

## **AEROSOLS RELEASED DURING THE LASER CUTTING OF A FUKUSHIMA DAIICHI DEBRIS SIMULANT**

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### **ABSTRACT**

One of the important challenges for the decommissioning of the damaged reactors of the Fukushima Daiichi Nuclear Power Plant is the safe retrieval of the fuel debris or corium. It is especially primordial to investigate the cutting conditions for air configuration and for underwater configuration at different water levels. Concerning the cutting techniques, the laser technique is well adapted to the cutting of expected material such as corium that has an irregular shape and heterogeneous composition. A French consortium (ONET Technologies, CEA and IRSN) is being subsidized by the Japanese government to implement R&D related to the laser cutting of Fukushima Daiichi fuel debris and related to dust collection technology. Debris simulants have been manufactured in the PLINIUS platform to represent Molten Core Concrete Interaction as estimated from Fukushima Daiichi calculations. In this simulant, uranium is replaced by hafnium and the major fission products have been replaced by their natural isotopes. During laser cutting experiments in the DELIA facility, aerosols have been collected thanks to filters and impactors. The collected aerosols have been analyzed. Both chemical analysis (dissolution + ICP MS and ICP AES) and microscopic analyses (SEM EDS) will be presented and discussed. These data provide insights on the expected dust releases during cutting and can be converted to provide radioactivity estimates. They have also been successfully compared to thermodynamic calculations with the NUCLEA database.

## KEYWORDS

Fukushima Daiichi, Aerosols, Debris cutting, Fission Product simulants

## 1. INTRODUCTION

The 2018 Technical Strategic Plan for decommissioning of the Fukushima Daiichi (1F) Nuclear Power Station [1] indicates that the policy on Fukushima Daiichi fuel debris retrieval will “combine optimum retrieval methods suitable for the part of each unit where fuel debris is expected to be present, instead of making an assumption that all the fuel debris is to be taken out using a single method”. Cutting fuel debris (solidified corium) is an important issue and several techniques including mechanical and thermal cutting are being studied for (see e.g. 2, 3). The laser technique is well adapted to the cutting of corium which has an irregular shape and heterogeneous composition. In addition, the laser cutting technique induces the lowest material mass removed and the lowest mass of re-suspended aerosol during the cutting, comparatively to others cutting techniques (grinder, plasma torch, arc air, arc saw, reciprocating saw) [4].

Several R&D projects have therefore been launched and subsidized by the Japanese government to study potential techniques. In this framework, a French consortium (ONET Technologies, CEA and IRSN) has been selected among others to implement R&D related to the laser cutting of 1F fuel debris and related dust collection technology [5].

Asides from experimental optimization of the laser-cutting technique on commercially-available samples such as electrofused zirconia, steel and zirconium plates, one specificity of our approach is to have specifically fabricated simulant of Fukushima-Daiichi fuel debris [6] that have in a second part been subjected to laser cutting in our facility while aerosol production [7] has been analyzed. As the laser cutting experimental works could not be carried out at this stage in a laboratory where uranium can be manipulated, a simulant corium debris has been manufactured based on hafnium oxide while the fission products were replaced by the same elements but with their natural isotopic composition [8].

In a first section the experiments will be described. Then, the aerosols analyses will be presented. Finally, thermodynamic calculations will be presented and compared with experimental results.

## 2. EXPERIMENTS

### 2.1. Corium Debris Simulant Manufacture

The ex-vessel debris simulant has been fabricated at PLINIUS platform during the test VF-03 (Vulcano Fukushima test number 3) [6]. It simulates a debris from interaction between the molten core and the concrete in the sump of Fukushima Daiichi Unit 1 (1F1) based on the MAAP LP case in Robb et al. [9] modelling of MCCI taking into account the Fukushima Daiichi concrete composition reported by Kitagaki et al. [10] and the fission product composition 10 years after shutdown from Nishihara [11].

To facilitate cutting and avoid radioactive releases, hafnium has been chosen as for uranium and plutonium has been replaced by cerium because their thermal properties are close. The replacement of uranium by hafnium has been made with respect to the assessment of the efficiency of thermal cutting by laser: indeed, uranium and hafnium dioxides have similar melting temperatures and thermal properties [8]. Unfortunately, it has not been possible to find a good simulant of uranium regarding the volatilization of oxides. Capriotti et al. [12] have shown that “many similarities exist between the system Pu-O and the system Ce-O, even in the very high temperature behavior” and that “CeO<sub>2</sub> displays ... a melting behaviour which has been recently proven to be typical of other similar metal-oxygen systems such as

Ca-O, Np-O and Pu-O". Therefore cerium has been used in this work as surrogate of plutonium. Ruthenium has also been removed because of its chemical toxicity in oxidizing conditions and rhodium because of its cost.

The ex-vessel fuel debris are made from:

- Fuel (uranium + non-volatilized fission products),
- Zircalloy (Zr + Sn) oxidized at a level depending on the unit accident scenario,
- Steel (containing 10.2 wt% Cr and 5.1wt% Ni) coming from the vessel internals, the vessel and concrete reinforcement bars ,
- Concrete decomposition products (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CaO...) and oxygen from concrete water.

Table 1 lists in details the materials which has been introduced in the load. Steel has been introduced as steel balls while the other elements have been introduced as powders. After melting, two phases have segregated: a small heavier metallic phase and an oxidic debris.

**Table I: Ex-vessel simulant load composition (in g per 10 kg) [6]**

	For 10 000 g	wt%		For 10 000 g	wt%
HfO <sub>2</sub>	2 036.62 g	20.366%	Fe <sub>2</sub> O <sub>3</sub>	286.37 g	2.864%
CeO <sub>2</sub>	18.47 g	0.185%	Nd <sub>2</sub> O <sub>3</sub>	8.93 g	0.089%
ZrO <sub>2</sub>	1 240.32 g	12.403%	MoO <sub>2</sub>	8.46 g	0.085%
SnO	15.80 g	0.158%	Cs <sub>2</sub> O	5.04 g	0.050%
B <sub>4</sub> C	17.36 g	0.174%	Ba	3.33 g	0.033%
Cr <sub>2</sub> O <sub>3</sub>	58.11 g	0.581%	La <sub>2</sub> O <sub>3</sub>	2.66 g	0.027%
Fe	630.09 g	6.301%	PdO	2.55 g	0.026%
FeO	1 177.76 g	11.778%	Pr <sub>2</sub> O <sub>3</sub>	2.45 g	0.024%
Ni	52.04 g	0.520%	Sm <sub>2</sub> O <sub>3</sub>	1.83 g	0.018%
SiO <sub>2</sub>	3 039.51 g	30.395%	Sr	1.47 g	0.015%
Al <sub>2</sub> O <sub>3</sub>	758.62 g	7.586%	Y <sub>2</sub> O <sub>3</sub>	1.15 g	0.012%

## 2.2. Aerosol Collection during Laser-Cutting of the Fuel Debris Simulant

Laser-cutting of this MCCI oxidic debris simulant (Figure 1) has been performed in air at CEA DELIA laser shot unit of the ALTEA platform (Figure 2 left). A Trumpf 8002-type 1030-nm laser source with continuous power of 8 kW is connected by optical fibers to CEA laser head . Two compressed air jet flows are provided, one around the laser head and one at 45° from the corium surface. The laser cutting has been conducted in air as well as under various depths of water.

Aerosol characterization is carried out through the measurements of the mass concentration, the particle size distribution and the composition of the aerosols that is sampled in the aerosol test section connected to exhaust line of the DELIA laser cutting cell [7]. Different instruments are implemented on the aerosol

test section to provide together real time and integrated measurements of aerosol characteristics (Figure 2 right).

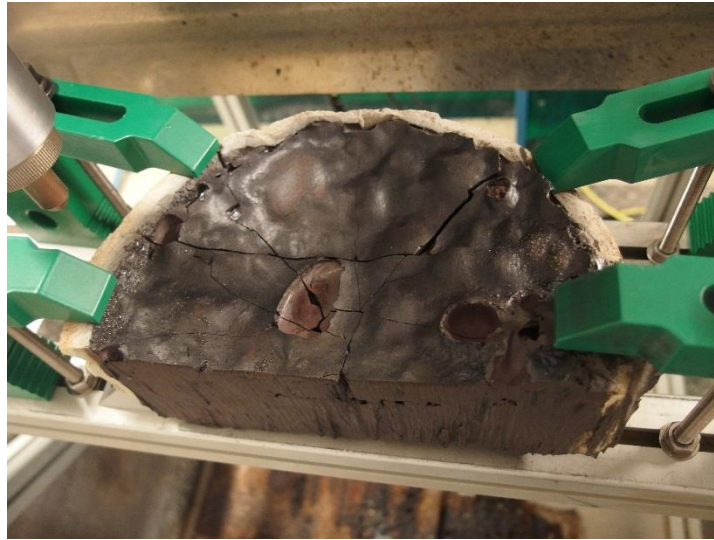


Figure 1: View of partially cut fuel debris simulat (in its ceramic crucible)

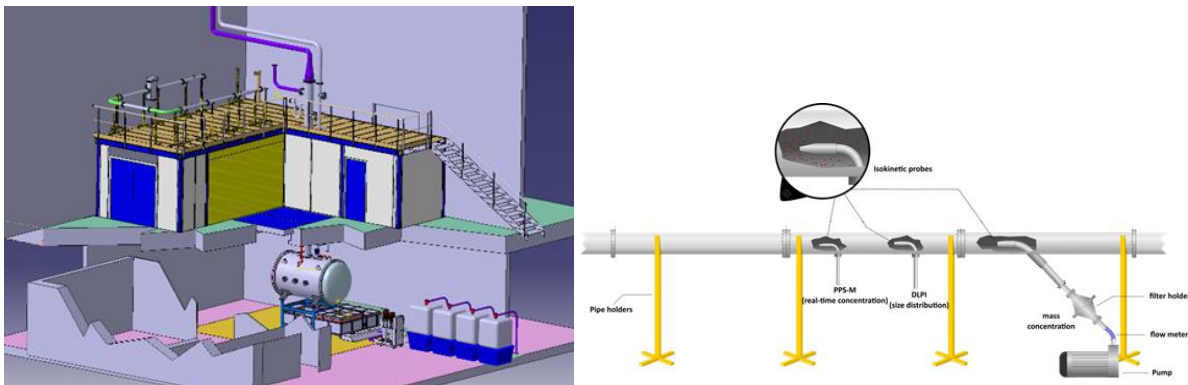


Figure 2: Sketch of the DELIA facility [7] Left: overall view – Right: Aerosol collection systems

### 2.3. Aerosol Collection and Analyses

The quartz filters (Figure 3 left) used for the global mass concentration measurement have been analyzed to determine the aerosol chemical composition (corresponding to the 30 nm-10  $\mu\text{m}$  range). After the retrieval of the particle deposits and dissolution of the material (Figure 3 right), the remaining solutions were analyzed by means of ICP-MS and ICP-AES techniques depending on the elements to be measured.

Results of the chemical analysis are presented in Figure 4 for three test conditions: one in air, two underwater with different pool heights above the sample. Results are expressed in terms of relative masses of each element considered in the analyzed samples.

For instance, for the case in air, the major constituents of the resuspended aerosols are iron (36 wt%), chromium (23 wt%), tin (8 wt%), boron (8 wt%), nickel (7 wt%), zirconium and calcium (4 wt%), caesium and molybdenum (both 3 wt%). Uncertainties of 1/10<sup>th</sup> of the measured concentration are estimated on these measurements. As the filter is made of quartz, it is not possible to measure the fraction of silicon in the collected aerosols. From the analysis of the aerosols collected on impactors, silicon represents 17 to 33 wt% of the aerosols depending on the test configuration.

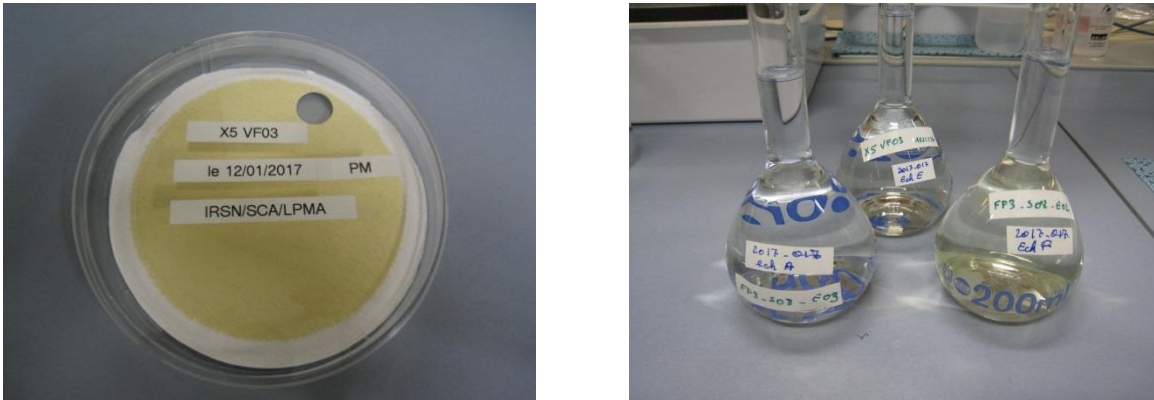


Figure 3 : Aerosol filter from VF03 laser cutting before and after solubilization

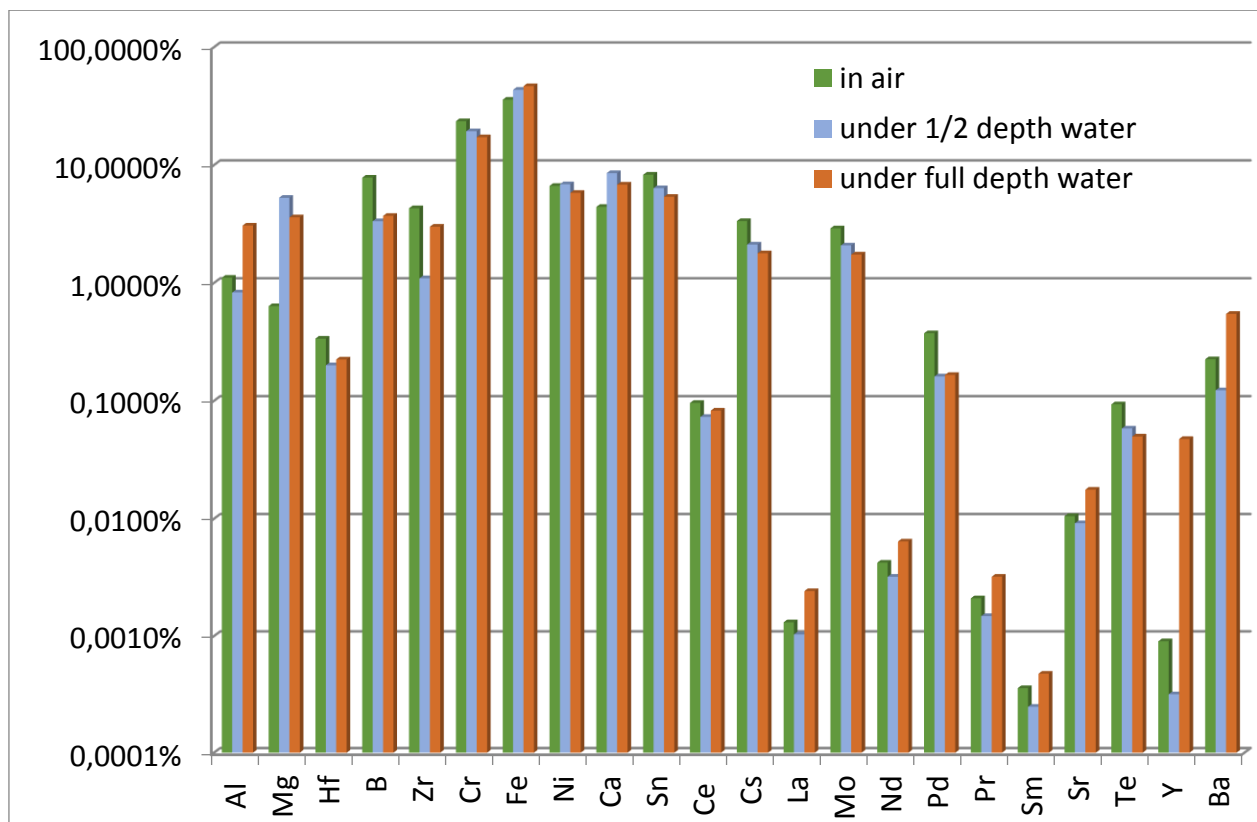


Figure 4: Mass fractions from the aerosols collected from MCCI debris simulant

### 3. MODELLING

The modelling is made under the assumption that the aerosols are formed from the condensation of the vapors produced by the fuel debris when it is heated by the laser beam. Thermodynamic equilibrium calculations have been carried out using GEMINI2 and the NUCLEA14 database [11].

These calculation assume that the molten material is at a homogeneous temperature which is fitted with experimental results. Oxygen and Argon are added to represent air. The element Argon was used as surrogate for the nitrogen in the air. In other terms, the effect of nitride is neglected. Some elements has been substituted by others because they are not present in the database:

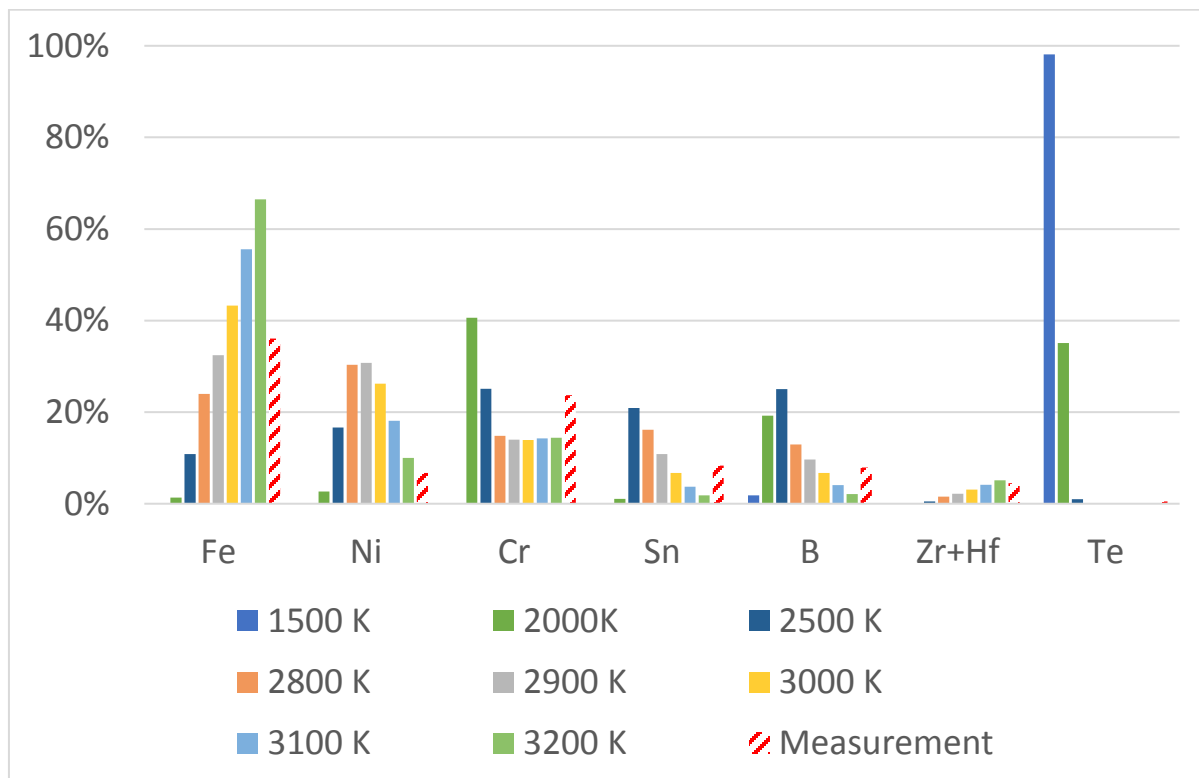
- Zirconium replaces, mole by mole, Hafnium,
- Chromium replaces Molybdenum,
- Lanthanum is surrogate for Praseodymium, Cerium, Yttrium, Samarium, Neodymium
- Silver replaces Tellurium and Palladium,
- Indium is simulating Tin.

The composition of the oxidic debris simulant has been determined from the load composition (Table I) and from measured compositions of samples from the oxide, metal and aerosols produced during the melting phase. Table 5 presents the load in grams for each element from the database in the cases considered for calculation. It corresponds to 8.2 kg of oxidic debris with 1.44 kg of air (1.2 m<sup>3</sup> at 298 K; 15 wt%). This quantity of air has been determined by trial and error in order to best fit the measured composition for the major elements. For this composition, the liquidus temperature has been computed to be around 1980 K

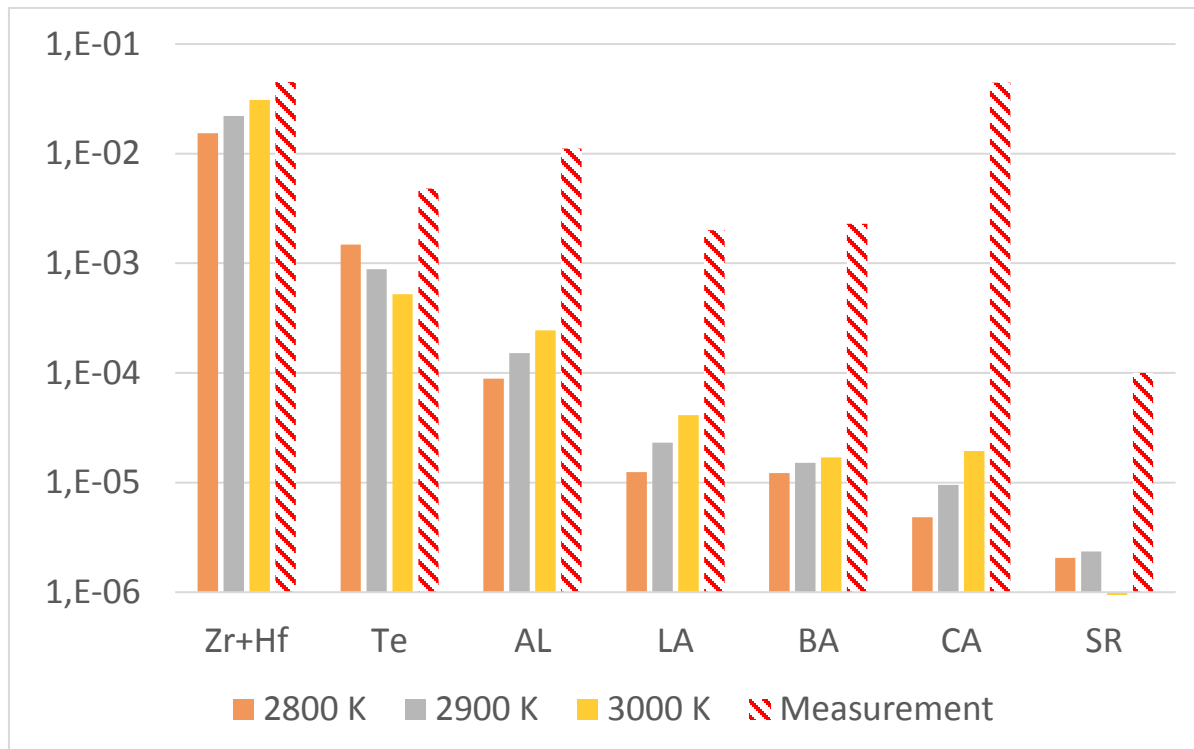
**Table II: Composition used for calculations of the ex-vessel oxidic simulant in air**

Element	Mass (g)
Zr	1628.16
Fe	1336.96
Si	1284.73
Ca	242.46
Al	359.64
Cr	246.96
Ba	2.67
Ni	49.29
La	25.88
In	8
Ag	0.06
B	10.03
Sr	1.44
Ar	1600
O	3208.00

Figure 5 shows the measured proportions of the major elements. The major element is iron followed by chromium tin and boron. Proportions in the vapor phase from thermodynamic equilibrium calculations at various temperatures are also plotted. At low temperatures (1500 K), silver (representing tellurium) is almost the only vapor. At higher temperatures (2500-3000 K) iron, chromium nickel, boron and indium have important contributions. Assuming equilibrium at 2800-2900 K (800-900 K above liquidus) provides a reasonable correspondence between calculation and experiment, except for Ni which is overestimated in these calculations. The major computed vapor phases at 2800 K are  $\text{BO}_2$  (5 mbar),  $\text{SiO}$  (3 mbar),  $\text{Ni}$  (2 mbar),  $\text{CrO}_2$  (1 mbar),  $\text{B}_2\text{O}_3$  (1 mbar) and  $\text{FeO}$  (1 mbar).



**Figure 5: Mass fractions of the major constituents of the aerosols: Calculations vs measurements**  
 In stands for Sn, Ag for Te, Zr for Zr and Hf.



**Figure 6: Mass fractions of the minor constituents of aerosols: Calculations vs measurements**  
**Zr stands for Hf and Zr, Ag for Te, La for all lanthanides**

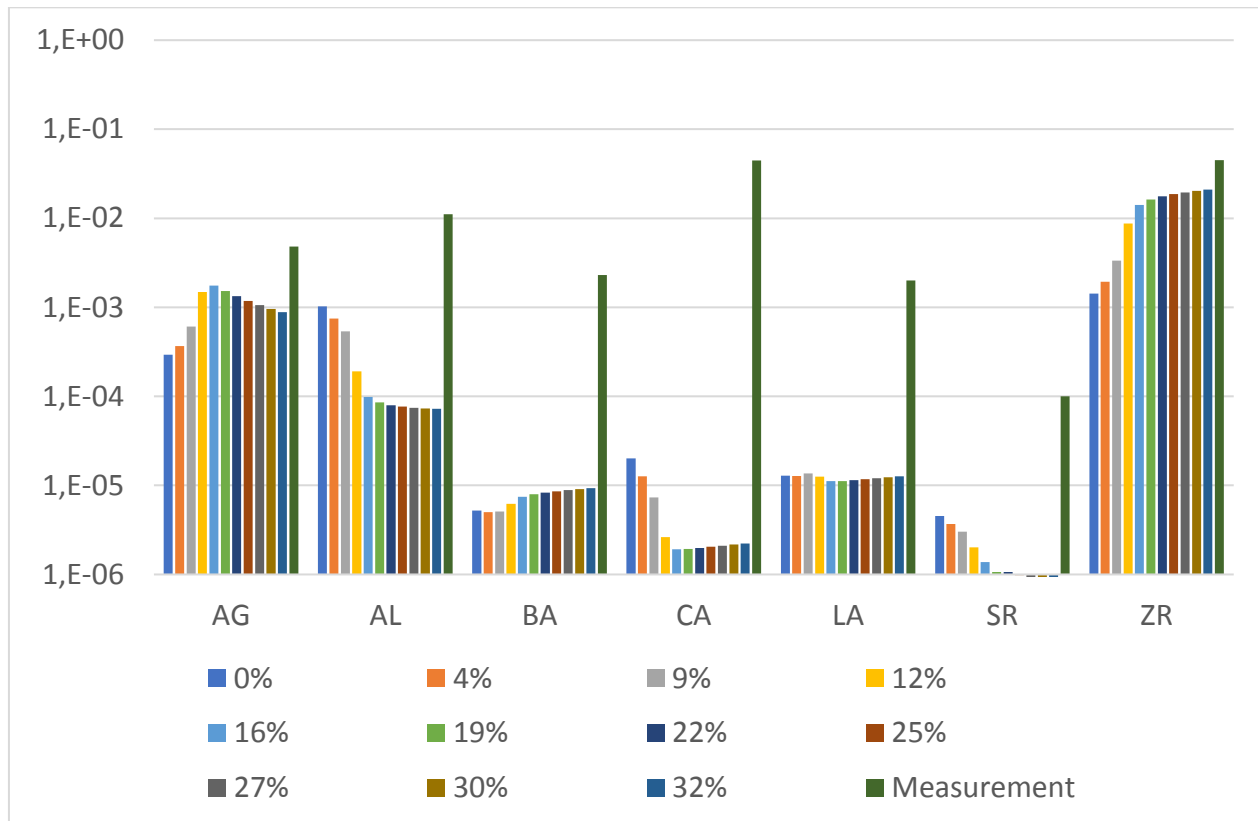
For the less volatile elements, Figure 6 compares computations and measurements. There is a clear underestimation of the released fraction of lanthanide, barium and strontium. This is only marginally modified by modifying the calculation temperature. Modification of the quantity of air in equilibrium with the heated fuel debris simulants (Figure 7) was also not able to sufficiently increase the fraction of these elements while it affected the ratios of the major components. Even though these fission product elements contribute to only 11 wt% of the aerosols, they carry most of its radioactivity. Further work is thus necessary.

The effect of the replacement of uranium by hafnium (or zirconium) has also been evaluated. Figure 8 presents two calculations for which the unique difference is that each mole of uranium has been replaced by a mole of zirconium (representing hafnium). Uranium becomes the major element of the vapour phase and with a 50-times increase in the computed mass fraction. The major uranium-bearing gas species is uranium trioxide (with a vapour pressure of 23 mbar), uranium dioxide being much less present (0.5 mbar), whereas only dioxide is indeed present for the composition with hafnium. Indeed, uranium dioxide is known to have an important non-congruent evaporation [15] leading in this case to the release of gaseous  $UO_3$ .

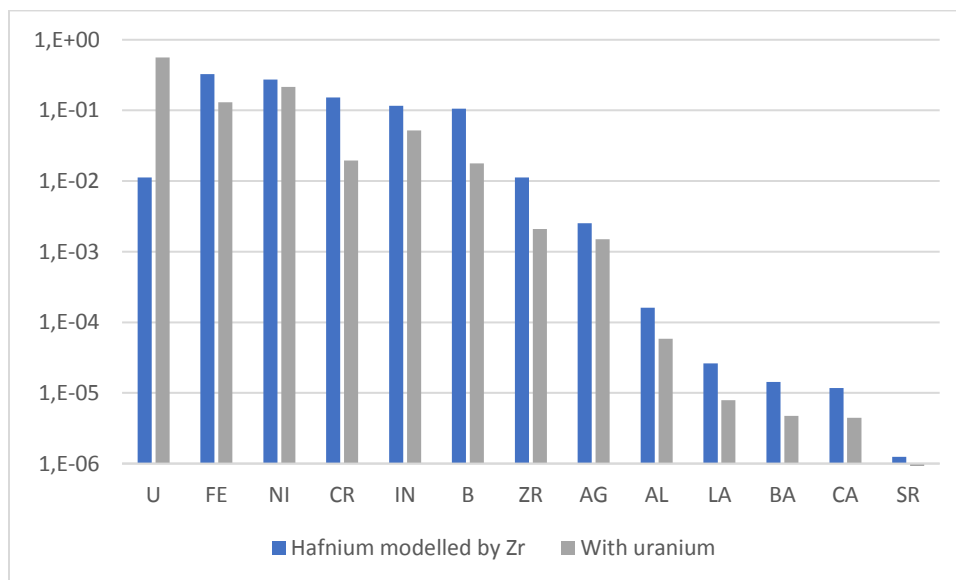
Being the major element of vapour phase, uranium-containing vapours also affects the releases of other elements, not only by modifying the total vapour mass fraction): for instance computed Lanthanide and Barium releases are divided by 3, while Boron releases are divided by 6. On the opposite, mass fractions of Nickel and Tellurium (modelled by Silver) do not significantly vary between these two calculations. As there are still large uncertainties on these calculations and no experiments on which to compare them, it is therefore recommended to conduct cutting tests on prototypic fuel debris simulants containing (depleted) uranium dioxide to confirm or infirm these



results. An intermediate first test could be to collect and analyse aerosols above pools of molten fuel debris simulants with uranium or hafnium at 2800 K.



**Figure 7: Effect of mass fraction of air in equilibrium with fuel debris simulant on the mass fraction of low volatility elements in the vapour phase (excluding Ar, O and Si)**



**Figure 8: Effect of uranium on the aerosol composition (mass fractions)**

## 4. CONCLUSIONS

In order to develop a safe laser-cutting technology for the retrieval of Fukushima Daiichi fuel debris, simulant fuel debris materials have been manufactured at CEA Cadarache and laser-cut at CEA Saclay. The emitted aerosols have been collected thanks to quartz filters which have been analyzed by ICP-AES and ICP-MS after dissolution at CEA Marcoule.

For a Molten Core Concrete Interaction simulant block cut in air, the major constituents of the aerosols are iron, chromium, silicon, tin, boron and nickel. Radioelements appear in much lower proportions.

Thermodynamic equilibrium calculations indicate that the major element proportions found in the aerosols approximately correspond to the fractions in the vapor in equilibrium with the molten fuel debris simulant at a temperature of about 2800 K. It must be stated that the collected fractions of the medium and low volatility elements (tellurium, lanthanides, strontium, barium) are larger than those computed with this equilibrium calculation, even when the temperature or the quantity of air in interaction with the melt is varied.

Another result of these calculations is the fact that uranium is expected to release much more vapor (that will later form aerosols) than hafnium while hafnium dioxide was used as simulant of uranium dioxide for its physical properties. This is linked to the important non-congruent evaporation of  $\text{UO}_2$  [15]. It is thus recommended to complement the presented results with new experiments on prototypic fuel debris simulants containing (depleted) uranium dioxide.

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