)$$

Commercial MoO₃ (99.5% purity, MERCK, **Figure 2**) was used as received and cesium uranate was synthesized according to the protocol described in [16]. CsNO₃ (MERK) and depleted UO₂ (Cogema) were mixed by grinding in an agate mortar and placed in a calcination furnace. The temperature was increased gradually and held at 700°C under air during 24h. The transformation of CsNO₃ was not complete at the end of the sequence (**Figure 3**) so the heating process was repeated a second time up to 800°C. A Rietveld refinement of the XRD patterns showed that a mix between Cs₂UO₄ (22%) and Cs₂U₂O₇ (75%) was obtained.

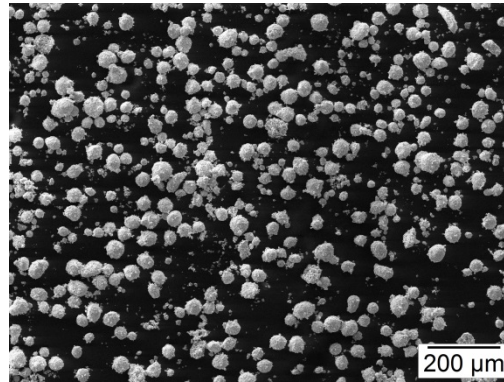


Figure 1: SEM-SE image of the pre-reduced UO₂ powder (mean ECD 30 μm)

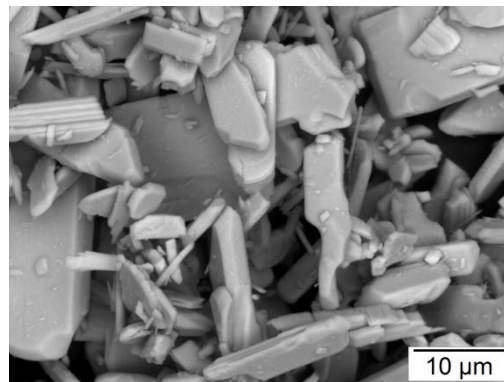


Figure 2: SEM-SE image of MoO₃ as received (mean size 12.7 μm)

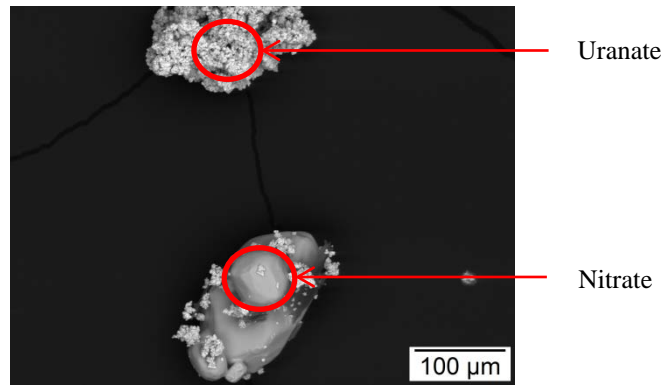


Figure 3: SEM-SE image of Cs nitrate and uranate after 24h at 700°C under air (mean agglomerate size 194.1 μm)

1.2. Syntheses of SIMFUEL samples

SPS is an electrical field assisted sintering technique that allows obtaining dense UO_2 pellets at lower temperature in a shorter time [17]. This enables the incorporation of volatile FP surrogates in the UO_2 matrix and has been deployed at the JRC-Karlsruhe to synthesize SIMFUEL samples [13].

Sample preparation was carried in a glovebox under Ar atmosphere. The additives powders were first ground separately in an agate mortar. The pre-reduced UO_2 was then added to the mixture and ground again. The powder was finally poured in a 6 mm SPS matrix containing a graphite foil. A pre-compaction was performed at 500 N (~17.7 MPa) and the following cycle was run:

- Evacuate to <10 Pa
- Press to 2.5 kN (~88 MPa) and fill the chamber with Ar
- Heat to 1200°C at 200°C/min
- Hold at 1200°C for 5 min
- Cool down at 200°C/min
- Release the pressure

The pellets were recovered and roughly polished to remove the graphite deposit on the surface. Their density was approximated by measuring their dimensions and compared to the theoretical density of the mix (equation (2)). The values varied between 68 and 90 % d_{th} depending on the mix considered: samples of batch n°4 have a density of 86.1 ± 4.3 % d_{th} .

$$d\% = 100 \frac{m}{\pi r^2 h} \frac{1}{d_{th}} \quad (2)$$

where $d_{th} = \sum_i^n d_i \text{ wt}\%_i$ is the theoretical density of the mix,
 d_i and $\text{wt}\%_i$ are the theoretical density and the weight percent of the chemical i in the mix,
 m , h and r are the mass, height and radius of the pellet resp.

1.3. Characterization of SIMFUEL samples

The first SEM observations were performed on a Tescan Vega LSH device equipped with an Oxford EDX detector. Fractured samples were used in order to get rid of the graphite layer on their surface. Acceleration tension was set to 20 kV. Semi-quantitative analyses have been performed for U, O, Mo and Cs.

2. Results and discussion

2.1. Chemical characterization

Image analysis was performed using the analySIS pro software v.5.0 from Olympus Soft Imaging Solutions. Polyhedral grains with a size from 1 to 4 μm can be seen. The average grain size was measured on 30 grains to be 2.11 ± 0.89 μm (Figure 4). A lot of pores are still visible between the grains. The observed microstructure matches the approximated density calculated for this sample (86.1 ± 4.3 % d_{th}) and confirms that the sintering was uncomplete.

Some grains containing Cs, which could be urinate precipitates, have been found in the samples (**Figure 4**). The solubility of Cs in UO₂ measured to be below 0.06wt% [6], [18] could explain the formation of Cs precipitates.

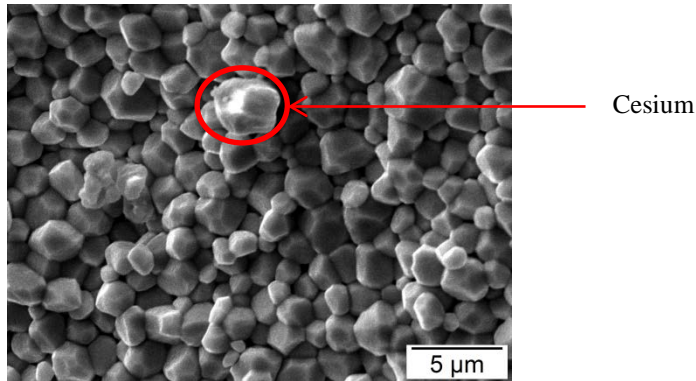


Figure 4: SEM-SE image of fractured surface of a sample from batch n°4. A grain containing Cs is indicated in red.

Melted area containing Mo can also be observed (**Figure 5**). This could be explained by the melting of MoO₃ occurring at 795°C which is well below the maximum temperature of 1200°C reached during the sintering. The atmosphere inside the SPS furnace might not have enabled the reduction of MoO₃ into MoO₂ or Mo metal (melting at 1100°C and 2617°C respectively). Furthermore, the solubility of Mo in UO₂ is below 0.002 wt% [6], [19]. The presence of Mo melted phases could thus have hindered the sintering to take place.

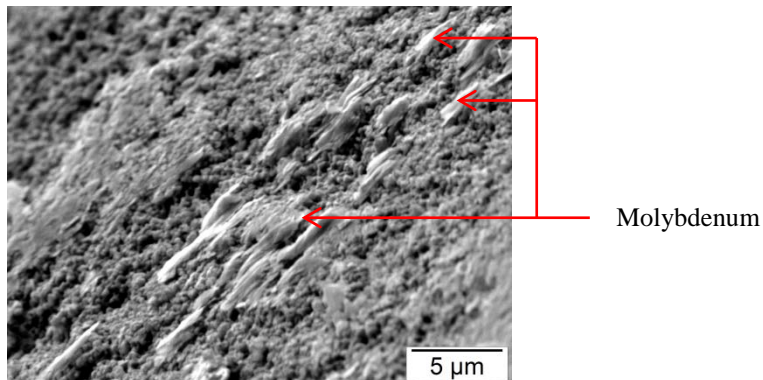


Figure 5: SEM-SE image of fractured surface from batch n°1. A melted area containing only Mo and is clearly visible.

SEM-EDX analyses and X-ray cartographies on polished samples have to be performed in order to determine accurately the initial FP state. Moreover, chemical analyses by mean of Inductive Coupled Plasma Mass Spectrometry (ICP-MS) will enable to determine the amount of Cs released during the sintering.

2.2. Thermodynamic predictions

The conditions in which the thermal treatments will be performed have been determined thanks to predominance diagrams calculated on the FACTSAGE software coupled with the TAF-ID [20]. These diagrams represent the oxygen potential vs the temperature (**Figure 6**). The brown lines correspond to the limits of the different domains. The ratio between H₂O/H₂ and CO/CO₂ are drawn as the red and blue dashed lines respectively. The black dashed line corresponds to the iso-concentration ratio between Cs₂MoO₄ and Cs in a logarithmic scale.

The objective of the thermal treatments is thus to probe the different domains of the diagrams to bring direct experimental evidence for the existence of the phases involving the FP of interest.

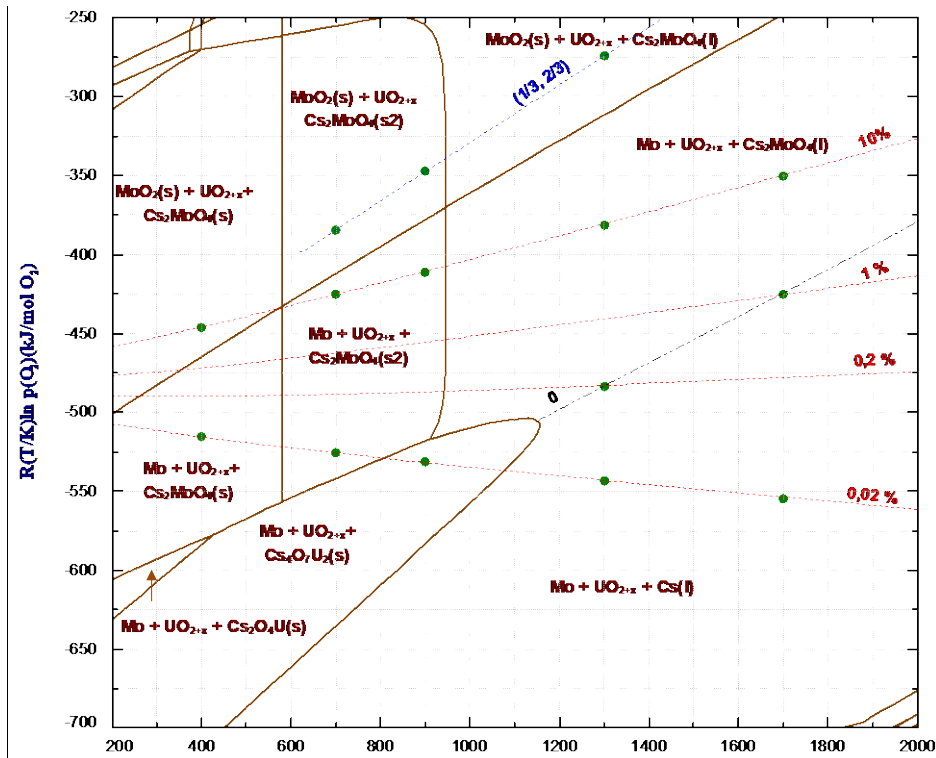


Figure 6: Mo-Cs-U-O predominance diagram, FACTSAGE coupled with the TAF-ID

2.3. In-temperature X-ray Absorption Spectroscopy

An in-temperature XAS experiment was developed in collaboration with the beamline FAME-UHD (ESRF, France). The set-up designed to perform the experiment has been extensively described in [21], [22] and used to carry out in-situ XAS experiments on radioactive materials at the INE beamline (ANKA synchrotron, Germany) [23].

The sample holder has been modified in order to handle and confine a 1 mg sample on a W-5% Re wire heated by Joule effect (Figure 7). A support has been added to avoid deformation of the wire at high temperature. The temperature is monitored during the test by both a thermocouple located beneath the sample and a pyrometer measuring the temperature at the surface of the sample. The atmosphere inside the furnace is controlled thanks to flowing gas mixtures (Ar, H₂O/H₂ or CO/CO₂).

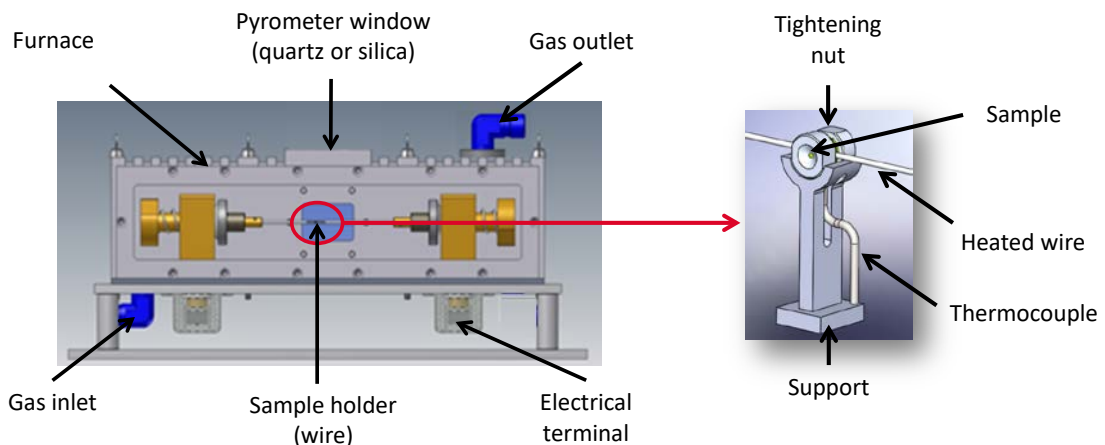


Figure 7: In-temperature XAS apparatus with a heated wire as a sample holder (left) and newly designed sample holder (right): the sample is maintained on the wire by two crimped nuts. A thermocouple is placed as close as possible of the sample. A hole in the nuts enables the X-ray beam to interact with the sample.

The experiment will be performed in High Energy Resolution Fluorescence Detection (HERFD) on FAME-UHD beamline (BM16) at the ESRF. XANES spectra will be recorded at the Cs L_{III} edge (5.012 keV). A Crystal

Analyzer Spectrometer (CAS) equipped with five Si(311) crystals will be used as it enables to probe very diluted elements in a heavy matrix [24], [25]. Successive isothermal plateaus corresponding to the green dots on **Figure 6** will be performed under different atmospheres.

To fulfill by the safety rules, a 1 mg sample (1x1x0.1 mm³) with a maximum activity of 14 Bq will be prepared and characterized through SEM before the experiment.

2.4. Additional thermal treatments

Additional thermal treatments will be performed in the DURANCE loop located at the UO₂ laboratory, CEA Cadarache, France (green dots on **Figure 6**). During these tests, the sample is placed in a metallic Mo crucible and heated in an induction furnace where the atmosphere is controlled by a gas mixture (H₂O/H₂). The temperature is measured and controlled by a thermocouple placed below the crucible and the oxygen partial pressure is monitored thanks to a MicroPoas probe (GENAIR) [26].

The samples will be then characterized through XAS, SEM-EDX and optical microscopy to complete the results obtained by in-situ XAS experiments.

3. Conclusion

An innovative method has been developed in order to study volatile FP speciation under SA conditions.

SPS syntheses

Simplified SIMFUEL samples containing Cs, Mo, Ba and Zr have been synthesized through SPS (1200°C, 5 min). Preliminary characterizations indicated that Cs is indeed present inside the samples after sintering. Further analyses, notably ICP-MS and SEM-EDX on polished samples, have to be performed in order to determine accurately the amount and initial chemical state of Cs.

The final density of the samples was roughly estimated to vary from 68 to 90 %d_{th} depending on the mix. This is consistent with the observed microstructure confirming the sintering was uncomplete. Nevertheless, measurements of the density by the Archimedes method have to be performed to get more accurate data.

Thermodynamic calculations

Thermal treatments conditions, representative of a SA, were determined thanks to thermodynamic calculations using FACTSAGE coupled with the TAF-ID.

In-temperature XAS

Predominance diagrams indicating the FP chemical states in the different conditions will be probed by in-temperature XAS analyses under controlled atmosphere performed on BM16 beamline at the ESRF. A specific sample holder and glovebox have been designed to handle and confine the sample during the experiment. This kind of analyses will enable the observation of potential intermediate compounds formed at high temperatures and improve the current knowledge concerning FP speciation.

Additional thermal treatments

Additional thermal treatments will be performed in DURANCE in order to complete the in-situ characterizations. The evolution of the samples' microstructure and the distribution of FP in the matrix will notably be studied by SEM-EDX.

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