



## **Ruthenium release at high temperature from irradiated PWR fuels in various oxidising conditions; main findings from the VERCORS program**

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### **ABSTRACT**

Fission product release and transport in case of PWR severe accident is a major topic in reactor safety assessment due to the potential radiological consequences for surrounding populations and the environment. In this context, the Institute for Radiological Protection and Safety (IRSN) and Electricité de France (EDF) have supported the VERCORS analytical test program which was performed by the "Commissariat à l'Énergie Atomique" (CEA). It is usually considered as complementary to the PHEBUS FP in-pile integral experimental program.

25 annealing tests were performed between 1983 and 2002 on irradiated PWR fuels under various conditions of temperature and atmospheres (oxidising or reducing conditions). The influence of the nature of the fuel (UO<sub>2</sub> versus MOX, burn-up) and the fuel morphology (initially intact or fragmented fuels) have also been investigated. These led to an extended data base allowing on the one hand to study mechanisms which promote fission products release, and on the other hand to enhance models implemented in severe accident codes. Among all the fission products investigated, ruthenium is of specific concern because of its high radiological effects due essentially to the combination of both its short and long half-life isotopes (i.e. <sup>103</sup>Ru and <sup>106</sup>Ru respectively), but also by its ability to generate volatile gaseous oxides (RuO<sub>3</sub>, RuO<sub>4</sub>) in very oxidising conditions, in particular in the case of air ingress accidents. Important uncertainties still remain on the release and transport of this element in such situations, and investigations on this open issue are notably carried out in the SARNET European framework.

The present communication gives a general overview of the VERCORS program and presents more deeply the main findings concerning the ruthenium release. Its global behaviour is analysed on the basis of several comparative tests:

- same UO<sub>2</sub> sample (35 and 50 GWd/t) under hydrogen or steam conditions,
- similar MOX sample (40 GWd/t) under hydrogen or mixed (steam and hydrogen) conditions,
- similar oxidising conditions for UO<sub>2</sub> samples at different burn-up from 35 to 70 GWd/t.

Significant ruthenium release has been evidenced in pure steam conditions from high burn-up fuels. A lack of data still exist under air conditions and will be completed in a future analytical program, the VERDON program, devoted to fission product release from high burn-up UO<sub>2</sub> and MOX fuels. This new program is part of the International Source Term Program (ISTP) launched by CEA, EDF and IRSN, and open to foreign collaboration.

## 1 INTRODUCTION

Fission product (FP) release and transport in PWR severe accidents (SA) is a major topic in reactor safety assessment due to the potential radiological consequences for surrounding populations and the environment. In this context, the Institute for Radiological Protection and Safety (IRSN) and Electricité de France (EDF) have supported the VERCORS analytical test program which was performed by the "Commissariat à l'Energie Atomique" (CEA). It is usually considered as complementary to the PHEBUS FP in-pile integral experimental program. 25 annealing tests were performed between 1983 and 2002 on irradiated PWR fuels under various conditions of temperature and atmospheres (oxidising or reducing conditions) [1], [2], [3], [4], [5].

This paper describes the experimental facility and gives an overview of this analytical program which allows to build an extended data base on FP release from irradiated fuel in SA conditions.

Among all the FP investigated, ruthenium is of specific concern because of its potential high radiological effects due to its two most important isotopes, <sup>103</sup>Ru in the short term (half-life of 39,3 days) and <sup>106</sup>Ru in the long term (half-life of 1,0 year). Ruthenium is present in irradiated fuel in the form of metallic inclusions [6] and is generally considered to be non-volatile. However, in very oxidising environments, in particular in the case of air ingress resulting for instance from bottom RPV (reactor pressure vessel) failure, or dry-out of spent fuel water pools, oxidation of ruthenium may occur and then generates volatile gaseous oxides, such as RuO<sub>3</sub> and RuO<sub>4</sub>. It has been clearly shown in the past by AECL tests conducted in Chalk River Laboratory, showing a rapid and complete release of ruthenium under air, with a faster kinetics than volatile iodine and caesium FP, whereas a very limited ruthenium release was characterised under steam conditions for rather low burn-up fuels [7], [8]. More recently experiments are performed in the context of the SARNET European network [9], dedicated to severe accident research, (i) by AEKI on RUSSET experiments, studying the release of ruthenium from non irradiated UO<sub>2</sub> containing FP as simulants [10], and (ii) by VTT studying the transport and behaviour of ruthenium oxides in nuclear accident conditions [11]. While RuO<sub>3</sub> appears to be rapidly decomposed to RuO<sub>2</sub> and deposited on surfaces of the RCS (reactor coolant system) at temperatures around 900 to 1100 K, significant amounts of RuO<sub>4</sub> could reach the containment atmosphere. Important uncertainties still remain on the ruthenium behaviour in oxidising conditions, such as delay of release due to the presence of other FP, competition and behaviour of different oxides (RuO<sub>3</sub>, RuO<sub>4</sub>), the possible role of hydroxides (e.g., RuO<sub>3</sub>OH<sup>1</sup>), and catalytic decomposition on surfaces which could increase the deposit fraction.

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<sup>1</sup> While several plausible ruthenium hydroxide species such as RuOH, Ru(OH)<sub>2</sub>, and RuO<sub>3</sub>OH have been hypothesized by various authors, and their thermodynamic properties have been estimated, none has yet been identified experimentally.

The VERCORS data base gives complementary results concerning ruthenium release from irradiated PWR fuels. Its behaviour is presented here on the basis of comparative VERCORS tests performed on UO<sub>2</sub> or MOX samples at different burn-up (from 35 to 70 GWd/t) and under various atmospheres (reducing in hydrogen, oxidising (i) in mixed hydrogen and steam, (ii) in pure steam and (iii) in air).

## 2 EXPERIMENTAL SETUP

The whole program was conducted in a dedicated shielded hot cell of the LAMA facility located in the Grenoble nuclear centre of the CEA. This section focuses on the experimental setup with special emphasis on sample preparation, loop description, on-line instrumentation and post-test analyses. The experimental loop was continuously improved along the 3 phases of the program (see next section), composed of the HEVA phase (8 tests performed between 1983 and 1989 at temperature up to 2100 K<sup>2</sup>) [1], the VERCORS phase (6 tests performed between 1989 and 1994 at higher temperature up to 2600 K just below fuel delocation) [2], and finally the VERCORS HT and RT phase (3 HT and 8 RT tests performed between 1996 and 2002 with systematic fuel melting and with a significantly improved instrumentation) [3], [4], [5].

### 2.1 Fuel sample

The fuel sample originated from a fuel rod section taken from a nuclear power reactor operated by EDF; it is generally composed of three irradiated pellets in their original cladding<sup>3</sup>. Two half-pellets of depleted uranium oxide<sup>4</sup> are placed at either end of the sample and held in place by crimping the cladding (figure 1). Thus the cladding is not fully sealed.

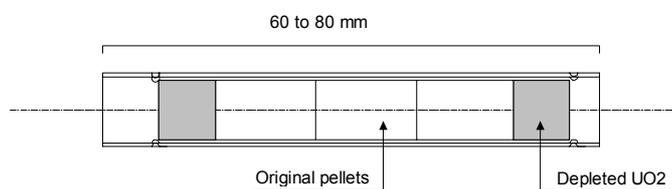


Figure 1: VERCORS fuel sample

In certain cases, the fuel sample was re-irradiated at low linear power (< 20 W/cm) in an experimental pool reactor for around seven days in order to recreate the short half-life FP without inducing any in-pile release. These short half-life FP, important for their radiobiological effects, include volatile FP (iodine and tellurium), gas (xenon) and less or low-volatile FP (molybdenum, barium, ruthenium, cerium, lanthanum, zirconium ...). Since the experimental sequence is performed less than 3 days after the end of the re-irradiation, these short half-life FP (including <sup>103</sup>Ru) are measurable by using on-line gamma spectrometry with a similar detection level to long half-life FP (including <sup>106</sup>Ru).

### 2.2 Experimental loops

The most sophisticated loop, devoted to the combined study of FP release and their transport and deposition along the circuit, is the HT loop [12] (figure 2).

<sup>2</sup> Except HEVA 6 performed up to 2400 K in reducing conditions

<sup>3</sup> Except two RT tests (RT3 and RT4) performed on fragmented fuels (debris bed configuration)

<sup>4</sup> These depleted half pellets are not irradiated in PWR

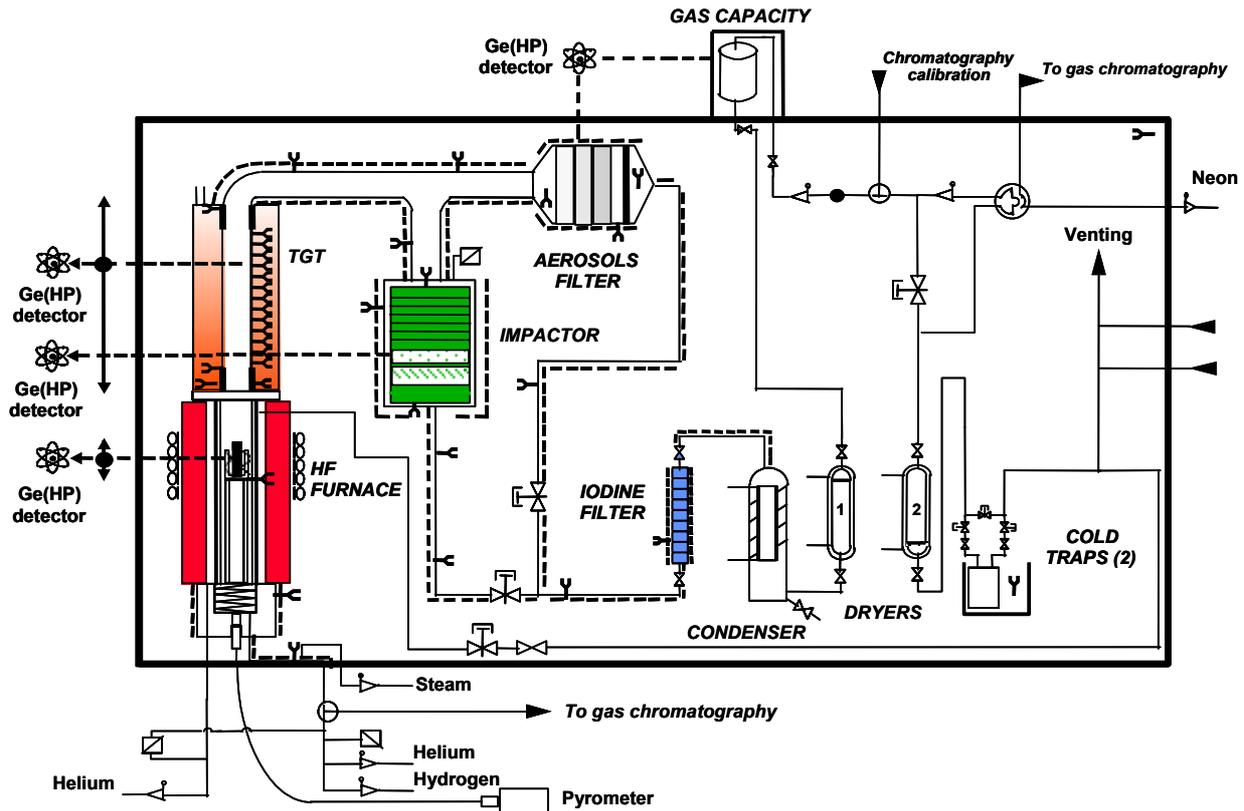


Figure 2: VERCORS HT loop in hot cell

Along the path of gas flow, the main components of the loop are:

- The fluid injection system (steam, hydrogen, helium, air).
- The induction furnace itself to heat the fuel up to meltdown. It comprises, from the inside to the outside (i) the crucible supporting the fuel sample (made of thoria or zirconia according to the cases), (ii) two concentric channels dynamically sealed by a stack of dense thoria (or zirconia) sleeves [*the internal channel containing the sample receives the steam and hydrogen flow, the external channel containing the tungsten susceptor (graphite in former tests) is swept by a helium flow with a slightly higher pressure than the internal channel*], (iii) a double-layer heat insulator (porous thoria or zirconia and alumina), (iv) a fused silica tube, constituting the furnace chamber, (v) and finally the inductor.
- A thermal gradient tube (TGT) 0.7 m long, just downstream of the furnace, devoted to the study of vapour-phase and aerosol deposition ; the axial temperature profile decreases from 1300 K to 400 K.
- A cascade impactor on a derived branch of the circuit with five stages, two granular beds and a back-up filter, used to trap the aerosols according to their size. It is located in a resistive furnace with an adjustable temperature range from 500 K to 1000 K and operates during a predefined period of the experiment (typically the last high temperature plateau). When the impactor is not open, the aerosols are collected in a high capacity filter composed of granular beds.
- A specific iodine filter (Maypack), aimed at separating the chemical iodine species, in particular aerosol, organic and molecular forms.
- A condenser and two dryers (silica gel and molecular sieve) for recovering the steam.

- A gas capacity to act as a buffer volume for on-line gas gamma spectrometry measurements.
- A cold trap (charcoal adsorber cooled by liquid nitrogen) to collect noble gases.

The RT version of the loop (RT for Release of Transuranics) is more compact. The furnace is similar to the HT furnace, but its handling is easier; thus it enables the frequency of the tests to be increased. In this simplified configuration, all FP and transuranic elements are trapped as near as possible to their emission point in a total filter (located in place of the TGT). The release quantification of actinides and pure  $\beta$  FP ( $^{90}\text{Sr}$  for instance) is then obtained by post-test chemical analyses, such as ICP-MS.

The original VERCORS loop had an intermediate configuration, slightly nearer to the RT version than to the HT one: above the furnace is placed the cascade impactor, then the condenser and the two dryers, the gas capacity (in place from the VERCORS 2 test onwards) and the cold trap.

### 2.3 On-line instrumentation and post-test analyses

Since the VERCORS tests are mainly aimed at characterizing the release kinetics (and total release for source term evaluations) of FP and aerosols, specific on-line instrumentation is needed. Consequently, complementary on-line gamma spectrometry stations are used:

- The first detector is focused on the top of the fuel and records directly the loss of the FP. Since this is a differential measurement, this station has the drawback of a rather low accuracy. The FP releases lower than 10% are only slightly significant on this measurement station. However, it has the advantage of quantifying the kinetics of all the FP, including those which do not reach the TGT and/or the impactor. Besides, it allows to follow the fuel degradation and to identify precisely the time of fuel delocation, since it “records” the loss of signal corresponding to non -or low-volatile FP (i.e.  $^{95}\text{Zr}$ ,  $^{140}\text{La}$  ...) due to the collapse of the fuel and its bulk relocation at the bottom of the crucible<sup>5</sup>.
- The two following detectors monitor the FP deposits on the TGT (or the impactor) and on the aerosol filter. Since this is a direct measurement (non-differential) on only slightly absorbing structures, the measurement sensitivity is very good (often less than 1% of the FP initial inventory) but limited to a fraction of the FP emitted, generally the more volatile ones.
- The fourth detector measures the fission gases emitted by the fuel (xenon and krypton) with a very good sensitivity and a great measurement dynamic (from  $10^{-6}$  to a few % per minute of the initial inventory).

These four gamma spectrometry units are composed of a portable liquid nitrogen-cooled Ge (High Purity) detector and an electronic device for signal shaping and storage, fitted with a rack unit for correcting pile-up counting losses in order to obtain spectra at a high rate (up to 1 spectrum/min). Compensation better than 5% is guaranteed up to 150 000 pulses/s, the limit of the counting rate defined for the tests.

After the test, the fuel is embedded in situ in an epoxy resin and X-rayed. A longitudinal gamma-scan of the fuel is conducted to determine the quantitative fractions of the FP emitted by the fuel during the test. All the components of the loop (TGT, separated impactor stages, filters, condenser, dryers, etc.) are then gamma-scanned to measure and locate the FP released during the test and to draw up a mass balance of these FP. For some tests, non-destructive transverse gamma-scans are carried out for several angles of incidence

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<sup>5</sup> From VERCORS RT5 onwards, a camera sighting the top of the fuel sample gives a complementary information of the time of fuel collapse.

to determine the spatial location of the FP remaining inside the fuel and analyze possible interactions of these FP with cladding components (for instance tellurium or barium trapped in the cladding, masking their emission) or their location inside the corium in case of fuel melting [13].

Ceramographic examinations are carried out on the remaining fuel sample to analyze the changes in the microstructure and/or the melting extent. Physico-chemical analyses are then carried out on samples of the loop after dismantling, especially on the impactor plates and on the thoria (zirconia) tubes linking the furnace to the TGT (impactor). The most frequently used techniques are SEM-EDS (Scanning Electron Microscopy-Energy-Dispersive X ray Spectrometry), and leaching followed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry).

### 3 EXPERIMENTAL GRID

The main parameters that have been changed from one test to another are the final temperature plateau and its duration, the temperature ramp, the fluid composition and flow rate (steam, hydrogen or air), the burn-up of the fuel, its nature (UO<sub>2</sub> or MOX) and its morphology (initially intact or fragmented). These parameters are synthesised table 1 (VERCORS phase) and table 2 (VERCORS HT/RT phase), as well as the total ruthenium release measured on each test.

Table 1: VERCORS 1 to 6 test matrix parameters

Test	VERCORS 1	VERCORS 2	VERCORS 3	VERCORS 4	VERCORS 5	VERCORS 6
Date of test	11-1989	06-1990	04-1992	06-1993	11-1993	06-1994
<b>Fuel</b>						
PWR irradiation	Fessenheim	Bugey	Bugey	Bugey	Bugey	Gravelines
Fuel burn-up (GWd/tU)	42,9	38,3	38,3	38,3	38,3	60
Re-irradiation	Siloe	Siloe	Siloe	Siloe	Siloe	Siloe
<b>Test conditions</b>						
Max fuel temperature (K)	2130	2150	2570	2570	2570	2620
Atmosphere (end of test)	Mixed H <sub>2</sub> O+H <sub>2</sub>	Mixed H <sub>2</sub> O+H <sub>2</sub>	Mixed H <sub>2</sub> O+H <sub>2</sub>	Hydrogen	Steam	Mixed H <sub>2</sub> O+H <sub>2</sub>
Last plateau duration (min)	17	13	15	30	30	30
Steam flow rate (g/min)	0,15	1,5	1,5	1,5 - 0	1,5	1,5
Hydrogen flowrate (g/min)	0,003	0,027	0,03	0,012	0	0,03
<b>Ru released fraction (%)</b>						
Ru			0,36	6	6	0,6

Table 2: VERCORS HT/RT test matrix parameters

Test	HT1	RT1	RT2	RT5	RT4	RT3	RT7	HT3	HT2	RT6	RT8
Date of test	06-1996	03-1998	04-1998	12-1998	06-1999	11-1999	04-2000	06-2001	04-2002	09-2002	11-2002
<b>Fuel</b>	UO <sub>2</sub>	UO <sub>2</sub>	MOX (AUC)	UO <sub>2</sub>	Debris bed UO <sub>2</sub> /ZrO <sub>2</sub>	Debris bed UO <sub>2</sub>	MOX (AUC)	UO <sub>2</sub>	UO <sub>2</sub>	UO <sub>2</sub>	UO <sub>2</sub>
PWR irradiation	Gravelines	Gravelines	Gravelines	Gravelines	Gravelines	BR3	Saint Laurent B1	Gravelines	Gravelines	Gravelines	Gravelines
Fuel burn-up (GWd/tU)	49,4	47,3	45,6	61	37,6	39	43,0	49,3	47,7	71,8	69,6
Re-irradiation	Siloe	No	No	Osiris	No	Osiris	Osiris	Osiris	Osiris	Osiris	Osiris
<b>Test conditions</b>											
Max fuel temperature (K)	2900	2570	2440	~ 2600	2520	2970	2890	2680	2420	2470	2670
Atmosphere (end of test)	Hydrogen	Mixed H <sub>2</sub> O + H <sub>2</sub>	Mixed H <sub>2</sub> O + H <sub>2</sub>	Hydrogen	Mixed "oxidizing"	Mixed "reducing"	Hydrogen	Hydrogen	Steam	Mixed H <sub>2</sub> O + H <sub>2</sub>	He + 10% air
Last plateau duration (min)	7	a	a	a	a	a	a	a	a	a	a
Steam flow rate (g/min)	1,5 - 0	1,5	1,5	1,5 - 0	0,876	0,075	0	0	1,5	1,5	
Hydrogen flowrate (g/min)	0,012	0,027	0,027	0,027	0,024	0,075	0,012	0,012	0	0,027	
Air flowrate (g/min)											0,048
<b>Ru released fraction (%)</b>											
Ru	8	9	5,4		7,7	~ 1	2	6	> 50	28	20

<sup>a</sup> Successive plateaus of 10 min each 100 K from 2100 K up to fuel delocation

Some of these tests are of particular interest in order to analyse the ruthenium behaviour:

- VERCORS 4 and VERCORS 5 were performed on the same UO<sub>2</sub> fuel rod (3 cycles, 38 GWd/t) with a pre-oxidising phase of the cladding in a mixed atmosphere of

steam and hydrogen of one hour at 1600 K, followed by a high temperature plateau of 30 min at 2600 K, in reducing conditions for VERCORS 4 and in pure steam atmosphere for VERCORS 5. The fuel sample remained intact at the end of the test, but severely damaged and probably close to its delocation.

- VERCORS HT3 and HT2 were performed on the same  $\text{UO}_2$  fuel rod (4 cycles, 50 GWd/t) with a pre-oxidising phase of the cladding in a mixed atmosphere of steam and hydrogen at 1800 K, followed by a succession of high temperature plateaus from 2100 K up to the fuel collapse temperature, in reducing conditions for HT3 and in pure steam atmosphere for HT2.
- VERCORS RT6 and RT8 were both performed on a high burn-up  $\text{UO}_2$  fuel (6 cycles, 70 GWd/t) with the same pre-oxidising phase than HT tests<sup>6</sup> and succession of high temperature plateaus up to the fuel collapse, under mixed oxidising atmosphere for RT6 and air ingress conditions for RT8.
- VERCORS RT2 and RT7 were performed on similar MOX fuels (3 cycles, respectively at 45,6 and 43,0 GWd/t) with the same pre-oxidising phase than HT tests, and succession of high temperature plateaus up to the fuel collapse, in mixed oxidising conditions for RT2 and in reducing conditions for RT7.

## 4 RUTHENIUM RELEASE IN VERCORS TESTS

### 4.1 VERCORS 4 and VERCORS 5, $\text{UO}_2$ fuel at 38 GWd/t in reducing and oxidising atmosphere

Ruthenium release in these 2 tests is low, but well quantified by gamma spectrometry, which can detect a level below 1% of the initial inventory due to the measurement of the separated components of the loop after dismantling. The total Ru release is the same (6%) in the two tests, despite the different oxidising conditions. Analysing in more details shows that Ru deposit:

- is totally located just above the fuel sample (along a few cm on the zirconia tube linking the furnace to the impactor, at temperature above 2000 K) for VERCORS 4,
- is mainly located above the fuel sample (5,5%), but with 0,5% of the initial inventory that reaches all the stages of the impactor heated at 870 K, for VERCORS 5.

Thermodynamic study has been performed on these tests with the GEMINI 2 solver and a recent data base, NUCLEA-IV, developed in the context of severe accidents [14]. The methodology used calculates the thermodynamic equilibrium (condensed and gas phase) at the final temperature of the test, considering the initial amount of  $\text{UO}_2$ , oxidised cladding, FP and the total volume of gas injected during the high temperature plateau. Based on thermodynamic equilibrium, it must be noted that this methodology is a preliminary approach which gives an upper value of the release. It leads to consistent results for VERCORS 4 (and more generally for all tests performed in reducing conditions), indicating that the ruthenium release in the gas phase is made of metallic Ru vapours which condense at high temperature, where Ru deposits have been measured. For VERCORS 5, GEMINI 2 calculation is not consistent with the measured value: it leads to 43% calculated release, 7% in the form of  $\text{Ru(g)}$  and 36% in the form of  $\text{RuO}_3(\text{g})$ .<sup>7</sup> However parametric studies decreasing the amount

<sup>6</sup> But in pure steam for RT8 during the plateau at 1800 K

<sup>7</sup> It should be noted that the species  $\text{RuO(g)}$  and  $\text{RuO}_2(\text{g})$ , which are poorly characterized but may contribute to ruthenium vapour pressure at temperatures above about 2000 K [18], are not included in the NUCLEA-IV database because reliable thermodynamic data are lacking. The highly volatile species

of Zr (the cladding is not linked with the  $\text{UO}_2$ -FP matrix) and the amount of  $\text{O}_2$  (the total steam injected does not participate to the thermodynamic exchanges) shows a resulting strong decrease of the  $\text{RuO}_3(\text{g})$  form. This seems to confirm that  $\text{RuO}_3$  gas formation could have been limited by kinetics aspects of fuel oxidation, and the small fraction of Ru deposit in the impactor could be consistent with some ruthenium oxide forms.

It is also useful to notice that in the case of VERCORS 6, performed at the same temperature and in oxidising conditions between VERCORS 4 and 5 (mixed steam and hydrogen), but with a high burn-up fuel at 60 GWd/t, the Ru release was very low (0,6%) ten times lower than the value of VERCORS 4 and 5. During this test, due to the high burn-up of the fuel and strong interaction with the oxidised cladding, the fuel sample collapsed quickly during the high temperature plateau and the resulting liquid phase limited the mass transfer of low-volatile FP, such as ruthenium.

#### 4.2 VERCORS HT3 and HT2, $\text{UO}_2$ fuel at 48 GWd/t in reducing and oxidising atmosphere

Ruthenium release in the HT3 test performed under hydrogen conditions is the same as in VERCORS 4 (6%), and also exclusively composed of Ru vapours which have condensed just above the fuel sample along the thoria tube linking the furnace to the TGT. This result is consistent with expectations.

HT2 test gives more surprising results: a very large release ( $> 50\%$ ) for a test performed under pure steam up to only 2420 K<sup>8</sup>. Moreover, this large released fraction is divided up to:

- a large deposit just above the fuel sample at temperature around 2000 K,
- 4% deposited along the TGT, mainly in its cold part,
- 1% in the filter which operates during the first phase of the test (up to the beginning of successive high temperature plateaus),
- 11% in the impactor which operates from the first high temperature plateau (2100 K) up to the end of the test.

It can be noticed that the fraction deposited at a rather low temperature is very significant (12% in the filter and the impactor heated at 400 K) and could be the result of the formation of volatile oxide forms of the ruthenium.

For the first time, a significant release rate of ruthenium was measured by the on-line gamma spectrometer sighting on the fuel sample (figure 3): Ru release began promptly at 2170 K and reached already 20% at 2300 K, when the fuel began to collapse at the bottom of the crucible.

Figure 4 illustrates the  $^{103}\text{Ru}$  distribution in the fuel sample before and after the test, as well as the strong deposit along the downstream thoria tube. Notice that the Ru location in the molten corium after the test is significantly different than the location of oxidised and non-volatile FP (represented by  $^{95}\text{Zr}$  on figure 4): it seems to confirm that the ruthenium in the corium is composed mainly of coarse-grained metallic precipitates.

It is important to explain the much higher release of Ru in HT2 than in VERCORS 5. One explanation is a new design of the crucible (open crucible for HT2, figure 5) which improves the access of the steam to the fuel<sup>9</sup>. Other phenomena which could have been favourable are: (i) the higher burn-up of the fuel sample, (ii) the effect of the successive plateaus at high temperature which favour thermodynamic equilibrium.

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$\text{RuO}_4$  (see main text) is stable at relatively low temperatures under strongly oxidizing conditions, but is not a significant contributor under VERCORS experimental conditions, according to the GEMINI 2 calculations.

<sup>8</sup> This temperature level is under re-evaluation and would probably be slightly increased

<sup>9</sup> This effect has also been evidenced for the kinetics release of volatile FP (iodine, caesium)

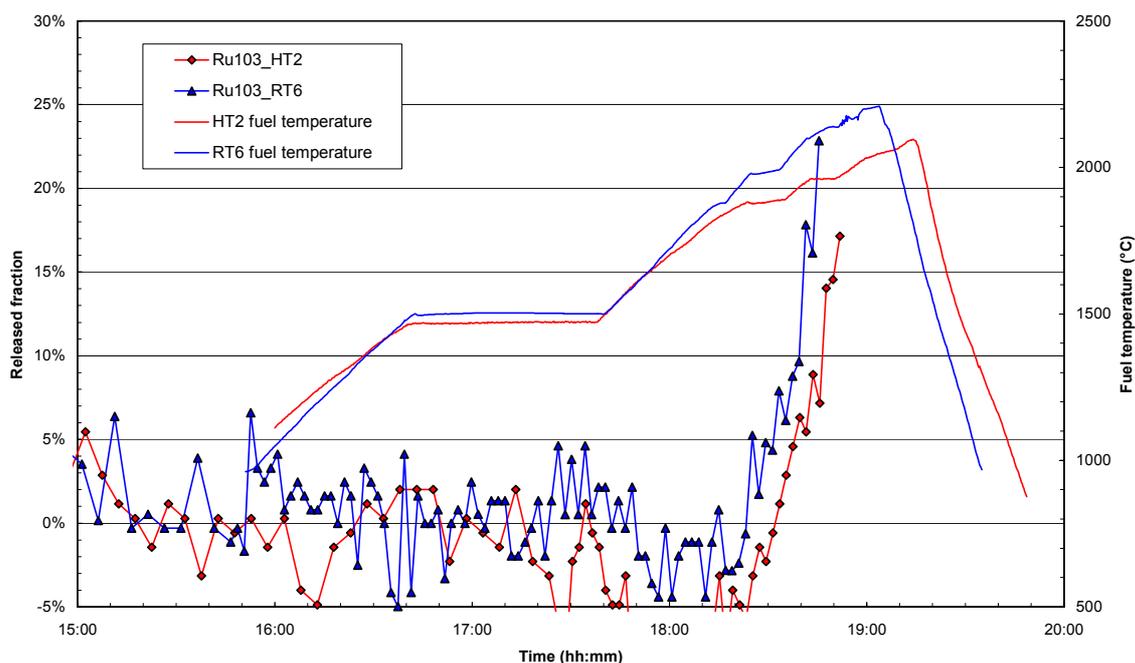


Figure 3: Ruthenium release kinetics from fuel for HT2 and RT6 tests

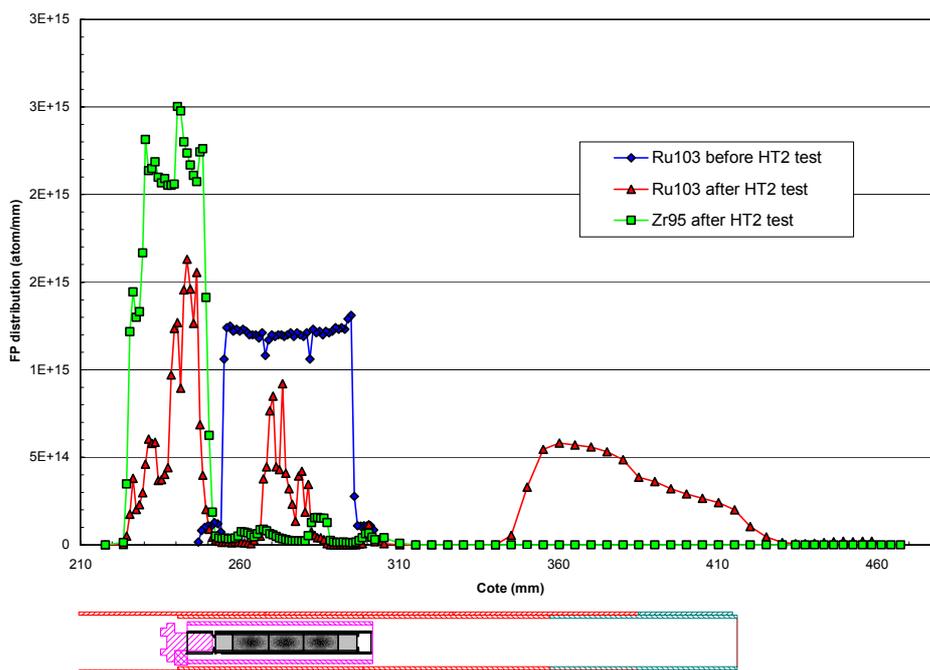


Figure 4:  $^{103}\text{Ru}$  and  $^{95}\text{Zr}$  distribution in the fuel and along the thoria tube for HT2 test

The oxidation state of the fuel, and by extension the kinetics of oxidation in air and/or steam, are important in controlling the release of ruthenium. Thermodynamic calculations indicate that ruthenium volatility is highest when fuel is oxidized to the maximum attainable value of  $x$  in  $\text{UO}_{2+x}$  (or to  $\text{U}_3\text{O}_8$  at temperatures below about 1878 K) [15]. This is consistent

with observations in Canadian tests on FP release from CANDU fuel in air. In a test with small, bare fuel fragments at 1883 K, a delay of about 250 s was observed before the onset of Ru release, as compared with Cs [7]. In a test with clad fuel segments at 2163 K, with a geometry resembling that of a VERCORS test, the delay was about 5000 s [16]. This longer delay could be attributed to the larger fuel specimen and the more constrained access of gas to the fuel.

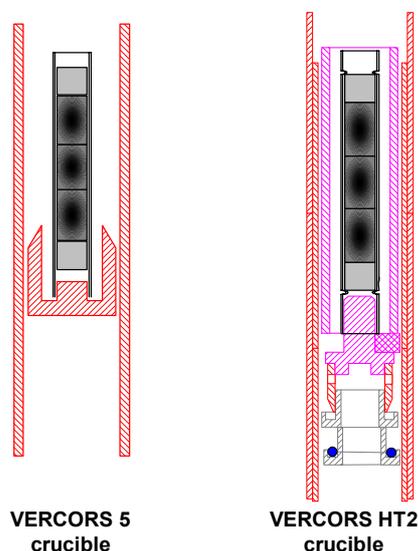


Figure 5: comparison between VERCORS 5 (closed) and HT2 (open) crucibles

#### 4.3 VERCORS RT6 and RT8, $\text{UO}_2$ fuel at 70 GWd/t in various oxidising atmosphere

These two tests highlight the effect of high burn-up fuel on ruthenium release.

##### a) VERCORS RT6

Compared with RT1 performed in the same mixed atmosphere, RT6 exhibits a Ru release which is 3 times higher (28% against 9%).

Compared with HT2 performed in more oxidising conditions (pure steam) than RT6 (mixed atmosphere), if the RT6 ruthenium release is smaller, it can be noticed that the kinetics release is the same up to the fuel delocation and reaches in both case 20% (figure 3). After the fuel collapsed at the bottom of the crucible, the more oxidising conditions of HT2 has had a more important impact than the higher burn-up of RT6.

Moreover, the 28% total RT6 release is divided at the end of the test into 21% deposited just above the fuel sample at rather high temperature and 7% deposited on the filter heated at 400 K. This suggests a tendency of higher fraction of volatile ruthenium oxide forms from high burn-up fuel (25% of the total release in this case). An interpretation of this observation could be proposed: high burn-up fuels have more fissions on plutonium and these fissions are more oxidising than fissions on uranium (the ratio O created by fission is 0,13 on  $^{235}\text{U}$  and 0,62 on  $^{239}\text{Pu}$ ). This effect could increase the oxygen potential inside the  $\text{UO}_2$  matrix and favour the formation of ruthenium oxides. This burn-up effect is relatively small, however, compared with the oxygen potential attained in pure steam or air-steam atmospheres; also, it is sometimes offset by oxidation of the internal cladding surface, which acts as an oxygen sink.

##### b) VERCORS RT8

RT8 is a test performed with a similar high burn-up fuel to RT6, specially dedicated to a simulation of an air-ingress accident. Total ruthenium release measured on this test (20%) is not so large as could have been expected in air ingress conditions. In fact, the conditions of the test were not so oxidising: for safety reasons the sequence was conducted in 3 successive phases, (i) a pre-oxidising phase of the cladding of one hour at 1800 K followed by (ii) a ramp temperature up to 2270 K under pure helium in order to be sure to sweep all the generated hydrogen from the loop, then (iii) the succession of several high temperature plateaus up to fuel collapse under a mixture of helium and air. The conditions in the final phase of RT8 were actually slightly less oxidising than in RT6, which could account for the somewhat lower ruthenium release.

Nevertheless the ruthenium release is significant and comprises 15% deposited at high temperature just above the fuel and 5% deposited on the filter heated at 400 K. We can observe that the fraction deposited on the filter represents 25% of the total release, the same value than RT6. This could reinforce the hypothesis of an increase of volatile ruthenium oxides from high burn-up fuel.

#### **4.4 VERCORS RT7 and RT2, MOX fuel at 45 GWd/t in reducing and oxidising atmosphere**

Ruthenium releases in these two MOX tests are very similar to results obtained on VERCORS 4 and 5.

Concerning RT7 performed under hydrogen conditions, Ru release is very low (2%), even noticing the fuel sample was heated up to 2890 K<sup>10</sup>, and the deposits are all located at high temperature along the thoria tube linking the furnace to the filter.

Concerning RT2 performed under mixed atmosphere of steam and hydrogen, Ru release is also low (5,4%), similar to VERCORS 5 and RT1 release. But we can notice that the release fraction is equally divided between the thoria tube above the furnace and the downstream filter, which seems to indicate a possible formation of more ruthenium oxides from MOX fuel than from UO<sub>2</sub> fuel and to confirm the more oxidising effect of the fissions on plutonium than on uranium.

### **5 THE FUTURE VERDON PROGRAM**

Among all these VERCORS tests, few were performed in very oxidising conditions and more particularly in air ingress conditions with significant amount of air. Since the end of the VERCORS experiments in 2002, a new program devoted to FP release and transport is being built, the VERDON program, which is included in a larger Source Term Separate Effect Tests Program [17]. This new analytical Source Term program is a joint IRSN/CEA/EDF project open to international participation. It contains out-of-pile experiments and fuel examinations aiming at reducing uncertainties remaining after the PHEBUS FP program.

The VERDON experiments will be performed in a future hot cell of the LECA/STAR facility located in the Cadarache nuclear centre of the CEA. The main uncertainties which remain regarding FP release concern high burn-up UO<sub>2</sub> and MOX fuels, as well as release in very oxidising conditions; they will all be addressed in the VERDON program. The experimental loop will be very similar to those used in the previous VERCORS RT and HT tests, with:

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<sup>10</sup> This temperature level is under re-evaluation and would probably be decreased

- one "simplified" configuration devoted to FP release from one pellet<sup>11</sup> or from a longer fuel section of about 10 cm in order to study the coupling between fuel degradation and FP release,
- one "complex" configuration, including, like VERCORS HT, a thermal gradient tube (TGT) aimed at studying FP transport and deposits.

Compared to the VERCORS program, the VERDON program will also be completed by detailed examinations of the fuel sample before and after the test, using micro-analytical techniques, such as SEM, EPMA and SIMS, in order to determine the location of FP in the various phases as well as the corresponding compounds if possible. This will help to better understand the mechanisms which promote FP release in such situations as well to support the associated modelling.

## 6 CONCLUSION

The VERCORS analytical program, conducted between 1983 and 2002 on irradiated fuels, has produced an extended data base on FP release and transport in PWR severe accident conditions. One typical feature is to have performed tests on freshly reirradiated fuels leading to a precise measurement of short half-life FP, whose radiobiological effects are the strongest in the short term just after a severe accident.

A presentation of ruthenium behaviour through this program has been highlighted, focusing more deeply on oxidising tests. The main important result is that for high burn-up UO<sub>2</sub> fuels, steam conditions, or even mixed steam and hydrogen conditions, can lead to important ruthenium release from fuel. Thus significant ruthenium release is possible under some conditions, even without air ingress. This observation has raised the question of the role of plutonium fissions which are more oxidising inside the UO<sub>2</sub> matrix, and could lead to similar and increased effects on MOX fuels.

Detailed analyses of ruthenium deposits along the VERCORS loop seems to confirm the existence of volatile ruthenium oxide forms in oxidising conditions, and an increase of their fraction on high burn-up UO<sub>2</sub> fuels and on MOX fuels.

This data base can now be used in support of the interpretation and modelling of ruthenium behaviour. Uncertainties still remain, in particular under air ingress conditions and for high burn-up UO<sub>2</sub> and MOX fuels. The future VERDON program, part of the new analytical Source Term program, jointly supported by IRSN, CEA, and EDF and open to international participation, will address this topic and correct the lack of data.

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<sup>11</sup> In this case of one pellet, it is intended to be able to perform a batch of 3 tests on the same reirradiated fuel under different accidental simulations (atmosphere, temperature sequence, etc.)

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