

Progress on Ruthenium Release and Transport under Air Ingress Conditions

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Summary

A particular concern in the event of a hypothetical severe accident is the potential release of highly radiotoxic fission product (FP) isotopes of ruthenium. The highest risk for a large quantity of these isotopes to reach the containment arises from air ingress following vessel melt-through. One work package (WP) of the SARNET Source Term topic is producing and synthesizing information on ruthenium release and transport with the aim of validating or improving the corresponding modelling of the ASTEC code. The WP includes reactor-scenario studies that can be used to define conditions of new experiments.

The experimental database currently being reviewed includes the following programmes:

- AECL Experiments conducted on fission product release in air; results are relevant to CANDU loss of end-fitting accidents;
- VERCORS tests on FP release and transport conducted by CEA in collaboration with IRSN and EDF; additional tests may potentially be conducted in more oxidizing conditions in the VERDON facility;
- RUSET tests by AEKI investigating ruthenium transport with and without other FP simulants;
- Experiments by VTT on ruthenium transport and speciation in highly-oxidizing conditions.

In addition to the above, at IRSN and at ENEA modelling of fission product release and of fuel oxidation is being pursued, the latter being an essential boundary condition influencing ruthenium release.

Reactor scenario studies have been carried out at INR, EDF and IRSN: calculations of air ingress scenarios with respectively SCDAP/RELAP5 and ICARE/CATHARE V2; SATURNE-MAAP; and ASTEC codes provided first insights of thermal-hydraulic conditions that the fuel may experience after lower head vessel failure.

This paper summarizes the status of this work and plans for the future.

A. Introduction

The {Ru-O} system has been studied in severe accident conditions since ruthenium tetraoxide has been observed to be highly volatile in air but also in steam with high oxygen potential [1-3]. A recently published review article provides a good overview of studies conducted previously in the field [4]. This paper presents progress made since the first ERMSAR meeting [5].

B. Ruthenium release from fuel

B.1 Modelling of ruthenium release and experiments with irradiated fuel

In ELSA module of ASTEC code v1.3, the modelling of ruthenium release from fuel is based on the assumptions that ruthenium volatilize from either $\text{Ru}_{(s)}$ or $\text{RuO}_{2(s)}$, depending on the oxygen partial pressure in the fuel, and that the main gaseous species to consider are RuO_x , with x from 1 to 4. Besides, the equilibrium oxygen potential in fuel is estimated using correlation based on data from [6] as recommended in [3].

Based on this modelling, the kinetic release of ruthenium has been estimated by IRSN for both clad and de-clad fuel samples through the AECL test series MCE1 [7] and HCE3 [8] and by ENEA for HCE3-H01 and HCE3-H02 experiments. These tests were conducted in vertically oriented zirconia furnace tubes in resistance furnaces (Table 1). The MCE1 tests [7] were performed on UO_2 fragments of burnup 10.7 MWd/kgU and masses between 0.191 g and 0.330 g. In tests 1, 2, 3, 4 and 7, the samples were heated to test temperature in nominally inert atmosphere ($\text{Ar}/2\%\text{H}_2$), and then subjected to air for about 900 s. Tests 5, 6 and 8 were conducted in $\text{Ar}/2\%\text{H}_2$ throughout the test, but test 8 experienced some oxygen ingress through the oxygen-permeable zirconia furnace tube.

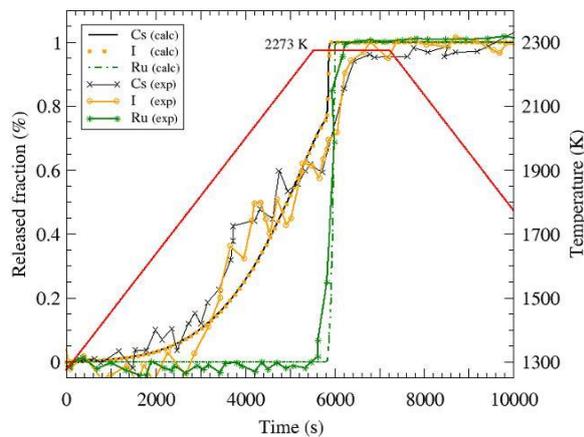
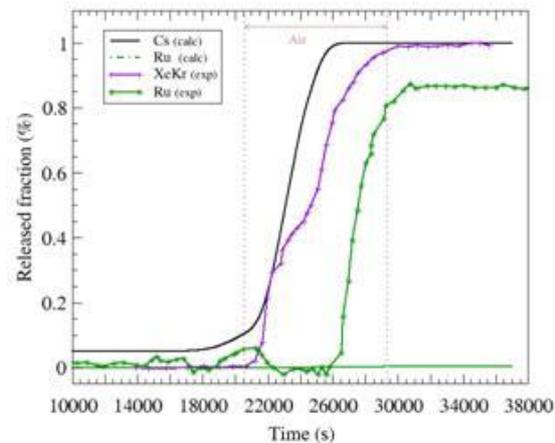
The HCE3 tests [8] were performed on 25-mm-long segments of a clad CANDU fuel element (burnup 9.8 MWd/kgU), with press-fitted Zircaloy end-caps. The nominal test environments were steam (tests H01, H03 and H06), air (tests H02 and H05) and $\text{Ar}/4\%\text{H}_2$ (test H04), but sufficient oxygen permeated through the furnace tube in test H04 to convert most of the hydrogen to steam. The samples were heated to about 1750 K or higher before being subjected to oxidizing environments for periods ranging from 8700 s to 2900 s.

We can notice on table 1 that for the MCE1 tests, i.e. for un-sheathed samples, the final released fractions of ruthenium are well estimated by ELSA module. Even if a discrepancy can be observed for test MCE1-8, one should keep in mind that for this test some additional oxygen was detected and that ruthenium release is highly sensitive to oxygen partial pressure. The kinetic release of ruthenium is, in the same way as the final released fraction, well estimated as it can be observed on figure 1 for the test MCE1-4. The delay between caesium release and ruthenium release is well reproduced by ELSA calculation. Then the modelling is quite well validated for de-clad fuel configurations.

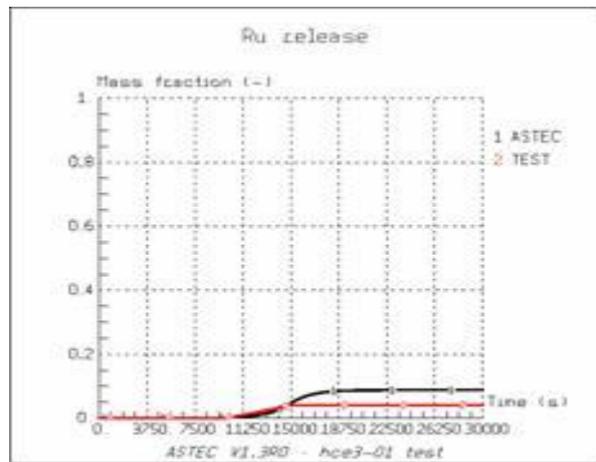
In calculations conducted at IRSN the final released fractions are always underestimated for clad sample (see table 1) in the same way as the kinetics (see figure 2 for test HCE3-H02). For clad sample, ELSA calculations take into account the geometrical barrier effect of the cladding that reduce the oxygen access to fuel (access is only enable through micro or macro fissures) but also the ruthenium access to gas flow. Consequently, fuel oxidation is slower and oxygen partial pressure may be underestimated by the calculation which implies a reduced ruthenium volatilization. A better understanding and estimation of the geometrical barrier effect of cladding under air ingress will be engaged in order to better estimate ruthenium release from clad fuel.

Table 1. Final released fraction of ruthenium for MCE1 and HCE3 tests from experiments and ELSA calculations.

	MCE1								HCE3					
	1	2	3	4	5	6	7	8	1	2	3	4	5	6
Peak T (K)	1973	2073	2173	2273	2073	2273	2350	2350	2200	2160	2110	2100	1780	1810
Atmos.	Air	Air	Air	Air	Ar/H ₂	Ar/H ₂	Air	Ar/H ₂	H ₂ O	Air	H ₂ O	Ar/H ₂ O	Air	H ₂ O
Exp. (%)	100	100	100	100	0	10	100	90	5	87	4	0	0	0
Calc.(%) IRSN	100	100	100	100	0	0	100	46	0	0	0	0	0	0
Calc.(%) ENEA	-	-	-	-	-	-	-	-	8.7	0	-	-	-	-

**Fig.1** Ruthenium kinetic release under air conditions for test MCE1-4.**Fig. 2** Ruthenium kinetic release under air conditions for test HCE3-H02.

In modelling conducted at ENEA in the case of steam atmosphere (HCE3-H01), Ru release fraction (table 1) and kinetics (Figure 3) as well as the release of volatile FPs agreed very well with the experimental data [9]. For the air ingress experiment (HCE3-H02), releases of ruthenium, barium or UO₂ were not predicted by the code although especially ruthenium release was very significant. Volatile FP releases were again in very good agreement with the experiments. In sensitivity studies varying oxygen partial pressure, gap and channel pressure or reducing oxidation of zircaloy cladding did not seem to have any effect on the release of ruthenium. Also results evidenced only low sensitivity on inlet flow rate. A slight effect was observed when the possibility of gas access to the fuel was modified.

**Fig. 3** Ruthenium release kinetics in steam flow for test HCE3-H01.

B.2 RUSSET ruthenium release experiments

In the frame of RUSSET experimental programme Ru oxidation and release were investigated to understand its release from spent fuel elements in high temperature air

atmosphere. Evaporation rate and content of Ru in escaping air flow at 300 K were studied. The results showed that Ru evaporates in form of RuO_3 and RuO_4 and the amount of RuO_4 in the escaping air was in the range of 10^{-6} bar, far above the value that would be expected from equilibrium ($\sim 10^{-10}$ bar). It was also observed that other fission products and UO_2 influenced the concentration of RuO_4 in escaping gas flow at ambient temperature and caused a time delay in appearance of its maximum values.

Previous RUSSET experiments (1-4) were performed with metallic Ru powder in inert matrix (ZrO_2) with or without inactive fission product elements or in UO_2 matrix containing also inactive fission product elements. In irradiated UO_2 Ru appears in form of small alloy precipitations together with Mo, Rh, Pd and Tc (white inclusions). The main objective of RUSSET-5 was to study the differences of ruthenium evaporation rate from pure ruthenium metal and from Mo-Ru-Rh-Pd alloy.

The experiments were conducted using ZrO_2 matrix with fine grains of Mo-Ru-Rh-Pd alloy as well as with other inactive fission product components (Cs, I, Se, Sn, Ag, Nd, Sb, Cd, Te, Ce, Ba and Zr). The applied concentrations of the alloy and other inactive fission product components represented a middle burn-up fuel. Reference measurements were conducted with pure Ru powder in ZrO_2 at 1000°C and 1100°C .

The scheme of experimental device is shown in Figure 4. High temperature conditions were established in a vertical furnace. The reaction chamber was a quartz tube with a larger diameter section in the middle containing the test mixture (1 g ZrO_2 with $\sim 18,52$ mg powdered alloy containing 5 mg Ru). With air flow rate of $171 \text{ cm}^3/\text{min}$ (NTP) the evaporation of Ru was fast enough to result in equilibrium partial pressures for ruthenium oxides in the beginning of the experiments. Isothermal experiments were performed at 1000°C and 1100°C . During the tests air injection was started when sample in the furnace reached the required temperature. Released Ru was first collected in an inner quartz tube placed at the outlet of the reaction chamber to determine the amount of deposited RuO_2 in the decreasing temperature zone. Gaseous ruthenium oxide components in the outlet gas were quantified trapping the gas in alkaline hypochlorite absorber solution at ambient temperature. Both the inner quartz tube and the absorber solution were changed at the same time to obtain time-resolved information about the RuO_x escape.

The present results showed that the oxidation rate of Ru from Mo-Ru-Rh-Pd alloy is about 50-60% of the evaporation rate of pure Ru at 1000°C and 1100°C . Slower reaction rate could be partly resulted by the larger grain size of the alloy compared to the commercial ruthenium powder. There were no significant differences in the partial pressures of RuO_x in the high temperature reaction chamber between pure alloy and alloy with other fission product components either at 1100°C or at 1000°C .

In case of pure Mo-Ru-Rh-Pd alloy, concentration of RuO_4 in the ambient temperature outlet gas decreased continuously in time. In presence of other fission product elements, a time delay appeared like at earlier experiments conducted with ruthenium powder and fission products. This time delay was about 30 min at 1100°C and about 60 min at 1000°C . However, there was no time delay in the escaping of Ru from the

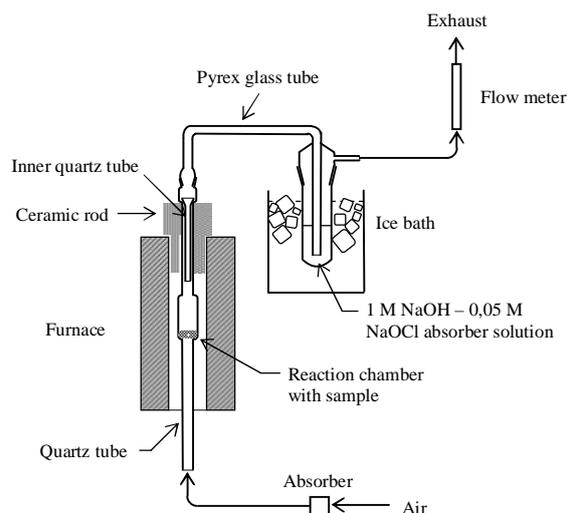


Fig. 4 Scheme of experimental facility.

high temperature reaction area. It suggests that reactions in the decreasing temperature area delayed the release of Ru in the escaping cooled down air. On the other hand, in presence of other fission product components the fraction of Ru appearing in the absorber solution was greater than in case of pure alloy. Moreover, in case of both pure alloy and alloy with other fission products, the fraction of escaping RuO_4 was greater than with metallic ruthenium powder. Presumably molybdenum oxide and other fission product elements deposited in the inner quartz tube reduced the decomposition of RuO_x to RuO_2 . The total amount of Ru collected in alkaline hypochlorite solution was greater in case of tests performed at 1000°C than at 1100°C . This maybe due to the longer reaction time, especially as the partial pressures of RuO_4 in the outlet gas were approximately the same in both temperatures.

B.3 VERCORS experiments

The particularity of the VERCORS programme is to provide data on fission product release, among them ruthenium, from genuine irradiated fuel rods under severe accident conditions. Altogether 17 separate effect tests were performed in hot cell of the CEA Grenoble between 1989 and 2002 on PWR irradiated fuel samples (around 30 grams), heated at high temperature under various atmospheric conditions. Thanks to a short re-irradiation of the fuel sample at low linear power in a MTR reactor, the elaborated data base covers a wide range of fission products, including those of short half life, and among them ^{103}Ru .

The programme is composed of 3 experimental phases: (i) VERCORS 1 to 6 tests performed on UO_2 fuels up to 2600K, (ii) VERCORS HT 1 to 3 tests performed on UO_2 fuels up to fuel melting temperature and devoted to study both the FP release and transport and (iii) VERCORS RT 1 to 8 tests, where the influence of the nature of the fuel (Burn-up, UO_2 versus MOX) as well as its morphology (initially intact or fragmented) on FP release have been investigated.

The main outcomes highlighted from these experiments are:

- In reducing conditions, low volatility of ruthenium is confirmed as expected. In all tests performed under hydrogen atmosphere, ruthenium mainly stays within the fuel sample and aggregates into coarse-grained metallic precipitates. Total release is always below 10% of the initial inventory, even when fuel melting temperature has been reached. Moreover, released ruthenium deposits immediately downstream the furnace at a rather high temperature.
- In oxidising conditions, ruthenium release may be more important, in particular from UO_2 fuel at high burn-up. Three experiments have exhibited a very significant ruthenium release, 17%, 28% and 65% respectively for RT8, RT6 and HT2 tests. They deserve to be described in more detail, since the release occurred not only in air atmosphere, but also in steam and even steam-hydrogen atmospheres.

RT8 was specifically devoted to simulate an air ingress accident on UO_2 fuel at 70 GWd/t. The relatively low ruthenium release (only 17% compared to the other RT6 and HT2 tests) can be explained by the conditions of the test: for safety reason the sequence was conducted in 3 successive phases; (i) a one hour long pre-oxidation phase of the cladding at 1800 K followed by (ii) a temperature ramp up to 2270 K under pure helium in order to sweep all generated hydrogen from the loop, then (iii) the succession of several high temperature plateaus up to fuel collapse under a mixture of helium (90%) and air (10%).

In comparison to RT8, RT6 was performed also on similar high burn-up UO_2 fuel (72 GWd/t). The sequence was composed of one hour long cladding pre-oxidising phase at 1800

K followed by a succession of high temperature plateaus from 2100 K up to the fuel melting. These phases were performed in a mixed atmosphere of steam and hydrogen. High release of ruthenium in this test (28%) is clearly a consequence of the high burn-up, since similar test (RT1) performed on UO_2 fuel at 47 GWd/t exhibits only 9% ruthenium release.

The most important ruthenium release (65%) comes from HT2 test, performed on UO_2 fuel at 48 GWd/t. The sequence was otherwise similar as RT6, but atmosphere after pre-oxidation phase was pure steam. Once again, oxidising conditions associated with a rather high burn-up fuel are responsible for this very important release. Ruthenium release in similar test (HT3) performed in pure hydrogen after the pre-oxidation phase was only 6%. Moreover, 12% of the released ruthenium deposited far downstream the loop at temperature below 400 K. At last, as shown in figure 5, ruthenium release begins promptly from 2150 K, when the fuel sample still remains solid and reaches 20-25% as the fuel begins to collapse.

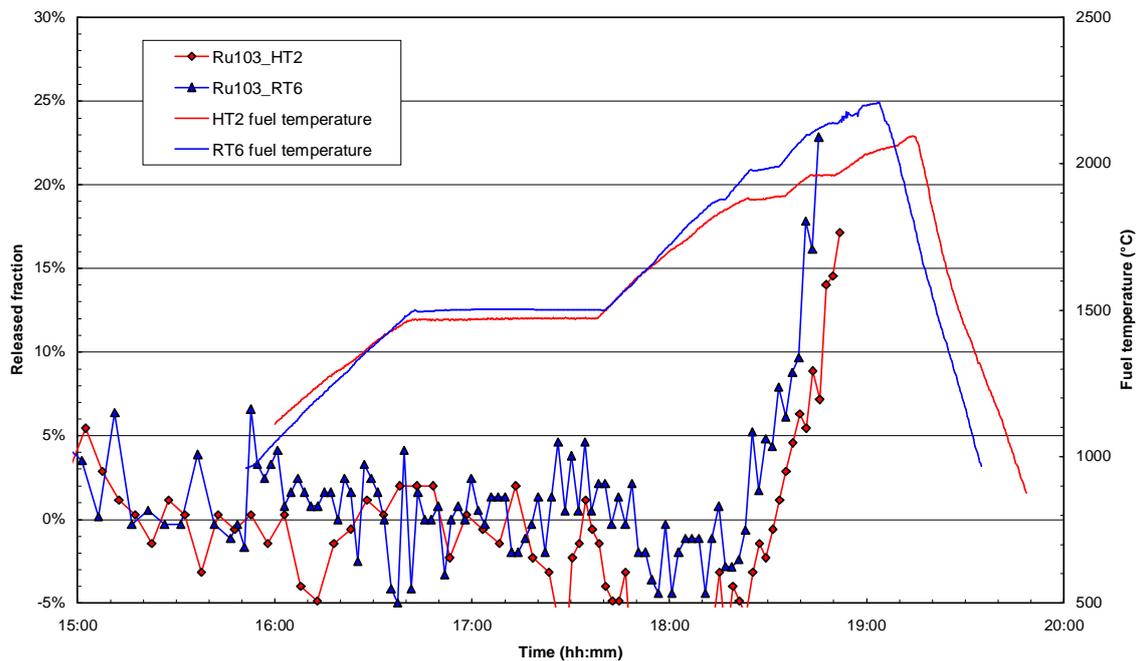


Fig. 5 Ruthenium release kinetics from fuel for HT2 and RT6 tests.

B.4 MERARG-Ru test

In order to complement ruthenium release from genuine irradiated nuclear fuel under air ingress, a so-called “Ru scoping experiment” has been undertaken in the MERARG facility. This device, implemented in a hot cell of the CEA Cadarache, is used to fulfil several analytical programs on Fission Gas Release. Results from the Ru scoping experiment are still under processing.

The annealing test facility is schematically depicted in figure 6. The main components of the loop are: (1) induction furnace located inside a shielded hot cell, (2) online γ -spectrometry device and (3) glove box. The induction furnace includes a metallic crucible heated by induction. Tungsten, molybdenum or platinum crucibles are available depending on the test. The sample temperature is monitored both by a pyrometer at the top of the pellet and by a thermocouple located in the crucible. Furnace containment is made of a quartz tube, in which the crucible is positioned. During the whole experiment, the specimen is swept by gas flow (helium, argon or air), which carries fission gas through aerosol filters before passing into the counting chamber situated in front of the γ -spectrometer. The γ -spectrometry station

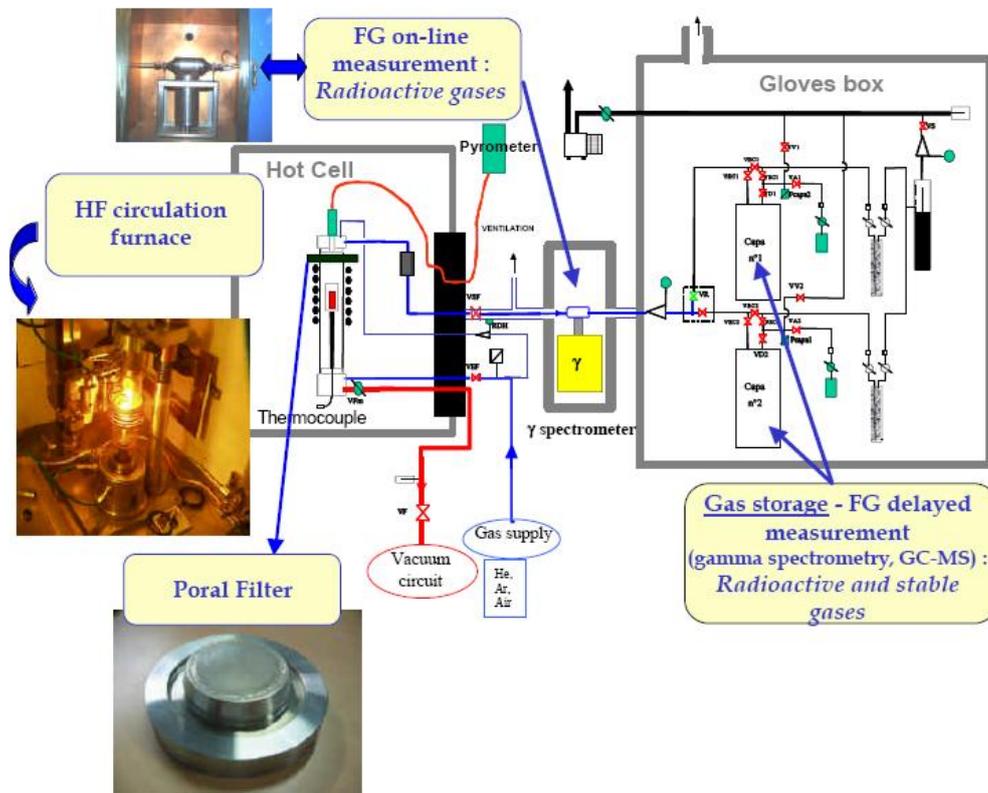


Fig. 6 A schematic picture of the MERARG facility.

monitors the fission gas release kinetics. Cumulative gas release is obtained at the end of an experiment by analyzing the gas, which has been trapped into the glove box.

In the “Ru scoping experiment” a poral filter was placed at the top of the furnace in order to trap the emitted aerosol particles. The sample, one pellet with its cladding, was taken from UO₂ fuel irradiated during six cycles in PWR (i.e. up to 72 GWd/t) operated by EDF.

In order to be able to calculate the release fractions of non gaseous fission products, the initial fission product concentration inside the samples has been measured by γ -spectrometry: several successive and joined spectra are made to explore the entire length of the sample and a classical γ -spectrometry data treatment is applied in order to determine the quantitative ¹⁰⁶Ru and ¹³⁷Cs distributions.

The sample, located inside the Pt crucible, has been heated up from room temperature up to 1350°C under air flow of 1 cm³/min. The temperature was maintained at 1350°C during 40 minutes. After the sequence, the crucible, the quartz tube and the poral filter have been stored separately in specific container, in order to be γ -scanned. This operation will allow determining the non gaseous fission products release (i.e. Ru and Cs) by comparison to the initial fission product concentration. Up to now, post test data treatment is under progress.

C. Ruthenium transport in primary circuit

C.1 Ruthenium transport and speciation experiments

In order to verify whether radioactive ruthenium would be transported within a nuclear facility, it is of interest to know how its volatile compounds are formed and how they behave. To this end 19 experiments were carried out at VTT between 2002 and 2006. In these experiments the formation and transport of volatile ruthenium oxides was studied by exposing

RuO₂ powder to diverse oxidising atmospheres at a relatively high temperature. The most important experimental parameters were temperature of the furnace, composition of the gas flow and material of the tubing.

In the experiments ruthenium source (RuO₂ powder) was placed in a ceramic crucible within a tubular flow reactor. The tube material in the reactor was high purity alumina. Depending on the experiment temperature of the reactor ranged from 1100 K to 1700 K. Downstream of the reactor the gas temperature decreased to about 360 K. The flow rate through the reactor was 5 L/min (NTP) and the flow consisted of different mixtures of air, argon and steam.

Upon cooling of the gas flow gaseous ruthenium oxides decomposed partly to solid RuO₂. Aerosol particles were filtered out at point 106 cm downstream of the reactor. Gaseous ruthenium was trapped downstream of the filter in a 1 M NaOH-water solution. The determination of ruthenium both in aerosol filters and in the liquid was made using instrumental neutron activation analysis (INAA). The amount of ruthenium deposited on the walls of the tube was quantified by carrying out some experiments with ¹⁰³Ru as radioactive tracer. The kinetics of ruthenium transport was studied in tracer experiments by measuring the activity of the filter and the trapping bottle online. The number size distribution of the transported aerosol particles was measured using Scanning mobility particle sizer (SMPS). Transmission electron microscopy (TEM) equipped with selected area electron diffraction (SAED) was applied in the analysis of the morphology and the crystal structure of particles.

As expected, the release of ruthenium from the reactor depended primarily on temperature ranging from 0.11 mg/min at 1100 K to 25.4 mg/min at 1700K. Release rate in different experiments is presented in figure 7. Ruthenium release rate increased with oxygen partial pressure especially at highest temperatures. Also doubling the gas flow rate to 10 L/min (NTP) increased the release rate by about 50%.

A large fraction of the release likely took place as gaseous RuO₃, which thermally decomposes to solid RuO₂ as temperature decreases below approximately 1000 K. Formation of RuO₂ aerosol particles competed with reaction on the tube surface. The fraction of released

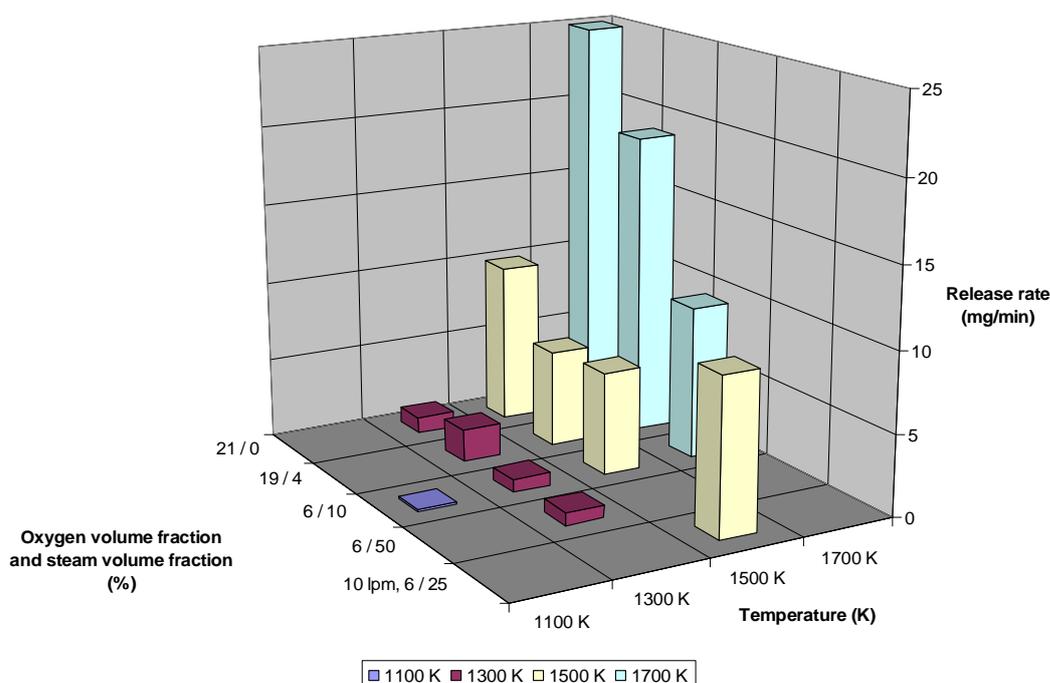


Fig. 7 Ruthenium release rate as a function of reactor temperature as well as oxygen and steam volume fractions.

ruthenium transported as RuO_2 particles increased with reactor temperature ranging from less than 1% at 1100 K to about 35% at 1700 K. Steeper temperature gradient at high reactor temperature favoured aerosol formation instead of reaction on the surface. The addition of seed particles into the flow increased aerosol transport by factor of 2 as a significant fraction of RuO_3 obviously decomposed on the surface of the seeds. Measured deposition profiles in all five experiments conducted with the radiotracer were almost identical regardless of the reactor temperature, composition of the flow or the amount of deposited ruthenium.

As much as 40% of the released ruthenium transported in gaseous form at 1300 K in dry air flow. The fraction increased to 66%-70% as the steam volume fraction was increased to at least 10%. As the temperature of the furnace was increased, the transport of gaseous ruthenium was almost limited to that reevaporated from the deposited RuO_2 at the outlet of the furnace. At 1500 K there were two cases, in which a significant fraction of ruthenium was transported in gaseous form. When tube material after the furnace was changed from stainless steel to alumina or silver seed particles were added to the gas stream, the fraction of gaseous ruthenium was increased to approximately 5% of the released amount.

C.2 Ruthenium transport in RUSSET experiments

The RUSSET ruthenium transport experiments were designed to represent the main phenomena taking place during a severe reactor accident with air ingress (Fig. 8). During isothermal oxidation of metallic ruthenium samples, the furnace temperatures were set to constant values between 1000-1800°C. The air injection into the furnace resulted in the formation of gaseous ruthenium oxides: RuO_3 and RuO_4 . The outlet section of furnace simulated the cold surfaces of the primary circuit with temperature decreasing to 100°C. As temperature decreased, RuO_3 and a fraction of RuO_4 decomposed leading to formation of RuO_2 crystals on the cold surfaces. When the air entering the outlet section was sufficiently hot, RuO_4 was produced again through the oxidation of deposited RuO_2 . A gas bubbler kept at room temperature represented the atmosphere of the containment or the environment. Here gaseous RuO_4 was collected by a chemically reacting solution.

The partial pressures calculated on the basis of the sum of deposited Ru mass and Ru in liquid solutions characterized the conditions in the furnace. As shown in figure 9, the calculated partial pressures were in very good agreement with the equilibrium partial pressure of $\text{RuO}_4+\text{RuO}_3$ system. The agreement showed that both RuO_4 and RuO_3 reached saturated concentration in the furnace, which limited the rate of Ru oxidation.

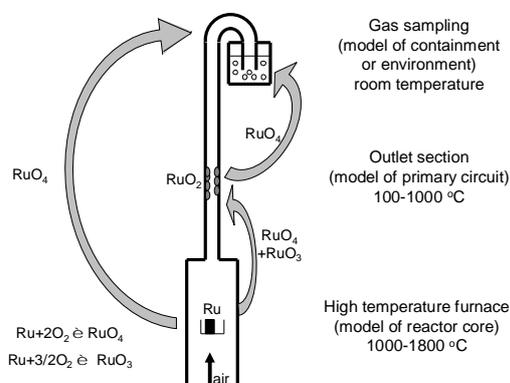


Fig. 8 Schematic view of Ru oxidation and release mechanisms.

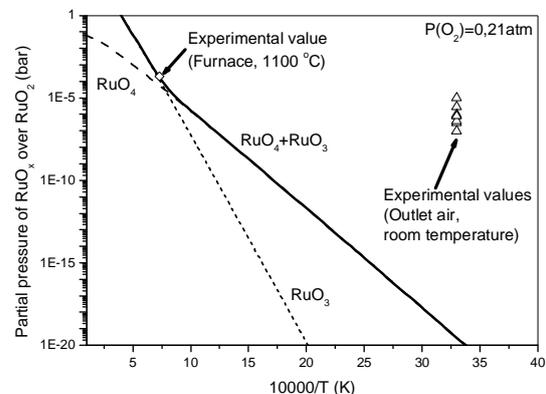


Fig. 9 Partial pressure of RuO_x as a function of reciprocal temperature in RUSSET-1.

Partial pressures calculated from the Ru mass trapped in liquid solutions characterized the Ru oxide concentration at room temperature. These partial pressures were in the range of 10^{-7} - 10^{-5} bar, while the equilibrium value of RuO₄+RuO₃ system is lower by several orders of magnitude. Obviously the decomposition process of RuO₄ to RuO₂ was not fast enough to follow perfectly the equilibrium. The rate of decomposition slowed down with decreasing temperature and stopped at about 600-800 °C.

D. Reactor scenario

Circumstances in which air can come in contact with irradiated fuel have been investigated and air ingress flows have been then evaluated with two independent approaches at IRSN and at EDF. The accidental situation leading to air/fuel contact in a Pressurized Water Reactor (PWR) which has been considered is when there is a lower vessel head failure (LHF), after core meltdown accident. Some previous studies were carried out at Sandia National Laboratories for evaluating in-vessel air flows, examining the “chimney” effect that develops after the reactor vessel is ruptured. It was first concluded that most of the flow regime was concentrated between 10 to 200mol/s [10]; more recent studies estimated the air flows range between 2mol/s to 20mol/s [11]. The approaches presented here are different from the previous ones as they are based on one hand on thermal-hydraulic calculations with a lumped-parameter code, namely ASTEC [12], and on another hand on CFD thermal-hydraulic calculations (Saturne code). Both are applied to 900MWe French PWR containment.

D.1 Air ingress scenario calculations with ASTEC

A quite detailed nodalization scheme was used for the reactor containment building modelling, i.e. more than 50 zones. The scenario investigated was a loss-of-coolant accident (LOCA) due to a 12” break located on a hot leg, water injection safety systems being not available. The reactor core underwent severe damage up to the lower head vessel failure. This scenario was chosen because it represents conditions, where air ingress may be favoured due to low pressure losses along the flow path. If no air ingress would be observed in such a situation, there is little “chance” to get it in other scenarios. In a first step, the whole severe accident transient has been calculated with the ASTEC integral code; boundary conditions coming from this first calculation were used as an input for a pure thermal-hydraulic calculation, with a detailed containment scheme, in a second step. Results for flow in the containment can be illustrated with three “snapshots” at different instants (figure 10):

- before LHF: steam coming from the RPV blow down at primary circuit break (F02V) induces rapidly containment pressurization, leading to the failure of the rupture disk connecting the cavity and the upper part of the containment (V25); during the in-vessel phase, a convective flow develops from the upper parts of the containment down to the ventilation chimney compartment through this connection and exits the cavity through the annulus space around the reactor vessel (V24).
- at LHF (F01V opens) and during about 11min, due to the significant gas mass flows produced by molten core concrete interaction (MCCI), all gases exit the cavity; the steel door connecting the ventilation room to adjacent rooms (P111) is assumed to leak as well. All oxygen initially present in the cavity is blown away, so there is no way for any air ingress in RPV.
- after a few minutes, flows is again reversed: natural circulation between the upper containment and the cavity through the RPV takes form, and lasts for several hours. Such a convective loop brings air into the RPV.

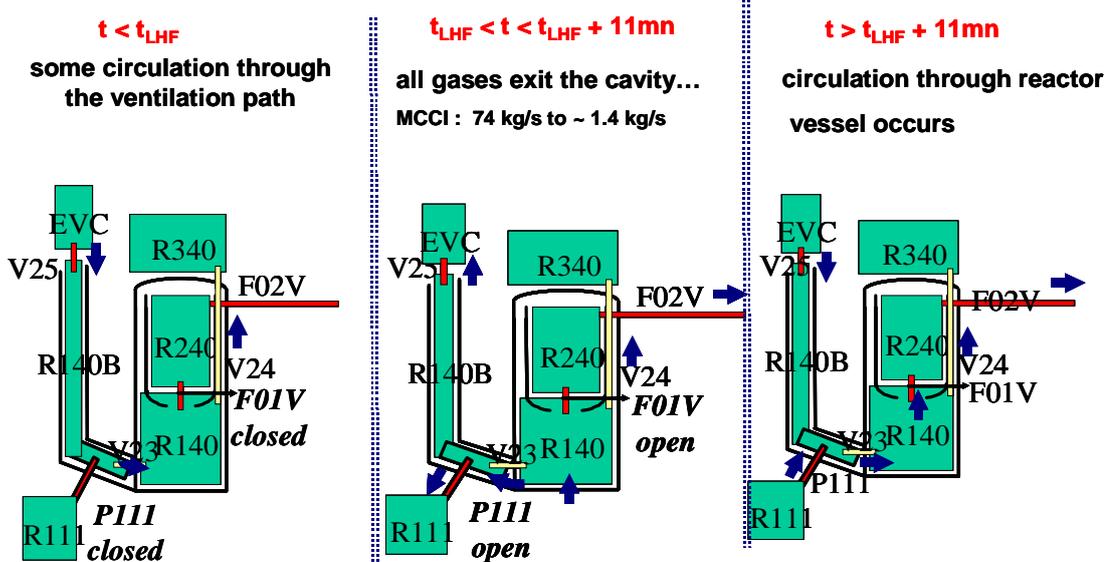


Fig. 10 Flow patterns in reactor cavity and adjacent rooms at different instants (blue arrows)

Explanation of the flow behaviour is the following: the cavity pressurization due to MCCI is overwhelmed by buoyancy forces between the ventilation chimney and the reactor cavity. The temperature difference between these zones is high enough to induce gas density differences. Considering the height of the ventilation chimney ($\sim 10\text{m}$), it is clear that pressure difference between these zones due to gravity drives the flow pattern. This situation lasts for several hours; a quasi-steady state seems to be established. Only 8% of the total mass flow entering the cavity passes through the RPV (F01V), while 92% exits the cavity through the vessel annulus space (V24). This is a particular feature of «French like open cavities», for which there is no major role of cavity pressurization. Gas composition (molar fraction) at about 4 hours after LHF is found to be about 50% air, 25% steam, 10% CO_2 , 10% H_2 , 5% CO. Air molar flow in the RPV can be estimated to be $\sim 7\text{ mol/s}$.

From this “base case” calculation, several sensitivity calculations were performed. Results indicate that in most cases, an air ingress in the reactor vessel is likely to occur some time after the beginning of MCCI, with a typical air molar flow of 10 mol/s. Surprisingly, there is a limited role of the RPV chimney effect itself: there is no significant increase of the up-draught flow rate when the temperature of the remaining fuel is increased in the vessel. On the other hand, temperature in the cavity and in the adjacent zones, namely zones above RPV and ventilation chimney, are of much higher importance.

D.2 CFD calculations of air inlet in vessel

The approach used by EDF to confirm air ingress is based on CFD calculation performed by Saturne –code, using standard $k-\epsilon$ model for turbulence. The whole reactor building has been meshed with 41.000 cells with a special refinement in the area of the vessel supporting ring in the annular space. The boundary conditions have been determined by simulation performed by EDF version of MAAP4 and crosschecked by Tolbiac calculations for molten core concrete data. The precise geometry of the remaining core inside the vessel is not accurately known. Thus the pressure drop inside the vessel is neglected compared to the pressure drop at the hot-leg breach. This is a conservative assumption.

In the calculation results a convection loop is well observed. Humid air goes down the venting duct and is heated by the corium pool in the reactor pit. Then, it goes up either through the annular gap or inside the vessel. The velocity field in the reactor pit is shown for

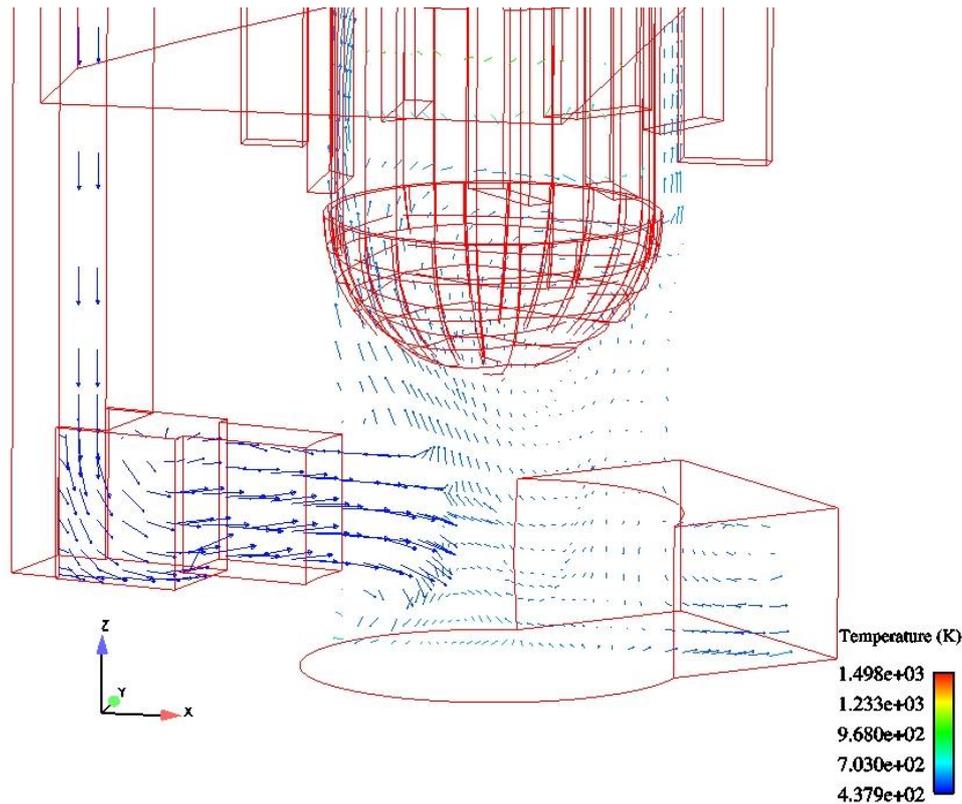


Fig. 11 Velocity field in the reactor pit

the reference case in figure 11. One can observe, thanks to the colour grid, that decay heat inside the vessel heats the gas passing through the RPV.

A sensitivity study has been performed for the following parameters:

- Meshing : 41.000 and 60.000 cells;
- Position of the vessel breach: unzipping at the pole or equatorial failure. The breach is maximized to bound the amount of air likely to enter inside the vessel;
- MCCI gas flow ranging from 0.05 to 0.5 kg/s, after initial phase of interaction;
- Hot leg breach size (double ended rupture 29" down to medium size 7" break).

The descending flow in the venting duct (~ 7 kg/s) is stronger than the MCCI gas flow. Therefore the latter has a weak impact on the results. The main parameter influencing the air ingress in the vessel is the hot leg breach size: it varies from 24 mol/s for a double ended breach to 1 mol/s for a 7 inches breach. The study confirmed the occurrence of air ingress scenario in the vessel. It has to be remembered that it requires failure first in the hot-leg and then in the RPV lower head. For bounding conditions, the amount of air ingress could not exceed 24 mol/s. From these calculations, it is recommended to consider that air can enter the vessel at a mean value of a few moles per second.

D.3 In-vessel calculations

The calculations are performed with ICARE/CATHARE v2, which has a model for zirconium oxidation by air. The objective was to analyze the conditions resulting from air ingress in the reactor vessel after the LHF. IRSN provided TMI2 input deck for the reactor pressure vessel, which was used in the calculations. Inlet boundary condition, mass flow rate, mixture composition and temperature were provided by previous containment calculations performed by IRSN for 12" break and by EDF for a 29" guillotine rupture of primary pipe.

Scenarios presented here focus on the analysis of a pre-degraded core composed of fuel and control rods segments as well as damaged structural components. The core is intended to be representative of TMI2 with a hypothetical rupture of the lower head. Sensitivity studies included cases, in which air-steam mixture was inserted on pre-oxidized and not oxidized core fragments. In some scenarios air was introduced after longer pre-degradation in steam [13]. The main assumptions for the calculations are:

- Air junction is located centrally right below the lower plate of the core. Assumption is conservative, because it will maximize the air flow rate through the core region.
- Area of the air junction corresponds to a circle with a diameter of 0.5 m [14].
- Non-condensable other than hydrogen is replaced by argon. Assumption is not conservative, because zircaloy could also be oxidized by CO and CO₂
- No by-pass is considered through the downcomer. This is a conservative assumption, because in reality natural convection should divert a part of the flow.
- Temperature of the gas mixture entering the vessel is 1700 K in the beginning and 1800 K at 29000 s [15].
- In the cases with pre-defined oxide scales the mass fractions are according to [16]:
 - a. On the fuel cladding ZrO₂ fraction increases linearly from 0 at the bottom to 0.2 at the top of the lower cladding segment and decreases linearly from 0.2 at bottom to 0 at the top of upper cladding segment. ZrO fraction is 5% of ZrO₂ fraction and the rest is β -Zr.
 - b. On control rod guide tubes the fractions are 0.94 ZrO₂, 0.01 ZrO and 0.05 β -Zr.

The first objective was to highlight the effect of air oxidation inside the core and to check its contribution to the core degradation process. Then oxygen circulation inside core was followed and its availability in different zones was determined. Finally, the status of the remaining fuel and cladding in the long run were outlined with the intent of investigating the possibility of fuel interaction with oxygen.

As a result, figure 12 displays the degradation status of the core and the temperature field in the two cases at 1 h after initiation of the air ingress. Figure 13 displays the oxygen availability inside the reactor pressure vessel at the same time. In the first thousands seconds, the flow of air mixture through the 12" break (336 g/s) produces roughly 1 MW by oxidation and the flow through the 29" guillotine break (1460 g/s) produces 5 MW. Degradation of the core is accelerated by increased flow rate. Oxygen starvation was observed at the beginning of oxidation and for low flow rate. Depending on the blockages and oxygen availability in each scenario, possibility exists for the de-cladded fuel and mixtures composed basically by UO₂ to get into contact with oxygen.

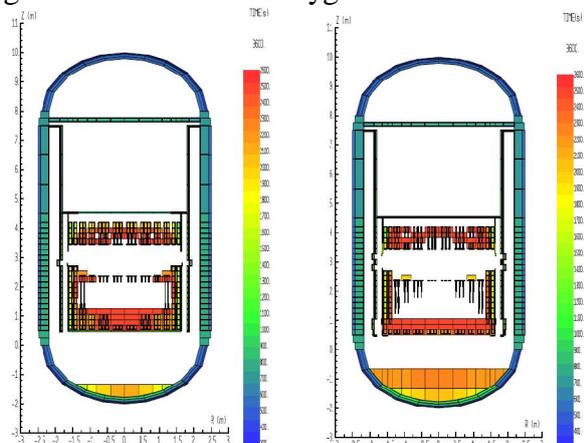


Fig. 12 Degradation of the core at 1 h for 12" break on the left and 29" break on the right.

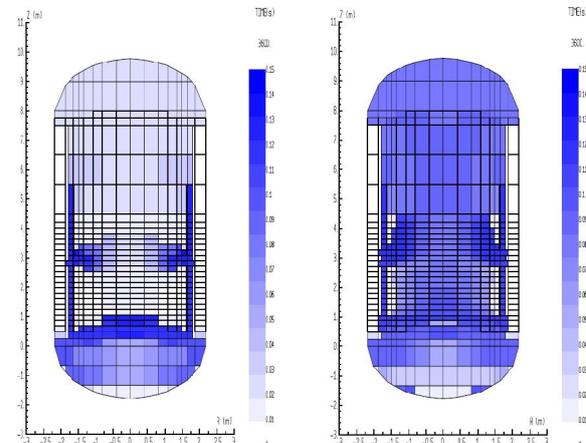


Fig. 13 Oxygen mass fraction at 1 h for 12" break on the left and 29" break on the right.

E. Conclusions and future work

The release of ruthenium has been studied using different types of PWR and CANDU fuel samples, fuel simulant materials as well as samples of ruthenium containing alloys and metallic or oxidised ruthenium powders. In reducing conditions ruthenium release has always been very limited. However, the release fraction of ruthenium has been found to be significant in pure steam atmosphere, in gas mixtures containing air and even in steam-hydrogen mixture. Release fraction and kinetics are greatly influenced by fuel burn-up and by the degradation of the fuel and cladding material. The release of ruthenium from bare fuel can be adequately modelled by current codes. The influence of the cladding especially in air ingress conditions need to be studied further.

Released ruthenium is transported in primary circuit conditions either as RuO_2 aerosol particles or gaseous RuO_3 and RuO_4 . Although a significant fraction of gaseous ruthenium oxides reacts on surfaces to form solid RuO_2 , measured partial pressures of ruthenium oxides have at room temperature been much greater than their equilibrium vapour pressure. Fission products or other materials released at the same time as well as revaporisation of deposited RuO_2 increase the fraction of ruthenium transported in gaseous form. The size of formed ruthenium particles ranges from few nanometres to less than 50 nm. Such small particles agglomerate rapidly with larger aerosol and are transported together with them.

Air ingress flows following hot leg break and lower head failure were evaluated in two independent studies. It was observed that natural circulation could bring air to RPV for several hours. The mean value of air flow to the RPV is expected to be few moles per second. Depending on the flow rate the air ingress was estimated to produce 1 – 5 MW by oxidation of the remaining core material during the first 1000 seconds. It seemed to be highly likely that the fuel would get into contact with oxygen.

The data base on Ru release under air ingress conditions from irradiated PWR fuel rods is still scarce, as in the VERCORS programme, few tests were performed in very oxidising conditions and more particularly under air ingress with significant amount of air. In this context, the future VERDON programme, recently launched by the CEA, will include a specific air ingress test on a genuine irradiated UO_2 fuel sample in its original cladding. As performed during the whole VERCORS programme, the sample will be previously re-irradiated at low power in a MTR reactor, in order to rebuild the inventory of short half-life fission products (including ^{103}Ru). This test will be conducted in a new dedicated hot cell, which will support an advanced instrumentation. The aim is at measuring not only the release of fission products, but also studying their deposit on thermal gradient tubes and their potential re-volatilisation induced by air injection. Compared to VERCORS, VERDON will also be completed by more detailed examinations of the fuel sample before and after the tests, using micro-analytical techniques, such as SEM, EPMA and SIMS, in order to determine the location of the fission products within the various phases as well as the corresponding compounds if possible. This will help to better understand the mechanisms, which promote fission products release in such situations, as well as to support the associated modelling. The VERDON programme is a part of the International Source Term Programme, which is composed of separate effect tests aiming at reducing uncertainties in severe accident analyses.

Beyond these results, it is also of prime importance to investigate, how ruthenium species behave in the reactor containment building. Whether there is any significant trapping on containment surfaces and whether RuO_4 is chemically stable in the containment. These questions have started to be addressed and several results are being produced [4, 17]. It appears that RuO_4 is not stable in gas phase but its decomposition is not as fast as expected from literature review. The kinetic rate law of RuO_4 reduction is found to be dependent on

temperature but above all on the presence of steam. Humidity as well as the presence of ruthenium dioxide deposits seems to catalyse the reactions. Also against all expectations, no specific affinity of RuO₄ for containment surfaces has been found, either for stainless steel or for painted substrates. In addition to ruthenium retention the production of gaseous ruthenium inside the reactor containment, i.e. by oxidation of RuO₂ deposited on containment surfaces or by oxidation of ruthenium species present in the aqueous phase is further studied.

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