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Ruthenium behavior in the reactor cooling system in case of a PWR severe accident

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Abstract

In the frame of severe accident topic for pressurized water reactor, the physical-chemistry of Ru fission products were experimentally studied to better understand their behavior inside the reactor coolant system in air or air/steam atmospheres. The tests consisted in vaporizing RuO₂ at 1200 °C and the ruthenium oxides are transported through a controlled thermal gradient tube made of quartz or pre-oxidized stainless steel. Results show that the major part up to 95% is deposited along the tube, the remaining part being transported almost under gaseous form attributed to RuO₄. Impact of carrier gas, temperature profile and nature of the tube are discussed.

AQ1

Keywords

Source term
Severe accident
Ruthenium transport
Reactor cooling system
Kinetics

Introduction

In the frame of severe accident (SA) occurring in a pressurized water reactor (PWR), some specific accidents with air-ingress lead to very oxidizing conditions [1]. Powers et al. [2] made first a review of the possible consequences of such kinds of accidents in assuming an air ingress flow rate of 100 mol/s, through the core, for station blackout accident with a surge line rupture. For such conditions, ruthenium which is a fission product with high yield radiation can be released in significant amounts from the melt core fuel as exhibited by several experimental programs. We can cite the past VERCORS (1983–2002) [3, 4] and ongoing VERDON [5] analytical tests performed by the “Commissariat à l’Energie Atomique et aux énergies Alternatives” (CEA) where some specific tests in high oxidizing atmosphere show some Ru releases higher from 20% up to 70%. A complete set of experimental data from CNL (Canadian National Laboratories) [6] also exists for Ru release from the fuel and confirm high releases for oxidizing conditions. These high releases result from formation of ruthenium oxides (RuO_x) much more volatile than metallic ruthenium present in the fuel. It appears that the Ru release begins when fuel temperature reaches at least 2000 °C and it is promoted by high burn-up fuel. Once released, ruthenium can be transported through the RCS and reach the nuclear containment building.

Ruthenium can contribute significantly to radiological damage in the human body in the short and medium term due to its two isotopes ^{103}Ru and ^{106}Ru [7, 8], if released in a significant amount to the environment. In addition to its high radiotoxicity, Ruthenium is of particular interest due its ability to form volatile oxides [9], noticeably RuO_4 which is volatile at room temperature. In Chernobyl accident, the following fission products: Te, I and Ru were measured to be partially under

gaseous forms [10] with the portion of ^{103}Ru in gaseous components made up 0.6–13%, that of ^{106}Ru made up 2.7–16%.

Chemical behaviour of ruthenium in the containment SA conditions was studied in the last decade [11, 12, 13] and from these works it appears that $\text{RuO}_{4(g)}$ can exist in the containment with quite long half-life and with possible formation from Ru deposits on the inner walls. For safety analysis, source term uncertainties have been discussed/assessed and as a result the high temperature chemistry in the RCS and its impact on the source term has been ranked with high priority by the Severe Accident Research Priority working group of the FP7 SARNET2 (Severe Accident Research NETwork of excellence) project [14]. Further, re-volatilisation of FPs deposited on the RCS and on the containment surfaces can also constitute a significant delayed source term which remains to be better understood. For Ruthenium, specific analysis [15] tend to show that radiological consequences will mainly depend on the amount of ruthenium transported, either under volatile form or aerosol in the containment. In the next section, available data in the literature on these phenomena are detailed. Next complementary experimental work carried out by the French “Institut de Radioprotection et de Sûreté Nucléaire” (IRSN) will be presented and discussed.

AQ2

Literature review

Recent experimental works [16, 17, 18, 19, 20] dedicated to the transport of Ru through RCS conditions were performed by AEKI (Atomic Energy Research Institute (Hungary), now MTA EK) and VTT (Technical Research Centre of Finland) organisations. In addition, VTT and Chalmers University of Technology (Sweden) studied in collaboration (under NKS-R programme) the effect of airborne compounds on Ru transport and speciation [21, 22, 23]. Main insights from these works are reported. Tests are based on Ru feed through a tube with a thermal gradient.

From AEKI studies, the standard sample configuration was 1 g ZrO_2 with approximately 5 mg of metallic ruthenium powder encapsulated in the ZrO_2 matrix, in some cases the Ru was present in the form of

powdered Mo–Ru–Rh–Pd alloy, and other elements (FP and UO_2) were also sometimes added [16]. Ru samples were heated up to 1100 °C and a carrier gas flowing through the tube to transport Ru (0.17 Nl/min); carrier gas was mainly air and sometimes moist air (5% steam content). The tube used was made with different materials (quartz, alumina, zirconium and more or less oxidized stainless steel) and the size was quite small with an internal diameter of 4 mm and a length of 185 mm. Test duration was fixed to 6 h. The tests performed were demonstrative in nature and the main objective was to assess impact of experimental parameter on the Ru transported at low temperature under aerosol or gas forms, with both forms being measured.

The main results obtained are:

- A high Ru fraction ($> 80\%$ of the released Ru) was deposited into the tube, the major part at higher temperature (about 900–600 °C); the remaining part was gaseous at the outlet (25 °C);
- With the quartz tube and dry air about 6% reached the outlet under $\text{RuO}_{4(g)}$, value enhanced for a SS pre-oxidised tube reached about 20%. It has been attributed to a better heterogeneous phase decomposition of RuO_4 and RuO_3 into RuO_2 by the quartz than by the SS surface.
- The Ru gaseous fraction was higher for wet air (5% steam) than for dry air;
- For Ru transport, some chemical surface processes are surely involved and have to be considered.

Hungarian study devoted to the effects of different surfaces on the transport and deposition of ruthenium oxides [17] showed that the heterogeneous phase decomposition of RuO_4 and RuO_3 into RuO_2 is catalyzed more efficiently by the quartz surface than by the stainless steel or alumina surfaces in air stream. Pre-oxidation of SS surfaces in steam had no significant effect on the ruthenium deposition.

In VTT tests [18, 19, 20] and in the collaborative tests between VTT and Chalmers [21, 22, 23], the source of Ru was placed in an alumina

crucible in the form of RuO_2 powder or Ru was fed directly in the form of $\text{RuO}_{4(g)}$. The thermal gradient tube is made of SS with an internal diameter of 22 mm and a length of about 1000 mm. The flow rate through the facility was mainly kept constant at 5 l/min (NTP). Ruthenium dioxide was exposed to oxidising environment at high temperature (827–1427 °C) in a tubular flow furnace with dry air or moist air (< 10% steam for the major part of experiments). Experiment duration time was between 20 and 60 min, except for the re-vaporisation tests which were longer (up to 360 min). At the outlet, ruthenium particles as well as gaseous ruthenium were quantified. For some tests Ru was labelled in ^{103}Ru in order to measure the Ru profile deposit along the tube. The main results obtained depend on the experimental conditions, up to 26% of Ru was released under aerosol and gaseous forms at 1427 °C and up to 6% as $\text{RuO}_{4(g)}$ at 1027 °C.

The main insights are:

- Humidity significantly increased the transport of ruthenium through the facility; mainly in the form of RuO_2 aerosol with a decreased RuO_4 fraction when compared to the dry air condition. At 1027 °C when steam volume fraction was further increased (above 10%) the transport rate decreased below that measured in dry air.
- Higher furnace temperature (1427 °C) promotes the aerosol formation and transport with respect to condensation processes onto surface;
- Persistence of $\text{RuO}_{4(g)}$ is promoted by alumina tube rather than a SS tube and also by the presence of NO_2 gas (50 ppm) and CsI particles. The feed of AgNO_3 droplets which are probably decomposed into silver and nitrous gas (NO_x) resulted in a significant increase of RuO_4 fraction, not as high as in the experiment with NO_2 gas as the only additive. Ag particles alone decreased the $\text{RuO}_{4(g)}$ transport.
- From revaporization but limited to only three tests, the $\text{RuO}_{4(g)}$ fraction observed is low, less than 1% of the Ru deposit (1227 and

1427 °C). However, the ratio of $\text{RuO}_4/\text{RuO}_2$ transported increased significantly.

From these data, it can be sump up that gaseous ruthenium tetroxide is formed in a thermal gradient tube and can persist at temperature in the range of the containment temperature in SA conditions, it means around 100 °C. Based on that, complementary information is needed to further develop a modelling concerning the chemical reactivity of ruthenium species through the RCS and to later implement it in severe accident simulation software.

IRSN launched experiments dedicated on Ru transport through a thermal gradient tube with two main specific objectives; the first being to study impact of steam in the gas mixture in relevant compositions because most of the past tests were performed in dry air or with a very low content in steam; and the second is to look at the revaporization processes which can happen and contribute to delayed releases; for that longer tests will be performed. Details are provided in the next section.

Experimental

The START (Study of the TrAnsport of RuThenium in the primary circuit) program is a part of the Source Term Evaluation and Mitigation (STEM) project [24] hosted by OECD/NEA/CSNI and operated by IRSN. The specificity is to provide a parametric study in which the effect of one single parameter can be precisely studied to be able to build later a mechanistic model which will be implemented in the ASTEC IRSN software package (Accident Source Term Evaluation Code [25]). The main experimental data to be measured are: amount and speciation of Ru species (gaseous and condensed forms) transported to the thermal gradient tube (TGT) outlet, amount of Ru deposits along the TGT as a function of the experimental conditions and amount of Ru transported during the revaporization phase from the deposits.

Hereafter are described the results obtained for six relevant experiments performed under different boundary conditions. The studied experimental parameters are the composition of the carrier gas (steam/air mixtures at various ratios), the thermal profile (abrupt or smooth) and the material of the TGT (quartz or stainless steel). The

comparison of the results obtained for the vaporization and revaporization phases, respectively, allows estimating the potential effect of each parameter studied.

Experimental set-up

The START set-up was designed to be quite representative at a small scale of the thermal phenomena of a RCS. The air/steam composition used is representative of air-ingress scenario [1]. The START facility is schematized in Fig. 1. The device comprised a high temperature tubular furnace (Nabertherm, RS170/750/12 with 13 cm of thermal insulation at both ends) and a transport tube simulating the RCS. Two tubes were used: made of quartz (Q) and stainless steel (SS). While the SS tube was representative of the RCS, the Q tube allowed the determination of deposits along the tube; it is assumed that deposits are not dependent on the nature of the surface. The Q tube had an internal diameter of 30 mm (thickness of 2.5 mm) and was 1.70 m long for an abrupt profile and 2 m long for a smooth profile. The materials of the SS tube were Inconel alloy 600 for the high temperature (HT) zone in the furnace and Stainless Steel 316L from the exit of the furnace to the TGT outlet. The characteristics of the SS tube were 1.80 m long and an internal diameter of 32.7 mm (thickness of 4.85 mm). A pre-oxidation of the SS tube was performed before the test with the same thermal profile as the test (furnace at 1200 °C and an abrupt profile) and with a gaseous mixture of steam/argon during 8 h 30 min (steam = 65.0 g/h and Ar = 53.5 g/h). At the end of this phase, the steam oxidation at high temperature led to a partial oxidation of the tube inner surface (thin black powder). So, to avoid pollution of the Ru reagent in the crucible with metallic oxides from Inconel material, an alumina tube of internal diameter of 23 mm has been inserted in the SS tube in the furnace zone only.

Fig. 1

Scheme of the START facility with a quartz tube

The facility was instrumented to enable on-line measurements and control of the thermal-hydraulic parameters (pressure, carrier gas flow rate, wall temperatures). The pressure in the line was around one bar. The gas mixture was introduced at 150 °C inside the transport tube. The steam generator (SG) allowed changing the composition of gas flow with different steam/air mixtures. For all the tests, the total flow rate was maintained constant at 1.84 Nl/min (0 °C, 101,325 Pa) in order to have a similar residence time for a given temperature profile, thus only the steam/air ratio was an analytical parameter. Ceramic heaters were implemented between the outlet of the furnace and the tube outlet to regulate the wall temperature and control the temperature profile. Two different thermal profiles between 1200 and 250 °C (Q tube) or 170 °C (SS tube) were tested: an abrupt one with a strong decreasing temperature gradient (with a maximum temperature drop estimated to be ~ 27 °C/cm) and a smooth one with a less sharp gradient (~ 12 °C/cm) (Fig. 2). During the commissioning tests, the thermal gradient between the high temperature zone and the tube outlet was experimentally measured with fluid and wall (top and bottom external) thermocouples. Thermal commissioning has been done with different gaseous mixtures (steam/air ratio). Only a negligible effect of steam has been observed on the two profiles, so it could be assumed that the profile was similar whatever the composition of the carrier gas was (in our range of experimental conditions). During the tests, the thermal gradient was measured by wall thermocouples only (upper ones). The residence time between the crucible and the tube outlet lays between 4 and 7 s (according to the thermal profile and the short or long tube configuration), which is quite well representative of an accident

situation, although these experiments are in laminar flow while turbulent flow would be expected in SA.

Fig. 2

Fluid thermal profiles with crucible at position 0 (furnace temperature at 1200 °C, air flow rate at 1.84 Nl/min)

The ruthenium source was placed in an alumina crucible (Al_2O_3 , 99.7%) containing 1 g of anhydrous RuO_2 powder (Alfa Aesar, purity 99.9%). This crucible was located inside the furnace (1200 ± 10 °C). At 1200 °C and in air/steam mixture, RuO_2 powder was mainly vaporized to RuO_3

(g).

The outlet of the tube was equipped with two successive liquid traps to condense steam and trap ruthenium species. These traps were filled with an alkaline solution (NaOH 1 M) which traps gaseous ruthenium tetroxide species with a good efficiency [18]. The first liquid trap was cooled down (around 4 °C) to improve the gaseous trapping [26], whereas the second one was at room temperature. In most of the cases, no gaseous Ru is detected in the second liquid trap, which confirms the efficiency of the cooled first trap. An ultimate filter (quartz fiber) was

placed downstream to catch the potential remaining aerosols of Ru passing through the liquid traps.

Experimental protocol

Two phases were studied, a first phase called vaporization phase in which Ru was generated from a crucible and a second phase, called revaporization phase, performed without any source of Ru but in presence of Ru already deposited along the TGT. The typical thermal-hydraulic experimental sequence for a START test is given in Fig. 3. For each vaporization test (with the crucible), the furnace was heated up to 1200 ± 10 °C with a rate of 300 °C/h under an inert gas (argon) flow. Then the temperature was maintained at 1200 °C during 1 h for thermal homogenization of the sampling tube, still under argon flow. After these 5 h, argon was replaced by oxidative gas (air and/or steam as carrier gas) and the vaporization began. The duration of a test was about 7 h for the vaporization phase. At the end of the vaporization test, the furnace was stopped and the steam and air mixture was replaced by argon with the same flow rate (1.84 Nl/min) during 10 min in order to stop Ru vaporization from the crucible. During the cooling down phase to room temperature, a low argon flow rate was used to sweep the tube. The next day, the argon flow was stopped to remove and to weigh the crucible containing the remaining reagent powder in order to assess the precise vaporized Ru mass.

Fig. 3

Thermal-hydraulic experimental sequences for a long duration START test

A revaporization phase was performed without reagent in the crucible but in presence of Ru deposits previously generated and with the same thermal-hydraulic conditions as those corresponding to the vaporization test. The revaporization test duration was between 10 and 29 h depending on the carrier gas used. For dry air, during the night, the thermal-hydraulic conditions were kept constant but no sampling was performed. In presence of steam, during the night, the carrier gas injection was stopped and the liquid traps were disconnected from the TGT, stored at low temperature (4 °C), while the furnace was maintained at 1200 °C.

Experimental matrix

The main test parameters were: the thermal profile (abrupt or smooth), the composition of gas flow (steam/air mixtures with 0/100% or 60/40% weight ratio) and the tube material (Q or SS). The START matrix is provided in Table 1. Test 1 was the reference case with dry air condition (0/100%), an abrupt thermal profile and a quartz tube. Test 2 focused on the effect of the steam/air ratio (60/40%_w). Tests 3 and 4 were dedicated to a less sharp thermal profile (“smooth”) with dry air

and steam–air mixture conditions respectively. Finally, the last two tests, numbered 5 and 6, were performed with a pre-oxidized 316L SS tube. The composition of the carrier gas mixture (60/40%_w) was 62.5 g/h for steam mass flow rate and 41.8 g/h for air mass flow rate.

Table 1

Experimental parameters of START tests

Test	Material, thermal profile	Vaporization carrier gas and duration	Revaporization carrier gas and duration
1	Quartz, abrupt	Dry air, 7 h 30 min	Dry air, 26 h
2	Quartz, abrupt	Steam + air, 7 h	Steam + air, 4 h 30 min and air, 22 h
3	Quartz, smooth	Dry air, 7 h	Dry air, 28 h
4	Quartz, smooth	Steam + air, 7 h	Steam + air*, 7 h and air, 22 h
5	316L SS oxidized, abrupt	Dry air, 7 h	Dry air, 28 h
6	316L SS oxidized, abrupt	Steam + air, 7 h	Steam + air, 12 h
*During the period from 150 to 270 min, the gaseous mixture was 36/64% _w , contrary to the expected 60/40% _w one and the total flow rate was only 1 NL/min (leak on the entry flange of the tube). Nevertheless, this problem should have a minor impact on the results			

Ru repartition

For each test, the released ruthenium was collected at different locations. The main part of the Ru released was deposited in the transport tube and the remaining part reached the tube outlet under gaseous and aerosol forms. Aerosols were trapped on the dipping tube of the first liquid trap, in the first trap solution (in addition to the gaseous fraction) and on the ultimate filter (assumed to be only aerosols).

Source of Ru

The Ru mass vaporized from the crucible, call later “crucible” vaporized Ru mass (“crucible” vap. Ru), was calculated by mass difference before and after the test. The initial Ru mass was obtained by the reagent analysis certificate (~ 75% of the initial weight of product). The final amount of Ru was obtained indirectly by analysis of the percentage of oxygen (high temperature pyrolysis coupled to the oxygen quantitative analysis, uncertainty of 1%). The Ru vaporization kinetics from the crucible was previously determined on calibration experiments for different test durations: from 20 to 420 min for a 60/40%_w steam/air ratio.

Deposits profile along the thermal tube

The deposits profile along the thermal tube was only measured on the quartz tubes (4 tests). After the test, the tube was radially cut in several pieces (about 2.5 cm). This step induced some Ru losses (up to 20% of “crucible” vaporized Ru mass). The pieces were weighed, crushed and dissolved by alkaline fusion in order to analyze the ruthenium concentration by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The uncertainty of the alkaline fusion process followed by ICP-AES analysis is ~ 10% of the total amount of deposited Ru and the quantification limit (QL) is ~ 10 ppm (~ 1 mg for a 100 ml sample).

Raman and XPS investigation analyses

The surface characterizations by X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy of Ru deposits were performed. Raman scattering depends on electron–phonon interactions that are very sensitive to local environments. Raman scattering can provide information about the material or device structure on the scale of a few lattice constants and is probably the most useful method available for studying lattice vibrations and their interactions with other excitations. While the Raman spectroscopic technique can be used to gain insights into the microscopic structural effects of materials, XPS provides valuable complementary information on oxidation states and stoichiometry of Ru oxides.

Micro-Raman spectra were obtained from a Renishaw spectrometer (RM1000 and in-Via model). Excitation was performed using the 514 nm green line of an argon-ion laser and the 785 nm of a near-IR laser, with a low power source (some mW). The acquisition time was 30–100 s and the spectral resolution was 4 cm^{-1} . The samples were pieces of quartz of test 3 (dry air).

The XPS analyses were performed using a Kratos Analytical AXIS Ultra^{DLD} spectrometer using a monochromatic aluminum source ($\text{Al K}\alpha = 1486.6\text{ eV}$) for excitation. The analyzer was operated in constant pass energy of 40 eV using an analysis area of approximately $700\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$. XPS allows getting chemical composition with less than 10 nm depth scale of the surface. Quantification and decomposition of the experimental photopeaks were carried out using CasaXPS software. Quantification took into account a non-linear Shirley background subtraction whereas Gaussian G (70%)–Lorentzian L (30%) product form or Lorentzian asymmetric LF line shapes were used for spectral decomposition of C 1s, O 1s and Ru 3d, respectively. The fitting parameters of the LF line shape given in CasaXPS were derived from [27]. The XPS elemental composition has an accuracy of $\pm 10\%$ and the detection limit is known to be 0.1 at.%. Due to post-test surface analysis, surface contamination cannot be excluded. In order to have a basis, a reference sample (RuO_2 anhydrous reagent, purity 99.9%, Alfa Aesar) was analyzed in the same conditions as described above. Some pieces of pre-oxidized 316L SS with Ru deposit after the revaporization tests (tests 5 and 6) and one piece of quartz (test 1) were characterized.

Kinetic gas and aerosols partition study

The kinetic evolution during the test was followed by analyzing periodically the liquid trap solution of the two traps by ICP-AES. The global uncertainty of the ICP-AES measurement was estimated at 10% and the detection limit at 10 ppb. In the second liquid trap, no Ru was detected.

The gaseous and some aerosol forms of Ru were trapped in the liquid traps while flowing through Ru aerosols were caught in the ultimate filter placed downstream of the sampling line. In the liquid trap, “outlet

Ru” is gaseous RuO_4 dissolved and aerosols in suspension. To determine the gaseous and aerosols partition, liquid trap solutions were centrifuged and filtered. Gaseous Ru forms in the solution were analyzed by ICP-AES and the filters with the aerosols from centrifuged solutions were dissolved by alkaline fusion in order to determine the Ru amount by ICP-AES analysis. So, the amount of Ru released under aerosol form was the sum of the Ru aerosol amount from the first liquid trap and from the ultimate filter.

In addition, a part of released Ru from the tube was also found on the dipping tube of the first trap. This deposit may result from aerosol deposit by impaction and also partly from the decomposition of $\text{RuO}_{4(g)}$ to $\text{RuO}_{2(s)}$ but probably in a lesser extent.

Ruthenium mass balance

For all the tests performed with a quartz tube, the Ru mass balance was evaluated by calculating the ratio of the “experimental” vaporized Ru mass which is the sum of the Ru collected amounts (deposits on the thermal tube and on the dipping tube, gas and aerosols in the liquid traps and aerosols on the ultimate filters) and the “crucible” vaporized Ru mass.

For the two tests with a SS tube, as the Ru deposit profile could not be determined, the amount of Ru deposits was deduced by the difference between the Ru amount vaporized from the crucible and the total Ru amount transported at the tube outlet (gas and aerosol in solution + Ru deposit on the dipping tube of liquid trap and on the ultimate filter).

Results and discussion

Ru mass vaporization kinetics

Analysis of the reagent (by X-Ray diffraction, see Fig. 4) showed that the final reagent is a mixture of crystallized Ru and RuO_2 while the initial product is amorphous RuO_2 . As the composition of the final reagent ranges from 9 to 70% of RuO_2 (Table 2), the vaporization rate could not be simply determined only from the reagent mass loss. This information was not presented in other studies [18].

X-Ray diffraction on Ru final product (Ru metal in red and RuO₂ in blue)

Final reagent composition (Ru weight percent)

Test	% Ru	% RuO ₂
1	65	35
2	30	70
3	80	20
4	60	40
5	91	9
6	58	42

In our protocol, the furnace was heated up to 1200 ± 10 °C under an argon flow. So, the impact of this heating phase on the reagent was studied. Two heating phase tests (complementary tests) were performed

to confirm the reproducibility of the vaporized Ru mass under argon. The pressure variation of the device and the Ru ultimate filter loading indicated that the vaporization of Ru starts around 700 °C. At the end of the complementary tests, the mass reagent is up to 95% in metallic form and less than about 1% of initial Ru mass was vaporized from the crucible during this phase. So, during the preliminary 5 h heating phase under argon, the RuO₂ powder in the crucible was reduced to Ru metal. To consider the oxidative phase only, the mass of Ru vaporized during the argon heating phase was removed from the measured vaporized Ru mass.

The Ru vaporization kinetic results showed no time dependence on the vaporization rate with 60/40%_w condition. The rate was considered constant (Fig. 5) and reproducible ($\pm 10\%$) for the other steam/air gas compositions. The total consumption of the Ru source (1 g) was never reached and allowed calculation of the vaporization rate. With the quartz tube, the mean values of the Ru vaporization kinetics have been calculated for the two steam/air gaseous mixtures used in the test matrix and for two additional conditions 35/65%_w and 85/15%_w. Figure 5 displays that the mean value of the Ru vaporization rate is linearly steam/air mixture dependent. The dry air condition promotes Ru vaporization. The rate decreases by about 49% with decreasing air mass fraction from 100 to 15%, consistent with Kärkelä et al. works [19] but nevertheless, vaporization rates obtained were ten times higher (for dry air) than ours. This is due to a higher flow rate (5 l/min) and a larger surface area of their crucible.

Fig. 5

Ru vaporization kinetics (a.u.) from the crucible as a function of the air weight ratio (quartz tube experiments only)

With the SS tube, the vaporization rates were slightly higher than those obtained with the quartz tube (20% more). It could be explained by the reductions of the internal diameter of the tube in the HT zone and of the height of the crucible containing the reagent powder which have been changed due to geometrical constraint.

Total ruthenium transported in vaporization and revaporization tests

The results are summarized in Table 3 where the Ru amounts transported at the tube outlet (gaseous and total with aerosol fraction) for vaporization and revaporization phases are presented. All the data are expressed as % of “crucible” vaporized Ru mass. Ru experimental mass balance based on Ru analysis reached about 80%, the remaining part was mainly due to some losses due to the cutting process of the quartz tube.

Table 3

Results at tube outlet ($\sim 250\text{ }^{\circ}\text{C}$, except for tests 5 and 6 $\sim 170\text{ }^{\circ}\text{C}$, outlet wall temperature) in % of “crucible” vaporized Ru mass

Test	Vaporization phase (%)		Revaporization phase (%)		2 phases (%)	Measured Ru tube deposit (%)
	RuO ₄ (gaseous) ^a	Ru total	RuO ₄ (gaseous) ^a	Ru Total	Ru total	
1	1.3	2.8	0.6	1.1 ^b	3.9	71
2	2	3.7	0.4	0.8	4.5	73
3	0.2	0.9	0.3	0.5 ^b	1.4	79
4	0.5	0.7	0.4	0.8 ^b	1.5	—
5	0.3	3.2	0.3	0.3 ^b	3.5	—
6	1.1	2.2	1.2	1.4 ^b	3.6	—
^a In 1st liquid trap without Ru deposit in the dipping tube						
^b The ending of revaporization phase was not observed at the end of experiment (see Fig. 9)						

There is a clear effect of the thermal profile on the total Ru transported (gas, aerosols and deposit into dipping tube) during the vaporization and the revaporization phases. For tests with an abrupt profile (Quartz or SS tube) the total Ru transported represents from 3.5 to 4.5% of “crucible” vaporized Ru mass while it represents about three times less for the two smooth tests. So, whatever the gaseous composition and the tube material, the abrupt thermal profile promotes the total Ru amount transported at the outlet during vaporization and revaporization phases. The revaporization phenomena are not finished at the end of START experiments and the values obtained are not final values. During a hypothetical nuclear accident, the vaporization phase is a short term phenomenon while the revaporization phase should be a potential long continuous phase. So, revaporization from the Ru deposit in the RCS must be taken into account to calculate the total Ru amount transported to the containment in the long term.

Transport during vaporization tests with the crucible

Figures 6 and 7 show the evolution of the total Ru amount including gas and aerosol forms during the six tests. As with the work of Vér et al.

with a low flow rate of 0.17 NL/min [16, 17], this study demonstrates that a part of Ru reached the outlet of the thermal gradient tube as gaseous RuO_4 even if it is not expected by pure thermochemical computations.

Fig. 6

Evolution of the Ru amount (gas and aerosols) collected during vaporization tests

Fig. 7

Evolution of the gaseous Ru fraction as a function of the total vaporized Ru forms collected in the first liquid trap during the vaporization phase

During the whole test duration, ruthenium transport kinetics (total amounts) were roughly linear. The lowest kinetic values of Ru transported at the tube outlet were observed for the smooth profile, especially in dry air. For the tests with an abrupt profile, there is no significant effect of the gaseous mixture and of the tube material on the transported Ru kinetics. As regards the gaseous evolution in the liquid traps (Fig. 7), for the test with a smooth profile, Ru transported to the tube outlet is only under gaseous form and with no aerosols measured. On the contrary, for the tests with abrupt thermal profile, whatever the tube material (SS/Q) and the gaseous mixture, there is a change in the gaseous/aerosols partition between the beginning and the end of the test. Globally, the Ru gaseous fraction increased significantly (except for test 5) and became the major contribution to the outlet Ru release. By contrast, for test 5 (SS, dry air), gaseous Ru is transported only during the first hour. Then the gaseous fraction was decreased by two thirds after 420 min. Transient phenomena in the short term (in the first hour(s) of experiment) are clearly evidenced in this study and might explain these changes. Therefore, this switch of the species transported over the test duration should be taken into account when considering a long term reactor scenario.

According to Backman et al. [18] high cooling rates increased the RuO_2 particle formation in the gas phase. In our study, except for test 5 (SS), aerosols were formed and transported at the outlet principally in the first hours of the experiment and decreased significantly in the course of the tests, possibly due to revaporization process of deposits. The

aerosol formation and transport depend on the thermal profile but also to other parameters such as surface materials and/or gas flow rate/content.

Figure 8 presents the final partition of Ru transported in the gaseous form, Ru aerosols and Ru deposited into the dipping tube that should be attributed to aerosol phase. The total Ru amount transported to the tube outlet represents up to 3.7% of the “crucible” vaporized Ru mass after the vaporization phase (Table 3). The higher values of Ru transported (total and gaseous) at the tube outlet were observed for the abrupt profile compared to the smooth profile (x4), linked mainly to kinetic limitations on $\text{RuO}_{4(g)}$ decomposition. Presence of steam promotes the gaseous Ru transported (black parts of columns in Fig. 8) whatever the tube material and the thermal profile. For the SS tube, Backman et al. proposed that the steam could passivate the stainless steel surface, hinder RuO_2 deposition on the surface and promote the Ru gaseous transport. Indeed, in our study, the gaseous fraction is more important in presence of steam (test 6) compared to dry air (test 5).

Fig. 8

Ru gas, aerosols and deposits in the dipping tube at the end of vaporization tests (% “crucible” vap. Ru) as a function of the thermal profile (abrupt or smooth, quartz or SS tube). Tests 1, 3 and 5 are in dry air, tests 2, 4 and 6 are in 60% steam/40% air mixture. Flow rate 1.84 Nl/min

To check the reproducibility, the test in dry air with a smooth profile (test 3) was performed twice. The results showed good reproducibility

of the vaporization tests results with a difference lower than 10% on the amount transported and kinetics, consistent with the expected uncertainties.

Transport during revaporization tests

The evolution of the Ru amount (gas and aerosols) in the first liquid trap during revaporization tests is shown in Fig. 9. For test 6, the gas (air + steam) injection was stopped during the night; the kinetic results obtained the next day were plotted just after those obtained the previous day. At the end of the experiments (12–29 h of revaporization), the revaporization phase was not finished. Kinetics were close to each other for all the tests, except for tests 1 and 6 with noticeably higher values. The total Ru amount transported to the tube outlet represents up to 1.4% of the “crucible” vaporized Ru mass for the revaporization phase (Table 3). As the total Ru transported at the tube outlet during the revaporization tests remains low, it is difficult to conclude on parametric effects but general trends can be highlighted.

Fig. 9

Evolution of the Ru amount (gas and aerosols) in the first liquid trap during long duration (LD) revaporization tests

For dry air condition (tests 1, 3 and 5), whatever the material tube, the kinetics of Ru transport at the outlet is linear. Completion of the revaporization phenomenon could not be reached after 29 h. In this study with dry air, the revaporization of deposited RuO_2 from quartz was higher than from SS material, contrary to [17]. These differences could be attributed to the different experimental device (geometry and sampling tube). For steam conditions (tests 2, 4 and 6), a tube material effect is observed. Contrary to dry air condition, the gaseous Ru amount transported at the outlet is substantially promoted with the SS tube (by a factor of 6.4 after 12 h). For test 6 with the SS tube (with the night stop), a decrease of the kinetic transport value the next day is observed (factor 4). So, the stop of injection of gas mixture has probably modified the conditions in the tube (Ru deposits) and could explain the lower revaporization kinetics observed. For quartz tube (tests 2 and 4), there is very little transport of Ru to the outlet tube. The change of carrier gas (60/40%_w to dry air) in tests 2 and 4 did not allow a resumption of the kinetics previously observed under dry air condition as in tests 1 and 3 respectively. This difference is most probably due to the effect of a steam excess on the Ru deposits. So it points out the

importance of the gaseous mixture composition during the Ru deposit formation process, and consequently on the revaporization phase.

Contrary to the vaporization tests, no transient phase is observed in the short term during the revaporization tests.

During all the revaporization tests, Ru is transported mainly in a gaseous form to the tube outlet (Fig. 10). Therefore, the Ru deposit in the dipping tube originated principally from $\text{RuO}_{4(g)}$ decomposition to RuO_2 . For test 1 (air, quartz and abrupt profile), aerosol fraction (grey part of 1st column in Fig. 10) comes from the dipping tube leaching at the end of the experiment. Some aerosol deposit fell into the solution during manipulation and this fraction corresponds to a part of Ru deposit in the dipping tube. So to avoid this false attribution/assignment to aerosol, no leaching was performed on the other tests. Small amounts of aerosols are found on the ultimate filter in the tests with SS tube. However, these amounts represent less than 0.1% of the “crucible” vaporized Ru mass. With such low values ($< 1.5\%$), it is difficult to conclude about the effect of the tube materials on the gas/aerosol partition. As the total Ru transported at the tube outlet during the revaporization tests remains in the same order of magnitude, it can be stated that the thermal profile (abrupt or smooth) has no significant effect on the revaporization whatever the gaseous mixture is (Fig. 10).

Fig. 10

Ru gas, aerosols and deposits in the dipping tube at the end of the long duration (LD) revaporization tests (% “crucible” vap. Ru) as a function of the thermal profile (abrupt or smooth), the tube material (Q or SS) and atmosphere (dry air: tests 1, 3, 5 and 60% steam/40% air mixture: tests 2, 4, 6)

For revaporization tests, the kinetics are lower than for vaporization tests. This decrease could be due to the experimental protocol. After the vaporization test, the set-up is cooled down to ambient temperature in order to remove the crucible with reagent. For one revaporization test (test 6) the stop of the gaseous mixture during the night led to a decrease of the kinetic transport value the day after. So, the final Ru amount is under-estimated. This point should be investigated deeper in the future with an improvement of the current START experimental protocol.

Deposit of ruthenium after revaporization

The deposit profiles in a quartz tube were measured. Ru amounts deposited in the quartz tube after revaporization tests represent more than 90% of the “crucible” vaporized Ru mass. The deposited amount is a bit higher than literature data ranging from 65 to 94% [16, 17, 18, 19, 20, 21, 22, 23]. In our study, no influence of the tube material could be observed but the thermal-hydraulic conditions are quite different.

Figure 11 shows two different Ru deposit profiles obtained after vaporization and revaporization phases under the two steam/air gaseous mixtures and with an abrupt profile. The reported temperatures are upper wall temperatures at the middle of the cut quartz pieces for the steady state conditions. At a given distance from the crucible, the wall temperature is generally 5 or 10 °C higher in the upper part than in the lower part of the tube and in any case this difference is lower than 20 °C. The main part of the Ru deposit is located on the thermal gradient zone, between 1000 and 500 °C. Ruthenium is deposited all along the

quartz tube according to the temperature profile and mainly on the upper side of the tube, due to the thermal convection in the horizontal device with a laminar flow rate, a phenomenon also observed in [20]. The peak of Ru depositions happens at high temperature (850 ± 40 °C), just after the outlet of the furnace, then the amount of deposited Ru decreases slowly down to the outlet (~ 250 °C). This trend is similar to Vr et al. 's observations [17] where most of the Ru species were deposited on the quartz surface between 865 and 510 °C. As already reported by [20], the bigger deposition peak at high temperature ($\sim 1000\text{--}500$ °C) could be due to the thermal dissociation of RuO_3 into RuO_2 followed by a smaller peak at lower temperature ($\sim 500\text{--}250$ °C) which could be due to reduction of RuO_4 into RuO_2 . For the tests performed with a smooth profile, the Ru deposit is spread out all along the thermal gradient with a long tube. The major part of Ru deposits is the zone ranging from approximately 1000 °C down to 600 °C.

Fig. 11

Ru deposit profiles after revaporization tests (1 and 2). Quartz tube with abrupt profile (1) dry air and (2) 60% steam/40% air mixture

The comparison of the Ru deposit profiles in the quartz tube obtained after the vaporization phase and after the revaporization phase shows a shift of the Ru deposit to lower temperatures during the revaporization phase for all the gaseous mixtures. This trend is observed with a higher effect in the zone of high temperature for the dry air condition, where the Ru deposit in between 950 ± 30 C to 880 ± 30 C was completely revaporized according to visual observations (Fig. 12). This complete

removal was not observed for the tests performed with steam/air mixtures. A comparison of the pieces of tube between 1000 and 500 °C for the two tests 1 and 2 shows that the Ru deposit is of different types, depending on the gas composition of the mixture studied. Especially for the condition with an excess of steam (60/40%_w), the Ru deposit is thicker and has a foaming aspect (Fig. 13). This deposit appearance might come from the experimental protocol (injection of 100% dry air after the steam injection during the revaporization phase).

Fig. 12

Ru deposits after the vaporization (top) and the revaporization (bottom) test 1 (dry air, quartz tube and abrupt profile), with wall temperatures at the end of the revaporization test and distances from the crucible

Fig. 13

Two quartz pieces with Ru deposits after the revaporization phase at the end of test 2 (left, between 850 and 700 °C and right, between 540 and 480 °C) (quartz tube, abrupt profile, 60% steam/40% air mixture)

The results of surface characterization obtained by the Raman and XPS techniques show that, whatever the Ru deposit locations (at high temperature or at low temperature), the deposit is mostly formed of RuO_2 species, except in two cases at about 880 °C (Ru metal, test 6 after vaporization phase with XPS results).

Raman spectra of Ru black deposit (temperature zone around 730 °C, Fig. 14) and green deposit (around 275 °C) onto quartz pieces of test 3 (0/100%_w) show the three major bands of single crystal RuO_2 which are located at 528, 646 and 716 cm^{-1} [28]. According to Music et al. [29], the shift and broadening of the Raman peaks for the RuO_2 anhydrous reagent (509, 626 and 689 cm^{-1}) are representative of less crystallinity and local disorder in comparison with the single crystal. The characteristic peaks of solid RuO_4 are attributed near 880 cm^{-1} [30, 31, 32] and those of hydrous RuO_2 at 470 and 670 cm^{-1} [32]. Room temperature Raman spectra of the RuO_2 thin films on Si substrate, using the solution chemical technique, annealed at 700 °C show three major bands at about 523 (E_g), 646 (A_{1g}) and 710 (B_{2g}) cm^{-1} [33]. An additional band at about 477 cm^{-1} was attributed by the authors to hydrated RuO_2 . It is generally known that RuO_2 behaves as a hygroscopic oxide. To better understand the unassigned band at 477 cm^{-1} , the temperature dependent behaviour of Raman spectrum was studied in detail by Bhaskar et al. [33].- This band appears at all temperatures below 27 °C and disappears completely above the

temperature of 77 °C, consistent with the assumption that the material transforms into the anhydrous form. The bands near 880 cm⁻¹ and near 477 cm⁻¹ are not observed for the samples in the current study, which confirms that these samples are characteristic of anhydrous RuO₂.

Fig. 14

Raman spectra of black Ru deposit on quartz tube at around 730 °C (test 3 with 100% dry air condition) and RuO₂ powder (initial reagent)

In general the XPS approach was found to be valuable in monitoring the surface concentrations of the ruthenium oxides and thus in characterizing their chemical compositions [34]. Nevertheless, the characterisation is rather complex because Ru 3*d* peaks are overlaid by C 1*s* peaks which come from carbon surface contamination (BE at 284.6 eV). Figure 15 shows XPS spectra of black Ru deposits on a piece of stainless steel from START test 5 after vaporization phase (dry air, corresponding temperature at about 430 ± 15 °C). The binding energy (BE) of the Ru 3*d*_{5/2} core level is pointed out at 280.5 eV, and at 529.1 eV for the O 1*s* peak. The sample from revaporization phase shows similar values (280.3 and 529.2 eV, respectively). These values of Ru 3*d*_{5/2} BE are in full agreement with the values cited in previous literature for anhydrous RuO₂, ranging between 280.7 and 281.0 eV [32]. It is known that RuO₂ behaves as a hygroscopic oxide and the BE of the Ru 3*d*_{5/2} peak of hydrated ruthenium dioxide is pointed out at 281.4 eV [34] or at 282.3 eV [35]. In a recent study [27], the difference between anhydrous and hydrated RuO₂ was explored. Experimental

Ru $3d_{5/2}$ BE were found at 280.6 and 280.8 eV respectively, and at 529.3 and 530.9 eV for the O $1s$ peak.

Fig. 15

XPS spectra of (a) Ru $3d$ and (b) O $1s$ core level lines of Ru deposit on SS for test 5 with 100% dry air condition (after vaporization test)

The Ru layers deposited on a piece of stainless steel were analysed by Mun et al. [35]. The BE of the Ru $3d_{5/2}$ level was pointed out at 281.4 eV and the O $1s$ region was completely dominated by the hydroxyl component, results characteristic of RuO₂ · x-H₂O. The decomposition of the O $1s$ peaks could be studied in a classical way, using three components (BE at around 529, 530.5 and 532 eV) attributed to oxygen atoms in three chemical environments: O²⁻, OH⁻ and H₂O, associated respectively to lattice oxygen, hydroxyl groups and water adsorbed at the surface of RuO₂ [13]. The presence of chemisorbed oxygen on the film surface could be associated with hydrated RuO₂ or RuO₃. As reported in [33], during the film preparation, the relatively rapid cooling process undergone by the film after deposition enhances the formation of RuO₃ species on the surface. The characteristic BE of RuO₃ are pointed out at 282.7 and 531.0 eV for the Ru $3d_{5/2}$ and O $1s$, respectively. Kim and Winograd [34] found that RuO₃ exists as a stable surface species on anhydrous RuO₂, as a defect structure. Two samples (upper and lower) of test 6 after vaporization,

corresponding to a temperature of about 880 ± 20 °C, show a spectrum characteristic of Ru metal (53–62%) with a Ru $3d_{5/2}$ peak at 279.8 eV [34], and with BE Ru $3d_{5/2}$ at 280.3 eV (47–38%) and BE O $1s$ at 529.7 eV characteristic of anhydrous RuO_2 (Fig. 16). One sample (upper layer) of test 6 after revaporization (near 560 °C) shows only peaks of anhydrous species (BE Ru $3d_{5/2}$ at 280.3 eV and BE O $1s$ at 529.0 eV).

Fig. 16

XPS spectra of **a, c** Ru $3d$ and **b, d** O $1s$ core level lines of Ru deposit on SS for test 6 with 60/40%_w mixture (after vaporization test **a, b**, and after revaporization test **c, d**)

To conclude, the XPS analysis of Ru deposit on pre-oxidized SS pieces showed that it is characteristic of anhydrous RuO_2 species in a major part of the cases with the possibility of Ru metal at high temperature. The difference of colour observed within a quartz tube seems to be linked only to the thickness of the deposit (lower thickness deposit is green near the exit of the device and higher thickness deposit is black in the gradient profile after the exit of the furnace). Thus, the surface analyses tend to show that all the Ru deposits along the thermal tube present in our experiments are forms of the RuO_2 species, similarly to previous works [19, 21, 22, 23].

Conclusions

In the frame of the OECD STEM project, small scale-experiments were performed on the START set-up to better understand ruthenium chemical behaviour in the RCS with SA oxidative conditions.

Our experimental results are quite consistent with previous works, i.e. ruthenium tetroxide is formed in air/steam by oxidation of ruthenium dioxide and a relevant amount, which mainly depends on thermal gradient, residence time and gas composition is measured at low temperature as well as a fraction in aerosol form.

Our experiments have shown that, whatever the tube material (Q/SS), the thermal profile (abrupt/smooth) and the gaseous mixture (with or without steam in the mixture), the major part of the vaporized Ru was deposited along the thermal gradient tube ($> 95\%$ of the “crucible” vaporized Ru mass) at the end of the tests after consecutive vaporization and revaporization phases, consistent with literature data. So, the total Ru transported downstream (gaseous and aerosols, including Ru deposited on the dipping tube of the first liquid trap) represents about a few percent of the Ru mass vaporized (1.5 up to 4.5%), mainly under gaseous form.

After a detailed characterization of the heating phase with argon, the Ru vaporization kinetics in the oxidant test was found to be linear for all the studied gaseous mixtures (steam/air) and can be considered as steam

content dependent. The dry air condition promotes the vaporization of RuO₂ from the crucible at 1200 °C.

During the vaporization phase from the crucible with reagent, the long duration tests pointed out the existence of transient phenomena in the short term (first hour(s)), whatever the gaseous mixture composition, that were never observed until now and thus reinforce the need to perform quite long tests (few hours). The abrupt thermal profile increases the total Ru amount transported at the outlet during the vaporization processes compared to a smooth one. In addition, it also favours RuO₂ particle formation (aerosols) in the gaseous phase whereas there is only Ru gaseous species with a smooth gradient profile. The precise steam effect on the total Ru transported could not be clearly determined in our vaporization tests. However, the large presence of steam does not change the phenomenology and could favor the Ru gaseous transport; this point needs confirmation by additional tests.

During the revaporization phase of the Ru deposited on the transport tube, Ru was transported mainly as a gaseous form to the tube outlet and no transient phenomenon was observed. Contrary to the vaporization tests, there is a possible gas composition effect linked to the tube material on the Ru transported during the revaporization tests: Ru transport is increased with an excess of air for quartz tube (abrupt profile) and with an excess of steam for SS tube (abrupt profile).

Moreover, this work underlines the importance of the gaseous mixture composition during the Ru deposit formation and consequently on the revaporization phase. This study allowed the measurement of the deposit profiles depending on the temperature wall and did not reveal a significant effect of the gas mixture (with or without steam) on the Ru deposit profile in the quartz tube.

Finally, in this study on the transport of ruthenium in conditions similar to those prevailing in the RCS, the total Ru transported at the tube outlet after vaporization and revaporization long duration experiments led up to 4.5% of the “crucible” Ru vaporized mass (in the tests conditions). With experimental conditions representative of a PWR

severe accident (Stainless Steel, abrupt thermal profile, steam in excess and an outlet temperature at about 170 °C), revaporization phase led to a similar gaseous Ru release at the transport tube outlet as the one observed during the vaporization phase ($\sim 1.2\%$ of the “crucible” vaporized Ru mass). However, this is not the maximum reachable value because the revaporization phase was not finished at the end of the experiment (only 12 h of revaporization). During a hypothetical nuclear accident, the vaporization phase is a short term phenomenon while the revaporization phase is potentially quite a long, continuous process. Further investigations on ruthenium revaporization processes with more oxidizing prototypic conditions, SS material and an improvement of the test protocol are currently carried out in the frame of the OECD STEM2 project [36].

These experimental results allow a better understanding of the Ruthenium transport in the RCS and will be used to implement an accurate modelling in the ASTEC code. This model will also allow improved source term assessments because, in terms of nuclear safety, a deeper understanding of Ru chemistry will be necessary for better severe accident countermeasures if needed.

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