Modelling of fission products release in VERDON-1 experiment with cGEMS: Coupling of severe accident code MELCOR with GEMS thermodynamic modelling package

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Abstract

The treatment of chemistry and thermodynamics in the integral severe accident codes is typically limited. A more accurate treatment of the chemistry during the severe accident modelling is, therefore, of great interest. For this purpose, the work is focused on the development of coupling of the MELCOR code with chemical thermodynamic calculations using GEMS codes and HERACLES database. Developed coupling between the two codes, called cGEMS, allowed for the improved thermodynamic description of the fission product release from the nuclear fuel under severe accident conditions. VERDON-1 test was selected as an experimental reference for the simulations. Experimental release behaviour of Mo, Cs and Ba observed in VERDON-1 experiment was reproduced by the developed coupled code. Performed simulations provided detailed information about the fission product speciation at different redox conditions. The obtained information and the developed code provides a more accurate description of the fission product behaviour and release during severe accidents.

1. Introduction

Since several years, the international community has been working on analysing accidents in the Fukushima power plant to develop and improve the methods of severe accident analysis (Nagase et al., 2016; Pellegrini et al., 2020; Nakatsuka et al., 2019). This requires knowledge of fuel debris characteristics and fission product (FP) behaviour, to evaluate the status and the physical/chemical conditions of fuel debris and the behaviour of fission products in the reactors and the subsequent transport in the plant. The major concern is to determine the Source Term, i.e. the speciation, release rate and released fractions of the fission products and other radioactive materials from the plant to the environment and their consequences. One of the major parameters affecting the source term is the release of FPs from the damaged nuclear fuel. This release behaviour of fission products from nuclear oxide fuels is influenced, among other factors, by the speciation of the fission products and temperature and oxygen partial pressure (oxygen potential) of the gas atmosphere. Under the conditions of a severe accident, temperature significantly exceeds the nominal one and the redox conditions can strongly vary depending on, for example, the oxidation of the Zircaloy cladding by steam (giving a large amount of H₂) followed by the ingress of steam or air. It is therefore of great importance to understand and to be able to model the speciation and release behaviour of volatile fission products in varying conditions.

Numerous research programs in the field of severe reactor accidents have been undertaken in various countries to assess the Source Term. Some of them like the PHEBUS programme (Bottomley et al., 2013) were devoted to integral tests while others have been devoted to separate-effect experiments. Among the latter, the VERCORS (Pontillon et al., 2010) and VERDON (Pontillon et al., 2017; Geiger et al., 2017) programs were composed of a series of analytical tests conducted on samples of irradiated Pressurized Water Reactor (PWR) fuels, in carefully controlled temperature and redox conditions. From these tests carried out in highly instrumented experimental facilities, extensive and invaluable data were collected and then used to improve the models for the Source Term evaluation.

The VERDON-1 experiment (Pontillon et al., 2017; Geiger et al., 2017) studied the fission product release from high-burnup PWR fuel under severe accident conditions as a function of temperature and under different atmospheres (consisting of varying ratios of steam/hydrogen) and transport in a laboratory scale. Extensive
characterisation of fission product behaviour was performed during and after the experiment (Pontillon et al., 2017; Geiger et al., 2017). Additionally, the chemical interactions between the phases formed during irradiation (caused by the formation of fission products), the fuel matrix (UO$_2$), and the Zircaloy cladding that may take place during a nuclear severe accident, were investigated (Geiger et al., 2019).

The experimental results are used to develop models for integral severe accident analysis codes, such as MELCOR. The severe accident code MELCOR (MELCOR, 2018) is used to assess the progression of severe accidents in Light Water Reactor (LWR) nuclear power plants, including fission product behaviour and release to the environment. Among others, the code is used to analyse the accidents at Fukushima Daiichi nuclear power plant (Gauntt et al., 2012; Robb et al., 2014; Sevón, 2015; Fernandez Moguel et al., 2019a, 2019b).

However, the representation of chemistry in MELCOR is rather simplistic: the thermodynamic stability of nuclear fuel, as well as reactions of fission products with each other or with structural materials (with the exception of Cs chemisorption to surfaces and $I_2$ pool chemistry models), are not accounted for with a chemical speciation being limited to a pre-set table of compounds or user-defined reactions.

At the same time, thermodynamic equilibrium modelling is a powerful tool for the description of complex chemical processes and systems, like those involved in irradiated nuclear fuels (Corcoran et al., 2016; Guéneau et al., 2011). Besides the fact that thermodynamic modelling provides information about the thermodynamic state of the system (speciation, activities, phases, etc.) it also accounts for the interactions between different species in the phases providing, therefore, a much more accurate description of a complex chemical system.

In this context, the current work was focused on a synergistic improvement of existing tools for assessment of fission products and core materials behaviour during a severe accident (SA) by combining the integral analysis code MELCOR with chemical thermodynamic calculations using GEMS codes and HERACLES database (Kulik et al., 2019, 2013; Shcherbina et al., 2012). This should lead to a significant advance in the understanding of chemical behaviour through a more accurate description of the chemical properties of fuel debris and fission products during a severe accident progression for the different parts of the reactor.

In this paper, we describe the method of coupling the GEMS code with MELCOR, and give first results regarding fission product release from fuel by using the VERDON-1 experimental results as a reference. Simulations were carried out using the standard MELCOR representation of the fission product release as well as using the coupled GEMS-MELCOR. Implications to severe accident analysis are given in the end of the paper.

2. Methods

2.1. Verdon test

The VERDON test loop was described in detail by Gallais-During et al. (2014). The irradiated fuel sample was placed in a heated high-frequency furnace on crucible made of HfO$_2$. During the experiments, fluid flow containing a mixture of helium, water vapour, hydrogen and/or air was used and the temperature of the furnace was increased gradually. The temperature inside the furnace was measured with three thermocouples at the insulator of the furnace and the temperature of the crucible was observed using a pyrometer.

A gamma spectrometer was aimed at the fuel sample during the test to continuously determine the FP concentrations (Pontillon et al., 2017). Additionally, FP release was investigated by collecting aerosol particles on filters which were analysed with either gamma spectrometry or by chemical analysis post-test. Gaseous iodine was trapped to Maypack filters and fission gases were analysed using micro gas chromatograph or sequentially by four sampling aliquots in a glove box outside of the high activity cell. The experimental facility also included a transport circuit, where the FP transport in the primary circuit in accidents was investigated using thermal gradient tubes, where the FP vapours and aerosol were deposited. In this work, we focus only on fission product release from the fuel, and the transport is not analysed.

In VERDON-1 test, the test sample featured two pellets of UO$_2$ encased in M5 cladding, irradiated to approx. 72 GWd/tHM. Two half pellets of unirradiated, depleted UO$_2$ were placed at top and bottom of the sample, similar to VERCORS RT6 test (Riglet-Martial et al., 2018). Before the experiment, the sample was re-irradiated in order to recreate the short-lived FPs (Pontillon et al., 2017). The fuel pellet diameter was 8 mm and the outer diameter of the cladding 9.5 mm.

The thermal–hydraulic sequence of VERDON-1 test is shown in Fig. 1. The test was divided into four phases. Phases 1 (neutral conditions) and 2 (oxidizing conditions) resemble the conditions in an initial phase of a loss-of-coolant accident and phase 3 (reducing conditions) corresponds to H$_2$ rich conditions due to cladding and metal-rich melt oxidation during core re-flooding (Pontillon et al., 2017) or core degradation in steam. In phase 4, the neutral atmosphere was used and at the end of the test, the temperature 2883 K was reached. The FP release in VERDON-1 test is shown in Fig. 2. The test did not result in a clear loss of fuel integrity.

2.2. MELCOR code

The integral analysis code MELCOR (MELCOR, 2018) is used by the utilities, academic researchers and the nuclear regulators to simulate the progression of the severe accidents in nuclear power plants and to assess the source term. MELCOR is being developed at Sandia National Laboratories for the U.S. Nuclear Regulatory Commission as a second-generation plant risk assessment tool. A broad spectrum of severe accident phenomena in LWRs, high temperature gas-cooled reactor and spent fuel pools is treated in MELCOR in a unified framework. These include the thermal–hydraulic response in the reactor coolant system, reactor cavity, containment building; core heat-up, fuel degradation, and relocation; core-concrete attack; hydrogen production, transport, and combustion; fission product release and transport behaviour.

![Fig. 1. VERDON-1 test thermal–hydraulic sequence (Gallais-During et al., 2017).](image-url)
In MELCOR the main fission products release and transport mechanisms, such as aerosol formation and transport as well as deposition, are modelled, but chemical reactions of fission products with each other or with structural materials are limited. Considering the fact that in severe accidents, temperatures may be very high and fission products may be partitioned between the gas phase and condensed phases (solids and liquid), it is expected that simulation of chemical reactions of fission products would be important for a reliable estimation of the source term.

### 2.3. CORSOR-Booth model

CORSOR-Booth model is used in MELCOR to model fission product release from the fuel. It comprises the Booth diffusion model (Booth, 1957) describing the fission product diffusion through the fuel grain to the surface and a gas-phase mass transport describing the evaporation of the materials from the grain surface. The total mass release rate by the CORSOR-Booth model is given by:

\[
m_{\text{tot},k} = \left( \frac{1}{m_{k,\text{diff}}} + \frac{1}{m_{k,\text{gas}}} \right)^{-1}
\]

(1)

MELCOR version 2.2.1.1923 allows the use of the revised version of the CORSOR-Booth model, “ORNL-Booth”, in which the release rate of class k from the fuel by diffusion is calculated using:

\[
m_{k,\text{diff}} = \frac{S_k}{F \Delta t} \left[ f(D(t + \Delta t)) - f(D(t)) \right] m_{0,k}
\]

(2)

In Eq. (2), \(m_{0,k}\) is the mass of FP class k in the fuel component, \(F\) is the fraction of k remaining in the fuel and \(f\) is the release fraction of Cs from the fuel grain by diffusion. Thus in the CORSOR-Booth model, the diffused mass of class k is obtained from the Cs diffusion applying the scaling factor \(S\), in Eq. (2). \(D\) is a temperature dependent diffusion coefficient of Cs, calculated by MELCOR during the simulation, and dependent of diffusion coefficient \(D_0\), activation energy \(Q\) and the equivalent sphere radius of the fuel grain \(a\). In the VERDON-1 simulations, we use the values for \(D_0\), Q and a for High Burn-Up (HBU) fuel, obtained from (Gauntt, 2010) and shown in Table 1.

The mass transfer from fuel grain surface to gas phase is described by

\[
m_{k,\text{gas}} = Nu \frac{D_k}{d} \frac{P_f}{RT}
\]

(3)

where \(D_k\) is the diffusivity of k, \(d\) is the fuel pellet diameter, \(A\) is the surface area of the fuel rod, \(Nu\) is the Nusselt number and \(P_f\) is the vapor pressure of the class k. MELCOR code will calculate \(D_k\) and \(Nu\) for every time step of the simulation.

### 2.4. MELCOR model of the VERDON-1 experiment

The schematic of the MELCOR model for VERDON-1 used in the simulations is shown in Fig. 3. The mixture of \(\text{H}_2\), \(\text{H}_2\text{O}\) and He is introduced to the test section (Control Volumes (CV) 101 to 105) from CVs 1–3 according to the sequence presented in Fig. 1. The core cells containing the fresh fuel were located in CVs 102 and 104, encircling the irradiated pellets located in CV 103. The temperature of the irradiated pellets was controlled using core heat structures, and it followed the temperature profile measured in the experiment (Fig. 2).

Since the information on the exact composition of the sample used in the VERDON experiments is not open, we have used the data published by (Geiger et al., 2019), who presented an elemental composition of a fuel similar to that used in VERDON-1 test, which they obtained from CESAR (Vidal et al., 2006) calculations. In MELCOR, the radionuclides considered in the FP release and transport simulations are divided into classes representing a collection of elements with similar behaviour mechanisms in reactor accident conditions. In the VERDON experimental results however, the data consist of release of separate radionuclides from the irradiated fuel pellets, as shown in Fig. 2 for VERDON-1. In order to compare the modelled releases to the experiments, we have added only the individual element masses to the corresponding MELCOR classes (Cs element mass to Cs class, etc.), shown in Table 2, that are taken from the work of Geiger et al. (2019). The masses of atmospheric gases during the simulation are shown in Fig. 4.

### 2.5. GEMS codes/HERACLES TDB

The Gibbs Energy Minimization Software for Thermodynamic Modelling (GEMS TM) has been developed for over 17 years at PSI. GEMS codes (http://gems.web.psi.ch), in part open-source, are widely used in various fields of application, including cement chemistry, radioactive waste disposal, and nuclear energy research.

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**Table 1**

| Parameter       | HBU                  |
|-----------------|----------------------|
| Diffusion coeff. \(D_0\)| 2.3E-9 m²/s     |
| Activation Energy \(Q\)| 2.411E5 J/kg,mol   |
| Grain radius \(a\)       | 6E-6 m             |

**Fig. 2.** FP release measured in the VERDON-1 test (Le Gall et al., 2017).

**Fig. 3.** Schematics of the MELCOR model of VERDON-1.
A critical issue of any thermodynamic model, independent of the code used, is the quality and completeness of the underlying thermodynamic database. For applications to nuclear materials and spent-fuel reprocessing, the HERACLES thermodynamic database (TDB) for low (ambient) pressure - high-temperature (normal up to 2500 K temperature) non-aqueous systems has been developed (Shcherbina et al., 2012). HERACLES TDB covers molar thermodynamic properties ($\Delta fH_{298}$ standard molar enthalpy of formation at 298.15 K, $\Delta fG_{298}$ standard molar Gibbs energy of formation, $S_{298}$ standard molar entropy at 298.15 K, $C_p(T)$ temperature dependence of molar heat capacity at constant pressure) of the solid, liquid (melt) and gaseous compounds of actinides, fission products, and minor actinides, and it is valid up to at least 3000 K, covering the majority of the elements of interest. Currently, the data for over 600 condensed compounds and over 400 gaseous species are provided.

### Table 2
| Element | kg          |
|---------|-------------|
| Cs      | 3.868e-5    |
| Ba      | 2.106e-5    |
| I2      | 5.918e-6    |
| Te      | 6.696e-6    |
| Ru      | 3.355e-5    |
| Mo      | 4.599e-5    |
| Ce      | 3.485e-5    |
| La      | 1.662e-5    |
| UO$_2$  | 1.512e-2    |
| Cd      | 2.134e-6    |

Fig. 4. Masses of the atmospheric gases in CV-103 in the MELCOR simulation of VERDON-1.

Fig. 5. General schematics of the cGEMS.

Fig. 6. cGEMS simulation workflow.

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### 2.6. Development of the coupled MELCOR/GEMS tool

For the coupling between MELCOR and GEMS, the cGEMS (coupled GEMS) (Nichenko, 2019) code has been developed. cGEMS serves as an interface between the GEMS and MELCOR and facilitates an exchange of information between both codes, Fig. 5. cGEMS can call both MELCOR and GEMS depending on the situation, and has a controlling function in the simulation process.

Since MELCOR 2.2 is a commercial package and PSI has no access to the source code, it was decided to make the coupling between MELCOR and GEMS through an external file system. This means that cGEMS supplies information to MELCOR through external input files. To pass the information, cGEMS has to restart MELCOR every time step with a new input file with the updated information. Continuous restart of MELCOR with intermediate calculations with GEMS leads to increased calculation time in comparison with stand-alone MELCOR calculations. In the simulations of the VERDON-1 experiment the total increase in the simulation time with cGEMS was about 10–20%. At the same time, cGEMS has direct access to the GEMS code through its Application -Programming Interface (API) which simplifies the data exchange in GEMS.

The general idea of the simulation flow is demonstrated using the diagram in Fig. 6 where the process is split into the steps:

1. Run the simulation in MELCOR for a pre-set time step (200 s in this study)
2. Collect data from MELCOR, containing elemental composition of the fission products in the fuel, as well as composition and temperature of the gas atmosphere, and pass it to GEMS for thermodynamic calculations
3. Run GEMS thermodynamic simulation
4. Collect and prepare GEMS results and pass them to MELCOR using a new input file
5. Repeat the cycle.

The 200 s time step used in this research was chosen so that the experimental parameters (temperature, atmosphere composition etc.) do not vary much within this time step. Several smaller time steps (from 10 s up to 500 s) were tested in the preliminary simulations, showing no noticeable effect on the obtained results.
The most important step in the cGEMS simulation flow is step 4. At this step, the cGEMS collects information from GEMS and passes it to MELCOR in the form of the newly generated input files with the updated information on the properties of interest. In this study, we are interested in the fission product release and, therefore, the information of interest is the speciation of the fission products as well as the vapour pressures of the species.

The vapour pressures \( P_k \) of different species are described in MELCOR following:

\[
\log P_k = A + \frac{B}{T} + C \log T
\]

(5)

Thereby the vapour pressures from GEMS to MELCOR are transferred in the form of the coefficients A, B and C in Eq. (5).

By keeping the MELCOR simulation time in each Step 1 relatively short compared to the rate of temperature change of the analysed sequence, as described above, the vapour pressures can be passed as constant values using only the "A" coefficients. Additionally, the continuous exchange of the information between MELCOR and GEMS ensures that the calculated vapour pressures of different species account for the composition evolution of the pellet and the atmosphere, as well as temperature and pressure during the experiment.

It should however be noted that GEMS thermodynamic package performs equilibrium thermodynamic calculations at every time step. During the modelling the changes in the atmosphere between the oxidizing and reducing conditions are set to change from one state to another by changing composition of the atmosphere at the relevant times in the modelling. This excludes the transition period from one atmosphere composition to another that during the experiment happens gradually, and will significantly depend on the parameters and geometry of the experimental setup. Besides, to be able to perform transient thermodynamic modelling we would need to know the reaction rates for different reactions at different temperatures and this information is, unfortunately, very limited. However, at high temperatures, such as considered in this work, the reaction rates are usually significantly faster, especially if compared to diffusion processes, and equilibrium thermodynamic calculations give accurate speciation results.

### 3. Results and discussion

In the current section, results of the modelling of fission product release in VERDON-1 test using MELCOR and cGEMS are presented and discussed together with modelling conditions.

#### 3.1. Modelling of the VERDON experiment with MELCOR

First simulations were performed using only MELCOR without coupling to the thermodynamic solver to simulate the release of FP from the irradiated fuel in VERDON-1 test. The simulation of the FP release was first performed using the default values for the FP vapour pressures (Table 3) and diffusion scaling coefficients (Table 4), Fig. 7. It can be seen that the default parameters reasonably predicted the release of Cs and I during the experiment. However, the release behaviour of Mo and Ba is significantly underestimated leading to almost complete retention of Mo and Ba in the fuel even at relatively high temperatures. Only at very high temperatures, above 2200 K, some noticeable release of Mo and Ba is observed.

In subsequent simulations, the parameters in MELCOR were adjusted for better agreement with the VERDON data. This was done by varying two parameters: the diffusion scaling factor and the vapour pressure of the fission products. The scaling factors which describe the diffusion inside the fuel were increased from the MELCOR default values, Table 4. This was done to reflect the degraded, porous structure of the high burn-up fuel which promotes faster release of fission products as seen in, e.g., VERCORS tests (Ducros et al., 2013). The vapour pressures of Mo and Ba were adjusted to reflect their expected behaviour under the oxidizing and reducing conditions in the VERDON test, respectively. According to the data, Mo is highly volatile under oxidizing conditions and Ba under reducing conditions. Consequently, Mo vapour pressure was set to that of Cs under oxidizing conditions, and Ba vapour pressure to that of BO2 under reducing conditions. BO2 was chosen as it was deemed to be sufficiently close to the vapour pressure of Ba(OH)2 which can be expected to be formed under reducing conditions. With these modifications, the simulations showed much better reproduction of the experimental results, Fig. 8.

These simulations were able to reproduce the experimentally observed behaviour of Mo and Ba. Mo forms species with high volatility under oxidizing conditions and would reduce to less volatile species under reducing conditions. In the case of Ba, species with very low volatility are formed under oxidizing conditions and species with higher volatility are formed under reducing conditions. However, this approach requires manual adjustment of the diffusion scaling factors and the vapour pressures which need a priori knowledge of the atmospheric conditions. Therefore, a more rigorous approach would be useful to apply the results in accident sequence analysis.

### Table 3

| Vapour pressure coefficients | A     | B     | C     |
|-----------------------------|-------|-------|-------|
| Mo                          | 9.68  | 32800.0 | 0.0  |
| Ba                          | 8.4   | 11000.0 | 0.0  |
| Cs (for T < 1229.5 K)       | 8.895 | 13600.0 | 0.0  |
| Cs (for T > 1229.5 K)       | 7.675 | 12100.0 | 0.0  |
| I2 (for T < 457.0 K)        | 23.666 | 3205.0 | -5.18 |
| I2 (for T > 457.0)          | 7.637 | 2176.91 | 0.0  |

### Table 4

| Diffusion scaling factor, SK | Default MELCOR | Adjusted MELCOR | Adjusted cGEMS |
|-----------------------------|----------------|-----------------|----------------|
| Mo                          | 1.0e-3         | 1.0             | 1.0            |
| Ba                          | 4.0e-4         | 0.15            | 0.02           |
3.2. cGEMS modelling with default diffusion scaling factors

The first simulations with cGEMS were carried out using the default modelling settings in MELCOR. In this case, the default diffusion scaling factors for different elements and the default partial vapour pressures corresponding to the actual atmospheric conditions were passed from GEMS to MELCOR at every time step and overwrote the default values in MELCOR. The total vapour pressure of every element has been calculated by summation of the vapour pressures of all the compounds containing a particular element (Sossi and Fegley, 2018). This allows accounting for different chemical states of any particular element during the experiment.

Due to the uncertainties in the sample holder geometry and the correct amount of atmospheric gasses to be used in the thermodynamic simulations, additional sensitivity calculations of the fission products release to the total amount of gases in the atmosphere had to be performed. The results of these calculations are described in details in the section on the atmospheric sensitivity considerations. These results allowed us to define the atmosphere scaling factor which defined how to map the quantities of the MELCOR calculated atmosphere gases in the CV-103 to GEMS for the thermodynamic calculation. In all the cGEMS simulations the H2O in the atmosphere was scaled by 0.2 when passed to cGEMS for equilibrium thermodynamic calculations.

It can be seen from the results, Fig. 9, that even though the vapour pressures are now being controlled by cGEMS and therefore account for different chemical conditions during the experiment, the results still do not reproduce experimental behaviour. In particular, cGEMS predicts only about 10% release fraction of Mo from the fuel during the oxidizing conditions in contrast to about 40% Mo release fraction observed in the experiment.

3.3. cGEMS modelling with adjusted diffusion scaling factor

To improve the agreement between the experiments and simulations, the diffusion scaling factors for Mo and Ba were adjusted to reflect the experimentally observed effect of burn-up on the release of fission products (Ducros et al., 2013). For Mo, tests with high burn-up fuels have shown almost total release from the fuel resembling the behaviour of Cs. Therefore, for Mo, it was decided to use the diffusion scaling factor of Cs, i.e. $S_{Mo} = 1.0$ (MELCOR, 2018).

The diffusion scaling factor of Ba is harder to estimate, partly due to the fact that Ba has a tendency to deposit close to the fuel sample after release. Due to this, the release fraction of Ba is difficult to determine experimentally (Ducros et al., 2013). However, experiments indicate also an effect of high burn-up on Ba release. In this case, the scaling factor was adjusted from the default $4/C2_{4}$ to $S_{Ba} = 0.02$ for agreement with the VERDON experiments. As already mentioned above, the higher than default diffusion scaling factor is credible based on experimental results for high burn-up fuels which show accelerated fission product release kinetics (Rondinella and Wiss, 2010).

In the Table 4 the adjusted diffusion scaling factors for Mo and Ba are presented. They affect the FP diffusion from the fuel as described in Eq. (2), as a function of the fuel temperature.

Results using the adjusted diffusion scaling factors are presented in Fig. 10. The results demonstrate a significantly improved agreement between the simulations and experimental results. It should be emphasized that in our modelling, only the diffusion scaling factors were adjusted to reflect the structure of the high burn-up fuel. The vapour pressures were supplied by the GEMS through cGEMS code. This approach allows for an accurate accounting of the thermochemical effects that take place during the experiment.

3.4. Cs and I behaviour

Concerning the Cs and I behaviour during the modelling with cGEMS there are no significant differences observed between the
This can be explained by the fact that Cs and I related species are volatile, Figs. 11 and 12, and the release behaviour is defined by the diffusion in the fuel as a limiting factor of the release behaviour. As can be seen from the vapour pressure plot in Fig. 12, most of the iodine is released as CsI during the oxidation phase. This coincides well with the current understanding that in SA conditions, a fraction of I is transported in the reactor primary system as CsI gas which condenses on aerosol particles when the gas cools down (Wright, 1994). Most of Cs is predicted to be present as cesium molybdate, which is in agreement with earlier thermo-dynamic investigations (Geiger et al., 2019). However, it should be noted that even though Cs2MoO4 is thermodynamically favoured under severe accident conditions, post-test analyses did not confirm the significance of this species during the VERDON-1 test (Le Gall et al., 2017).

Additionally, the MELCOR “Best practice” guidelines (Ross et al., 2014) suggest that most of the Cs (89% of the initial inventory) exists as Cs2MoO4, which coincides well with the results of the oxidising conditions in the VERDON-1 experiment, obtained in this study.

It is noted that even though the calculated total release of Cs and iodine in the end of the calculation is in agreement with the experimental data, the release in the experiment is slower than in the simulation. This is caused by the high volatility of Cs and iodine. Throughout the experiment, Cs and iodine vapour pressure is very high and the release from the fuel is controlled by the diffusion of these elements from the fuel as described by Eq. (2). The different transient behaviour of the release is thereby a result of the diffusion model used to calculate the transport in the fuel pellet, in this work CORSOR-BOOTH, which can not capture the detailed release dynamics as observed in the experiment.

3.5. Mo behaviour

As shown by the Fig. 8, MELCOR calculations using the default parameters cannot reproduce the experimentally determined Mo release in the VERDON experiment. In particular, Mo is released during the VERDON experiment in two steps: a) a significant release is observed during the oxidation phase and stops right at the end of the oxidation phase; b) release of Mo at high temperatures at reducing conditions. This kind of behaviour indicates that Mo should be released in different forms, compounds, during different phases of the experiment. Due to a lack of thermochemical routine, these effects cannot be produced in MELCOR alone.

cGEMS can provide the detailed information about the speciation during the experiment and shed some light on the Mo behaviour. As it can be seen from the vapour pressure plot of the Mo related species, Fig. 13, the dominant species during the oxidation phase is Cs2MoO4, which has a high volatility and, therefore, vapour pressure. Formation of the Cs2MoO4 compound explains the initial Mo release during the oxidation phase. During the reducing phase of the experiment, Mo is present mainly in the form of pure Mo, which has quite low vapour pressure (fugacity) which, however, rises rapidly and finally causes Mo release at high temperatures at the end of the experiment (25'000 s onward). This last Mo release behaviour does not coincide with the experimental observation and indicates that the diffusion of Mo, at least at the higher temperature, is not correctly reproduced by the current model. It should be noted that the Mo speciation during the experiment significantly depends on the atmospheric conditions. The sensitivity of the speciation to the atmosphere changes shall be discussed below.

3.6. Ba behaviour

From the Fig. 14 we can see that during the oxidation phase, Ba forms BaMoO4 compound as the main Ba related species. At the same time partial vapour pressure of BaMoO4 is rather low which does not lead to a noticeable release of Ba in contrast to Mo.
During the reducing phase of the experiment, Ba is released mainly in the form of pure Ba, Fig. 14. A significant increase in Ba release during the reducing conditions can be explained by the fact that the boiling point of pure Ba is lower than those of Ba oxides and BaMoO₄. During the oxidation phase Ba is mainly in the oxide or molybdate phase what makes Ba less volatile during the oxidation phase. During the reducing conditions the metallic Ba is formed, which is much more volatile than its oxide or molybdate counterparts. Thereby, Ba speciation during the experiment significantly depends on the atmosphere and redox conditions. Experimental results from the VERDON and VERCORS programs have also indicated that Ba is being released readily in reducing atmospheres (Le Gall et al., 2020; Pontillon and Ducros, 2010), coinciding with the modelling results presented in this paper.

### 3.7. Atmosphere sensitivity considerations

One of the main difficulties with cGEMS modelling of the VERDON-1 experiment is the correct consideration of the atmosphere. In the VERDON facility, only a fraction of the gas flow which is fed into the facility will reach the sample surface and react with the sample. To determine the fraction of the gas flow which reacts with the sample, a detailed analysis of the flow path under the test conditions would be needed. Such an analysis is beyond the scope of this work. Therefore, as a part of this investigation, we have added a sensitivity study on the effect of different atmosphere gases quantities, namely H₂O.

The H₂O amounts in the CV-103, obtained from the MELCOR simulation were scaled by scaling factor, scH₂O in cGEMS before it was passed to GEMS. The idea behind this approach is to understand what fraction of the gas supplied to the volume reacts with the pellet. This is important because if we pass all the H₂O amount on every time step to the GEMS calculations, which are equilibrium thermodynamic calculations, this will lead to a significant deviation from the real dynamic process, where not all of the supplied atmosphere takes part in the chemical reactions and thermodynamic processes. Only part of the atmosphere close to the pellet is involved in the thermo-chemical reactions and the rest of the atmosphere passes through the volume without reacting with the pellet.

Therefore, these calculations can provide a rough assessment of the gas fraction in the volume which is passed to GEMS to provide realistic results. However, it should be noted that these results are preliminary and detailed analysis of this issue should be performed, which is not a subject of this study.

### 3.8. Release behaviour at different redox conditions

The results of the sensitivity calculations are presented in Figs. 15–16.

It can be seen from the Fig. 15 that the Mo release behaviour noticeably depends on the scaling factor of the H₂O. At high (>0.5) as well as at low scaling factors (<0.02) the deviation from the experimentally observed behaviour is significant. However, at the scaling factor 0.02 < scH₂O < 0.5 the behaviour of Mo is independent on the scaling factor and, therefore, not sensible to the atmosphere.

At the same time the release behaviour of other fission products of interest (Ba, Cs and I) does not show any dependence on the H₂O scaling factor, Fig. 16, at least in the studied scaling factor range.

Based on the obtained results the scaling factor of the H₂O in cGEMS of 0.2 has been selected for all the cGEMS modelling in this work. The 0.2 atmosphere scaling factor can be understood as a part (20%) of the atmosphere that is reacting with the pellet material. However, as it was already mentioned above, the question of the correct atmosphere treatment in the cGEMS modelling, namely determination of the gas flow distribution in the VERDON facility needs further study.

### 3.9. Speciation at different redox conditions

cGEMS calculations of the release behaviour using different atmosphere scaling factors allowed for a better understanding of the influence of the atmosphere on the speciation and volatility of different elements in the VERDON-1 experiment. The main effect of changing the scaling factor is to change the amount of oxidizing agent, H₂O, which reaches the sample surface. Thereby a low atmospheric scaling factor would indicate more reducing conditions, and a high atmospheric scaling factor would indicate more oxidizing conditions.

The vapour pressure plots for Mo related species at two different atmosphere scaling factors are presented in Fig. 17 (at scH₂O = 0.02) and Fig. 18 (at scH₂O = 2.0). The difference in the H₂O content in the atmosphere between two plots, therefore, is 100 times.

During the oxidising phase (from 13’000 till 20’000 s) of the experiment at both scaling factors, scH₂O = 0.02 and scH₂O = 2.0, we can see that Mo is predominantly in the form of Cs₂MoO₄ and its activity does not depend significantly on the atmosphere scaling factor. At this phase, the activity of Cs₂MoO₄ changes significantly (reduces) only at low atmosphere scaling factor, below scH₂O = 0.01. This explains the lower Mo release in the oxidising conditions.
A different behaviour is observed during the reducing phase (from 20'000 until 30'000 s) of the experiment. With a higher scaling factor, above \(Sc_{\text{H}_2\text{O}} = 0.5\), the Mo partitioning noticeably changes. It can be seen in Fig. 18 that the activities of the Mo related oxide species significantly increase in comparison with a lower scaling factor, Figs. 13 and 17. This explains why there is no noticeable release of Mo during the reducing phase at atmosphere scaling factors below \(Sc_{\text{H}_2\text{O}} = 1.0\).

At very high temperatures in the experiment, above 2300 K (from about 25'000 s), Mo is released even at reducing conditions, i.e., when very low atmosphere scaling factors are used. At this temperature, the activity (fugacity) of metallic Mo is high enough to cause its release from the pellet.

Such a variation of the Mo oxides activities (volatilities) with the atmosphere composition indicates significant sensitivity of the FP release behaviour and speciation to the redox conditions, i.e., availability of the oxidizing agent, in this case \(\text{H}_2\text{O}\).

In case of Ba, the release, as was mentioned above, does not depend on the atmosphere scaling factor [Fig. 16]. This can be explained by the fact that Ba related species, including metallic Ba, are much more volatile than, for example, Mo species. [Figs. 19]
and 20). It is, therefore, the diffusion that acts as a limiting factor and defines the release behaviour of Ba during the experiment.

4. Conclusions

This work presents an attempt to improve the modelling of fission products release using MELCOR by coupling MELCOR with thermodynamic modelling package GEMS. Developed coupling code, cGEMS, which serves as an interface between MELCOR and GEMS allows for an improved representation of the chemical effects on the fission products release behaviour. Improvement in the modelling predictions is associated with a more accurate description of chemistry and thermodynamics. In particular, GEMS provides MELCOR with information on the activities and vapour pressure of different species in the system during a simulation. Being a powerful thermodynamic modelling package, GEMS allows to predict activities and vapour pressure of different species depending on the temperature, pressure and chemical environment, taking into account mixing effects and chemical reactions that take place during the experiment/modelling.

The developed coupling code allowed to reproduce fission products release during the VERDON-1 experiment. In particular, the coupled simulations resulted in a credible description of Mo and Ba release during the experiment, without manual adjustment of vapour pressures of Mo and Ba species by the user. In addition, information on the speciation during the experiment was obtained, which sheds light on the release behaviour of Mo and Ba related species. In particular, the simulations have confirmed the observation by other studies that Mo is mainly released in the form of Cs2-MoO4. Ba is first released in small quantities as BaMoO4 during the oxidizing phase and mostly in the form of pure Ba later in the experiment. The particular partitioning between different species and, therefore, release behaviour of different species during the simulation strongly depends on the redox conditions and composition of the fuel.

The tool presented in this work improves the modelling of fission products release using the CORSOR-Booth model in MELCOR taking into account not only temperature effect but also the chemical composition of the fuel and redox conditions. Current work serves as an initial attempt to improve the description of thermochemical effects during severe accident modelling. Further research will be carried out to address not only fission products release behaviour but also the behaviour of the core during the severe accident as well as phenomena during molten core concrete interaction (MCCI).

However, it need to be taken into account that the application of the developed tool, cGEMS, increases the total simulation time due to the continuous restart of the MELCOR and intermediate GEMS calculations. In the case of VERDON-1 experiment simulations the increase in time was about 10–20%. In case of the full plan simulation the simulation time could increase significantly. In order to improve the calculation performance of the coupled code the possibility of integration of the thermodynamic calculation routine into the MELCOR analysis code should be considered in the future work.

CRediT authorship contribution statement

Sergii Nichenko: Conceptualization, Methodology, Software, Investigation, Formal analysis, Writing - original draft, Visualization.
Jarmo Kalilainen: Conceptualization, Methodology, Validation, Investigation, Visualization, Writing - review & editing.
Leticia Fernandez Moguel: Conceptualization, Methodology, Investigation, Writing - review & editing.
Terttaliisa Lind: Conceptualization, Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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