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Ruthenium behavior in the RCS in case of a PWR severe accident: study of oxidative conditions with stainless steel tube

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Abstract

In the research field on severe accidents in Nuclear Power Plant, a specific scenario correspond to accident with oxidative conditions for which damaged fuel can be highly oxidised with significant releases of ruthenium oxides. Ruthenium chemistry is complex, and the current knowledge has to be deepened to better assess ruthenium Source Term with potential radioactive releases to the environment as volatile ruthenium tetroxide. In this work, experimental studies are focused on ruthenium behaviour along a stainless-steel thermal gradient tube, with maximum temperature of 1200°C, simulating the reactor cooling system in oxidizing conditions with mainly steam/air gas mixtures. Results showed that few % of ruthenium oxides (< 10% with SS tube) can reach low temperature, representative of containment temperature, even with low oxygen content in the carrier gas. The ruthenium revaporization process from the Ru deposits along the tube on mid-term was studied. Influence of carrier gas composition (steam %), flow rate and NOx feed are discussed.

Keywords Source term, Severe Accident, Ruthenium transport, Reactor Cooling System, NO_2

Introduction

During a hypothetical severe accident (SA) with a core melt down and under oxidizing conditions in a Nuclear Power Plant (NPP), ruthenium may be released from the nuclear fuel and partially transported as gaseous ruthenium oxides to the reactor containment building. Ruthenium is of particular interest because of its high radiotoxicity and its ability to form volatile oxides. It can contribute significantly to radiological consequences on the short and mid-terms due to its two isotopes ^{103}Ru and ^{106}Ru, if released in significant amount to the environment [1]. A previous OECD project, called STEM (Source Term Evaluation and Mitigation) operated by IRSN, investigated the Study of the TrAnsport of RuThenium in the primary circuit (START) [2]. The objective was to provide experimental data to better understand the phenomena leading to gaseous ruthenium release at the break of the reactor cooling system (RCS) [3]. The main objective was to build a first experimental database to guide ruthenium modelling improvements and thus later be able to refine the evaluation of source-term for a SA occurring on a pressurized water reactor (PWR), and to reduce uncertainties on specific phenomena related to the physical-chemistry of one major fission products ruthenium. This experimental project has provided new insights concerning the Ru

transport/chemical behaviour in the RCS, focused on medium- and long-term releases during a severe NPP accident.

During the START experiments, two phases were studied, a first direct phase called vaporization phase in which Ru was generated from a crucible at 1200°C and a second phase, called revaporization phase, performed without any source of Ru but in presence of Ru deposits along the thermal gradient tube (TGT). The major experimental data measured were amount and identification of Ru species (gaseous and condensed forms) transported at the "cold leg break", amount of Ru deposit along the TGT as a function of the experimental conditions and amount of the Ru transported during the revaporization phase from the deposits. The purpose was to supply a parametric study to better understand the effect of each single parameter. The first phase of the program gave information on the key parameters impacting the transport kinetics, the partition between gaseous RuO_4 and particles of RuO_2 at low temperature and the extent of the revaporization process of deposited species [3], most of the tests were performed with a glass tube to ensure a better mass balance and exclude/limit possible surface interactions. In START program, with an abrupt thermal profile, steam in excess and a pre-oxidized stainless steel (SS) tube, it was shown that the total Ru transported downstream the TGT led up a maximum of 4.5% of the Ru mass vaporized, mainly under gaseous form. This work showed that the precise steam influence could not be clearly determined for the two phases (direct vaporization and revaporization) and needs additional tests.

To complete this first project, complementary tests based on ruthenium revaporization process with representative oxidative conditions (including atmospheric radiolysis simulants) have been performed in the frame of the follow-up OECD STEM2 project (2016 to 2019) [4]. In START2, role of oxidative agents and surface state with SS transport tube were examined on ruthenium tetroxide (RuO_4) formation and stability. This paper summarises the main outcomes.

First, the revaporization phase required more investigation and an improvement of the test protocol was carried out in START2 with longer duration tests.

Second, nitrogen oxides are of special interest regarding ruthenium chemistry. RuO_4 is known for its ability to form different nitroso and nitrosyl compounds after reacting with nitric acid, NO_2 or NO gases [5-7]. RuO_4 can also be trapped into the water phase after reacting with NO_2 or NO gases [8]. Estimation of the amount of NOx in the containment atmosphere predicts that representative concentrations of NO_2 and N_2O will be a few tens of ppm at most depending on e.g. temperature, dose, gas composition [9, 10].

Third, the tests were carried out with a pre-oxidized stainless steel thermal gradient tube to include the potential surface effect (covering a better representativeness of the surface deposition).

In the present article we address the influence of steam, ~~gaseous~~ flow rate and NOx feed on the Ru transport at the TGT outlet, after consecutive vaporization and revaporization phases, for ten relevant experiments.

Experimental

The experimental set-up and the test protocol were described in a previous article [3]. For these new experiments, details are provided hereafter.

Reagents

The ruthenium dioxide powder (RuO_2, purity 99.9%) was purchased from Alfa Aesar. The weight percentage of Ru in RuO_2 powder is 75.8% given by the analysis certificate.

The source of NO_2 or N_2O gas in air was purchased from Air Liquide® (450 ppm NO_2 or 400 ppm N_2O in the source bottle).

Equipment

The START2 facility (Fig. 1) has been designed as an open flow reactor with a controlled TGT. Temperature gradient, reagent concentrations and residence time are representative of an accidental break of the primary circuit of a nuclear reactor, right up to the measurement point (simulating a cold leg break). A gas supply system with a steam generator (SG) is placed at the entrance of the tube and gas mixtures (H_2O/air) are introduced at 150°C upstream of the furnace. The two flow rates studied are 1.84 NL/min or 4.65 NL/min (at 0°C, 101.3 kPa). The tube materials representative of RCS surfaces were Inconel alloy 600 for the high temperature zone in the furnace and Stainless Steel 316L from the exit of the furnace to the TGT outlet (Fig. 2). The tube is 1.80 m long and has an internal diameter of 33 mm. The SS tube was pre-oxidized before the test at 800°C with a rich steam mixture (steam = 80 g/h and air = 14.1 g/h), during 24h to form representative oxide layers [11].

The device comprised a high temperature furnace and ceramic heaters to control the thermal profile. During the first part of the program, two thermal profiles (abrupt and smooth) were studied with the furnace temperature at 1200°C [3]. All the START2 experiments were performed with an abrupt profile (~27 °C/cm) favoring the gaseous transport at the outlet in accordance with the results obtained previously [3]. In the SS-316L part, the measurement of fluid temperatures between the position at 0.45 m from the crucible and the exit of the device (middle of gas flow, with a step of 5 cm) was performed by six thermocouples during all the duration of the test (Fig. 3). With a tube (0.70-0.75 m long between the crucible and the outlet) and a furnace reference temperature at 1200°C, the fluid temperature at the exit flange of the TGT was around (290 ± 20) °C and the residence time from crucible to exit tube ~5 seconds with a total flow rate at 1.84 NL/min. With a higher flow rate at 4.64 NL/min (x 2.5), the fluid outlet temperature was around (410 ± 30) °C and the residence time decreased to 2 seconds.

The test bench was instrumented to allow continuous measurements and control the thermal-hydraulic parameters such as pressure, carrier gas flow rates, wall and fluid temperatures.

The NO/NO_2 measurements were performed with a PORTASENS II portable gas leak detector (precision of ± 0.1 ppm for the 10-200 ppm NO_2 range and precision of ± 1 ppm for the 40-500 ppm NO range, with a response time of about 40 sec.). A G200 analyzer dedicated to measure N_2O gas was also used (precision of ± 2% for the 0-1000 ppm, with a response time of about 40 sec).

Method

The START2 test protocol (thermal-hydraulic sequence) was adjusted to get a total consumption of the reagent in the first two hours of the experiment. The objective was to conduct the vaporization and revaporization phases without interruption of the furnace heating and of the gas mixture injection in the tube during the night. The goal was reached with reducing the amount of Ru in the crucible (about 10 times less) and using a bigger first liquid trap of

1.5 L (Fig. 2). So, this new protocol is more reliable without any disturbing during the long test and results are more confident.

The source of Ru, call later "crucible" vaporized Ru mass (i.i.), was previously determined in START project at 1200 °C by mass difference before and after the test. In START2 test protocol, at the end of a long duration test, the crucible was empty. So, the Ru vaporization rate from the crucible obtained in START with 1.84 NL/min were used to determine the duration to consume the entire RuO_2 reagent in the crucible with the gaseous mixture used in the START2 tests. With a total flow rate of 4.65 NL/min, complementary experiments with SS tube, a short duration of 1 hour and 300 mg of reagent (anhydrous RuO_2) were performed to determine the Ru vaporization rate from the crucible at 1200 °C with 1%-99%$_w$ and 67%-33%$_w$ of H_2O-air gaseous mixtures. For each test, a mass of 100 mg (flow rate of 1.84 NL/min) or 200 mg (with 4.65 NL/min) of anhydrous RuO_2 powder in the alumina crucible was weighted and placed in the furnace the day before the test. This mass allowed a crucible empty at the end of the test. The furnace was heated up to high temperature (1200 °C) under argon, due to low vapor pressure of RuO_2 an infima/negligible amount of RuO_2 is vaporized. When the device was thermally stable, the argon flow was replaced by the oxidizing gaseous mixture (H_2O/air) during 20 h for long tests and 6 h or 7 h with NOx feed. For the conditions with higher flow rate and without NOx feed, it was not necessary to extend the test duration to second day. The total flow rate (laminar flow) was the same in a set of tests to have a similar residence time for a given temperature profile allowing comparison between tests. At the end of the test, during the set-up cooling down, a low argon flow rate was used to sweep the tube.

Separation and quantification of gaseous and condensed (aerosols) ruthenium species was achieved by trapping them into two liquid traps containing NaOH (1M) mounted in series and on an aerosol filter (quartz fiber) located downstream of the liquid traps to avoid parasitic trapping of gaseous Ru. The first liquid trap was cooled down (around 5 °C) to increase the gaseous trapping, with a good efficiency whereas no gaseous Ru is detected in the second liquid trap. For test with steam in excess, the temperature in the first liquid trap increased to 11 °C together with the liquid volume increase. Kinetics evolution of Ru transported at the outlet along the test was followed by sampling regularly the liquid trap solution.

For tests performed with NO_2 feed with 1.84 NL/min, it was decided to inject NO_2 gas at the furnace exit, after the high temperature zone, to avoid possible thermal decomposition of NO_2. Therefore, the flow rate over the crucible was 1.64 NL/min completed by 0.2 NL/min of NO_2 feed injected at the exit of the furnace (about 930 °C). In our conditions of gas dilution (flow rate of the NOx line adapted), we injected about 50 ppm of NO_2 or 40 ppm of N_2O in the tube, respectively. A test like the test with dry air and NO_2 feed at the exit of the furnace was repeated with NO_2 feed at the entry of the TGT. No significant influence was observed on the Ru amount transported at the outlet. Based on previous literature works [12, 13], it was assumed that the low concentration of NO_2 did not have a significant effect on the Ru vaporization from the crucible. So, for tests performed with the higher flow rate, the NOx feed was done at the entry of the TGT with the flow rate over the crucible of 4.15 NL/min completed by 0.5 NL/min of NO_2 feed (50 ppm).

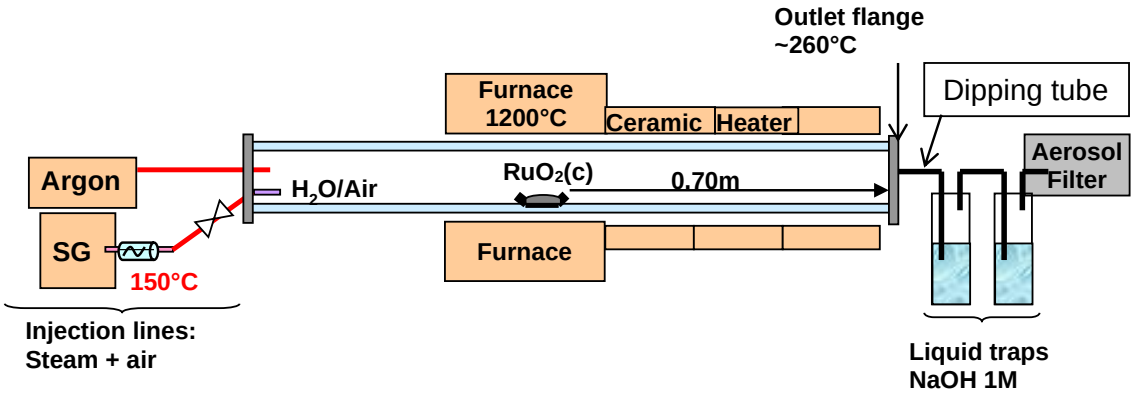


Fig. 1 Scheme of the START2 facility [3].

Fig. 2 START2 test facility (left) and RuO_4 dissolved in alkaline solution with the higher liquid trap – steam conditions (right)

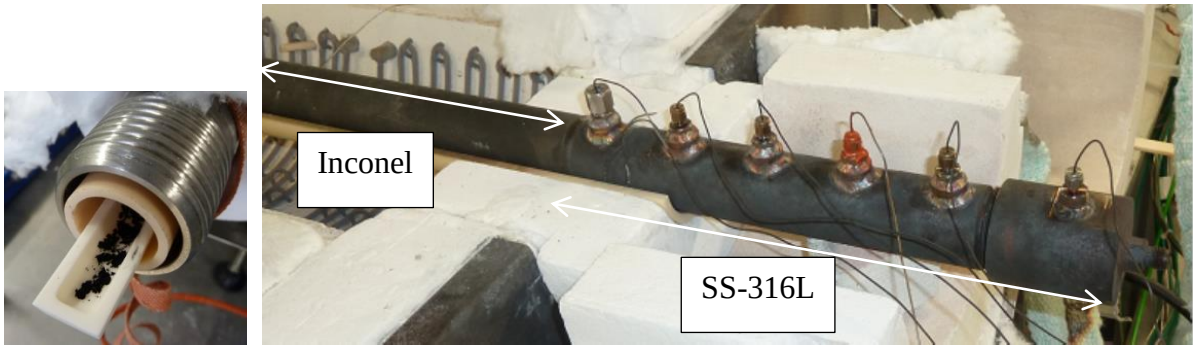


Fig. 3 Crucible of RuO_2 powder at the entrance of the SS tube (left) and exit part of the pre-oxidized SS tube with fluid thermocouples, without final insulation

Experimental matrix

The matrix composed of 10 tests covers influence of gas compositions, flow rates and test duration. The gas composition H_2O-air is reported in Table 1, with some tests with NOx feed (NO_2 and N_2O). The reference flow rate is fixed to 1.84 NL/min with variation with a factor x 2.5. Test 1 was the reference case with dry air condition (0%-100%$_w$), an abrupt thermal profile and SS tube. Tests 2 and 3 focused on the effect of the steam-air proportion (60%-40%$_w$ and 85%-15%$_w$). Tests 4 and 5 were dedicated to NO_2 influence with dry air and steam-air mixture conditions respectively. The next tests (6 to 10) were focused on the increase of the flow rate and the NO_2 feed to observe any influence of shorter residence time and Ru concentration. Finally, the last test, numbered 10, was performed with a N_2O feed. With 1.84 NL/min, 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, and 80.0 g/h for steam and 14.1 g/h for air for (85%-15%$_w$). With 4.65 NL/min, the reference test (6) was performed with (1%-99%$_w$), 4.1 g/h for steam mass flow rate and 352.8 g/h for air mass flow rate. The composition of the carrier gas mixture (67%-33%$_w$) was 171.0 g/h for steam and 83.6 g/h for air.

Table 1 Experimental parameters of START2 tests (316L SS oxidized, furnace temperature 1200°C and abrupt thermal profile, RuO_2 source).

Test	Carrier gas H_2O-air (%$_w$ weight proportion), NOx feed	Flow rate (NL/min)	Test duration (min)	Vaporization duration (min), ± 10 min
1	0-100 (ref)	1.84	1170	52
2	60-40			87
3	85-15			67
4*	0-100, NO_2 (50 ppm)		420	52
5*	52-48, NO_2 (50 ppm)			87
6	1-99 (ref)	4.65	390	94
7	67-33			170
8	1-99, NO_2 (50 ppm)			91
9	67-33, NO_2 (50 ppm)		360	186
10	67-33, N_2O (40 ppm)			169

*: For tests 4 and 5, the flow rate over the crucible was 1.64 NL/min (52%-48%$_w$ H_2O/air) completed with 0.2 NL/min of NO_2 feed (at about 930 °C) injected at the exit of the furnace. So, total flow rate of 1.84 NL/min with (60-40) mixture for test 5.

Ru analysis

Despite a major part of the Ru released was deposited in the TGT, a significant part was transported to the tube outlet under gaseous and aerosol forms. So, the ruthenium released from the crucible was found on the dipping tube (DT) of the first liquid trap (deposited Ru), in the trapping solution (gaseous and aerosol particles) and on the ultimate filter of the device (assumed to be only aerosol particles). The Ru measurements for these different places (essentially performed with ICP-AES) are detailed in [3]. To determine the Ru amount in gaseous phase and in aerosols particles, liquid trap solutions were centrifuged and filtered at the end of the experiment. The final solution filtered was analyzed by ICP-AES (gaseous RuO_4 dissolved in NaOH) and the filter with aerosol particles was dissolved by alkaline fusion and analyzed by ICP-AES.

Contrary to the tests performed with quartz tube in the first part of the program, the Ru deposit profile along the SS tube could not be measured. This material does not allow dissolving the deposits by alkaline fusion. So, the amount of Ru deposits is determined by the difference

between the Ru amount vaporized from the crucible and the total Ru amount transported at the tube outlet (gas + aerosol particles + Ru deposit on dipping tube of liquid trap).

For each test, the partition of Ru transported during the vaporization and revaporization phases, respectively, is determined. There is no gas / aerosol particle differentiation in this partition as it is carried out from the total Ru data (gas and aerosol particles) transported in the trapping solution (1st liquid trap). The amounts transported in each phase are expressed in percent of the vaporized Ru mass (i.i.). Concerning the revaporization contribution, the percentage transported is also expressed in term of the i.i. and not of the actually revaporizable amount deposited into the tube because it is not possible to determine it with accuracy.

First, the time required for the total consumption of the reagent in the crucible is estimated (vaporization phase duration) with the vaporization kinetics (in mg / min) of the tests carried out and the initial mass of Ru in the crucible. Then, according to the graph "Evolution of the Ru amount in the first trap", the transport kinetics (in µg / min) of the ruthenium transported is established. The duration of the vaporization phase is used in the transport equation to know the Ru amount transported only during this phase.

For the revaporization phase, two cases may occur:

- Either the revaporization is finished before the end of the test, characterized graphically by a stabilization of the Ru amount transported in the liquid trap;

- Or the revaporization is not completed at the end of the test, characterized graphically by an increase in the amount trapped in the liquid trap.

In the first case, the beginning of the stabilization (end of transport of Ru) is determined graphically. The real revaporization duration is the difference between the end of the vaporization phase and the beginning of the stabilization. The Ru amount transported during this phase is the difference between the Ru amount transported at the end of the test and the value determined at the end of the vaporization phase.

In the second case, it is not possible to estimate the duration of the revaporization phase while it is not achieved. The Ru amount transported during the revaporization is estimated in the same way (final amount minus amount at the end of vaporization). The calculated percentage will therefore be a minimum value of the contribution of the revaporization.

This partition is based on the graphical estimation of the Ru (gas and aerosol particles) and the average kinetics. So, a difference could be observed between the sum of the percentages attributed to each phase and the percentage of final transported Ru which considers the gas / aerosol particle partition.

According to the feedback of the previous program, RuO_4 trapped in NaOH 1 M is not stable in time and tends to precipitate as insoluble RuO_2. Thus, the last sample of day 1 is analyzed and then stored at 4°C (temperature like that of the liquid trap 1). This same sample is analyzed again the next day to estimate the "loss" linked to the instability during the night. When the loss is greater than 10% (uncertainty criterion), the values obtained during the ICP analysis are corrected by the percentage previously determined.

RESULTS AND DISCUSSION

The following sections are dedicated to the comparison of the test results according to the studied parameters to evaluate the potential influence of each one. All the results obtained in the START2 test matrix are summarised in **Table 4**.

Ru mass vaporization kinetics

The Ru vaporization rate from the crucible at 1200°C and a flow rate of 1.84 NL/min with quartz and SS tube was determined previously [3]. The values are detailed in **Table 2**. The dry air condition was the most favorable condition for Ru vaporization. The release of Ru from the crucible at 1200°C in a SS tube with 1.84 NL/min flow rate is ranging from 0.8 to 1.5 mg/min. With a higher flow rate at 1200°C, dedicated tests were performed in START2 (**Table 2**). The modification of geometry between the SS and Q tube induced an increase of the kinetics for the SS tube (*factor 1.2*). It is probably due to the reduction of the internal diameter in the hot zone (from 30 to 23 mm [3]) and the height of the crucible containing the Ru powder which was decreased by half (compared to START experiments with a quartz tube) thereby improving the surface air/reagent exchange in the SS tube configuration. It was highlighted that the crucible used in START2 tests had a limiting interface effect on the Ru release behavior, with a maximum value close to 1.8 mg/min compared to 6.1 mg/min with a flow rate of 5 NL/min in VTT-NKS studies [13]. The vaporization kinetics for 85%/15%$_w$ H_2O/Air gaseous mixture with SS tube and 1.84 NL/min was not experimentally determined but was estimated from the average of the quartz tube and 85%/15% mixture condition tests (0.67 x 1.2 = 0.8 mg Ru/min).

Previously [3], it was demonstrated that the release rate of Ru decreases with the oxygen partial pressure. The same tendency is observed with 4.65 NL/min as expected.

Therefore, the durations of vaporization phase estimated from the total Ru consumption of RuO_2 reagent for each test are presented in **Table 3**. The duration estimated for test 5 was 87 min, as test 2. This value is probably slightly over-estimated because the flow rate over the crucible was smaller (1.64 NL/min) than for test 2 (1.84 NL/min). For test 4 with dry air, this duration was estimated to about 50 min, like test 1.

To conclude, the flow rate, the crucible geometry with gaseous flow rate leaching the reagent powder surface or not, and the gaseous composition (O_2 %) are important parameters for the Ru vaporization rate at a given temperature.

Table 2 Experimental values of the Ru vaporization kinetics for different gaseous mixture studied with SS tube.

Gaseous mixture H_2O-Air ($\%_w$)	Average kinetics (mg/min) 1.84 NL/min	Kinetics (mg/min) 4.65 NL/min
0-100	1.50 ± 0.02	/
1-99		1.75 ± 0.02
60-40	0.93 ± 0.02	/
67-33	/	0.90 ± 0.02
85-15	0.80 ± 0.13 (estimated)	/

Table 3 Vaporization kinetics and estimated duration for the total Ru consumption.

Test	Gaseous mixture H_2O-air ($\%_w$)	Kinetics (mg/min)	Initial mass of reagent RuO_2 (mg)	Ru mass vaporized (to express all results as % i.i.)	Duration for the vaporization phase (min)
1	0-100	1.50	104	79	52
2	60-40	0.93	106	81	87
3	85-15	0.80	71	54	67
4	0-100	1.50	104	79	52
5	52-48	0.91	105	79	87
6, 8	1-99	1.75	218, 210	165, 159	~92
7, 9, 10	67-33	0.90	201, 201 221	153, 152, 168	169-186

Total Ruthenium transported in vaporization and revaporization phases

The results are summarized in **Table 4** where the Ru amounts transported at the TGT outlet (gaseous and total with aerosol particle fraction and dipping tube deposits) are presented with

the repartition of Ru coming from vaporization and revaporization phases. All the data are expressed as % of "crucible" vaporized Ru mass. The results of the long tests 1 and 2 (1770 min) have been expressed at the end of the first day of experiment (420 min) to be compared easily with others tests at similar duration.

All the tests performed with SS tube and an abrupt profile conducted to Ru transport at the tube outlet. For tests with the lower flow rate and without NOx feed, the total Ru transported represents from 4% to 8% of "crucible" vaporized Ru mass while it represents about three times more for the higher flow rate (13% to 18.5%). When the revaporization phenomena are not finished at the end of the experiments (tests 3, 7 and 10), the values obtained are minimal values.

Table 4 Results at tube outlet in % of "crucible" vaporized Ru mass (i.i.), for long time duration (tests 1, 2 and 3) and after the first day of experiment (other tests).

Test	Test duration (min)	RuO_4(gaseous) [a] (%)	Ru Total [a] with DT deposit (%)	Ru during Vaporization [b] (%)	Ru during Revaporization [b] (%)
1	1770	6.6	7.9	1.3	4.9
	420	*4.5*	*5.2*	*1.3*	*2.9*
2	1770	3.4	6.2	0.4	3.3
	420	*0.9*	*2.1*	*0.4*	*0.8*
3	1770	3.1	4.3 [c]	0.6	2.5 [c]
4	420	1.0	3.5	1.3	1.6
5	420	1.0	2.9	0.4	0.5
6	390	11.4	18.5	6.5	5.3
7	390	7.7	13.5 [c]	6.4	1.9 [c]
8	390	10.1	13.1	7.0	5.2
9	360	1.85	10.5	2.4	0.7
10	360	5.1	13.6 [c]	2.4	3.0 [c]

[a]: Uncertainties for Ru amount transported at the outlet: ± 0.2% for tests 4 and 5, ± 0.3% for tests 3 and 7, ± 0.4% for test 2, ± 0.7% for test 1, ± 0.8% for test 9, ± 1.3% for tests 6, 7 and 10.

[b]: Gas and aerosol particles in 1st liquid trap without Ru deposit in the DT.

[c]: The revaporization phase was not finished at the end of tests 3, 7 and 10.

Gaseous composition effect

The START2 tests allowed completing information on the effect of gaseous composition with pre-oxidized SS tube and on revaporization process. With a furnace temperature at 1200°C and abrupt profile, a flow rate at 1.84 NL/min, kinetics of Ru transport at the tube outlet were linear and similar for the two phases: vaporization and revaporization in condition mixture with steam (Fig. 4). Kinetics of Ru transport at tube outlet was equal to 2 µg/min and 0.67 µg/min for tests 2 and 3, respectively. For the test with dry air, the kinetics was higher than for the two other tests performed with steam mixtures, equal to 23 µg/min to 90 min (vaporization phase) and 4 µg/min in the range 90-420 min with end of revaporization around 800 min. Revaporization process could take place during the vaporization phase but kinetics of revaporization is lower than kinetics of vaporization. The Ru transport was completed before the end of the test (~1400 min) for 2 tests (0%-100%$_w$ and 60%-40%$_w$) while it was not reached for the 85%-15%$_w$ test (~1800 min).

The mixture H_2O-air composition influences the total Ru amount transported at the TGT outlet. Air content promotes the Ru amount transported at the outlet (Fig. 5, **Table 4**.

In long duration test 2 (60%-40%$_w$), the Ru plateau revaporization was reached with a final gaseous value of 3.4 % i.i., value higher than that observed in previous tests [3] but for shorter duration without plateau.

To conclude, the maximum gaseous Ru amount measured of 6.6% of "crucible" vaporized Ru mass was obtained with dry air condition (including both vaporization and revaporization phases). With steam in large excess in the gaseous mixture (85%-15%$_w$), which are the most representative conditions of a hypothetical severe accident occurring on a PWR, this value was about half (3.1 % i.i.), in the same order of magnitude with (60%-40%$_w$) mixture. A major part of the Ru source term came from the revaporization process on the "long term" (Fig. 5).

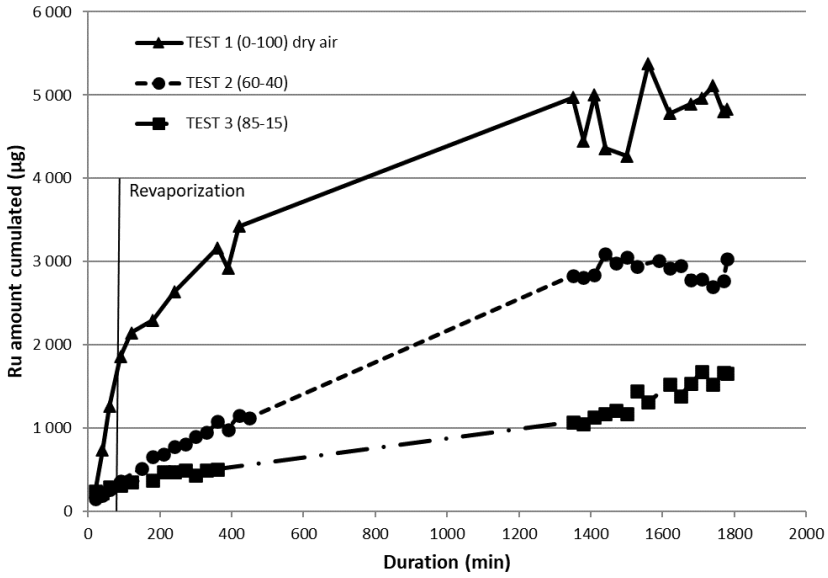


Fig. 4 Evolution of the Ru amount in the first liquid trap as a function of the H_2O-air gaseous mixture

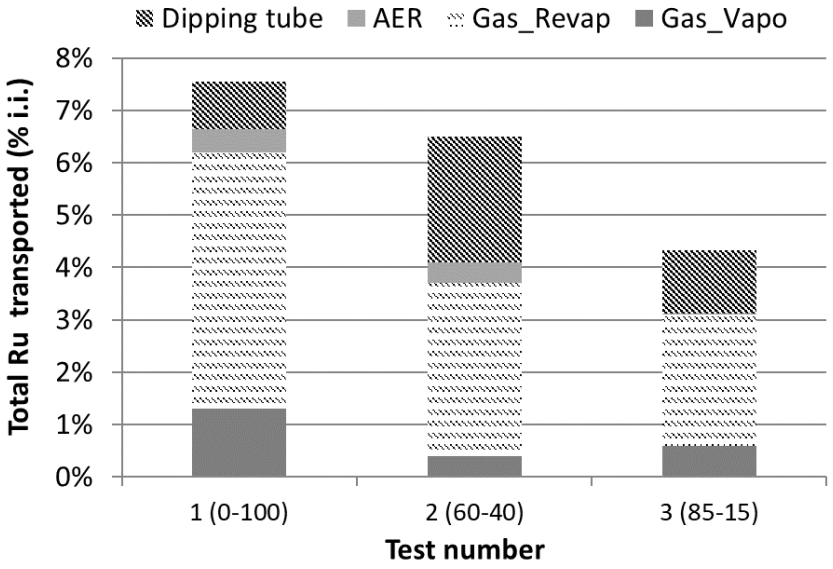


Fig. 5 Ru gaseous partition from vaporization and revaporization, aerosols (AER) and Ru deposited into the Dipping Tube at the end of the tests 1, 2 and 3 (% i.i.) with a pre-oxidized SS tube

Recent NKS (Nordic nuclear safety research) studies on transport of ruthenium in thermal gradient tube had been performed by I. Kajan *et al.* [13] and previously by T. Kärkelä [14]. The experiments were realized with a flow rate of 5 NL/min (TGT internal diameter of 22 mm) and the results obtained are quite different from those of START2 with 1.84 NL/min, with mostly aerosols at the outlet except with NO_2 which favors the gaseous phase. So, we have performed some START2 tests with a higher flow rate to be closer to NKS-VTT condition and allowing a better comparison.

Flow rate effect

Two complementary tests without NO_x (tests 6 and 7) were performed at 1200°C to evaluate the impact of a higher carrier gas flow rate (factor of 2.5) on the Ru transport at the tube outlet (**Table 4**).

With dry air (test 6), kinetics of Ru transported was linear for the two phases with about 117 µg/min for the vaporization phase (0-90 min) and 25 µg/min for the revaporization phase (105-270 min), to reach a plateau (300-420 min). With steam condition (test 7), kinetics of Ru transported was linear for the two phases with about 54 µg/min for the vaporization phase (0-170 min) and 16 µg/min for the revaporization phase (210-390 min). With the two mixture compositions, there is a break of the slope between vaporization and revaporization phases (Fig. 6). The contribution of gaseous Ru amount transported to the outlet is similar during the vaporization and the revaporization process (about 6% i.i.) with dry air. While with steam mixture, the revaporization is significantly decreased (~2%) but the revaporization was not finished at the end of the test.

With a pre-oxidized SS tube, a furnace temperature of 1200°C, an abrupt thermal profile and a flow rate of 4.65 NL/min, most of the vaporized Ru was deposited in the thermal gradient tube (> 80% i.i.) whatever the carrier gas composition. With a steam rich mixture (67%$_w$), after 6h30 of experiment, the total Ru amount (gaseous and aerosol particles) transported to the tube outlet represented up to 13.5% i.i., with 7.7% i.i. under gaseous form (Fig. 7). This value is higher by a factor of about 7 versus the test with 1.84 NL/min on the total transported Ru (1.9% i.i. in test 2 after 6h30) and on the gaseous transported Ru (0.9%). With almost dry air (1% H_2O), the total Ru amount transported to the tube outlet represented up to 18.5% i.i., the major part being in gaseous form (11.4% i.i. without DT deposits). This value is higher by a factor of 2.5 versus the test with 1.84 NL/min on the gaseous transported Ru (4.5% i.i. in test 1 after 7h). The steam condition decreased the total Ru transported at the outlet, similarly to the results observed with the lower flow rate (Fig. 5).

With the higher flow rate, the fluid temperature at the exit flange was hotter (+ 70°C for test 7) and the Ru deposit in the DT was more important (x10) because of a stronger thermal gradient in the pipe of the first liquid trap.

The main conclusion is that there is a positive impact of the flow rate increase on the total Ru amount transported at the outlet, principally on the gaseous form (Fig. 7). Nevertheless, the revaporization phase was less efficient and shorter, leading to smaller formation of gaseous ruthenium on the long term.

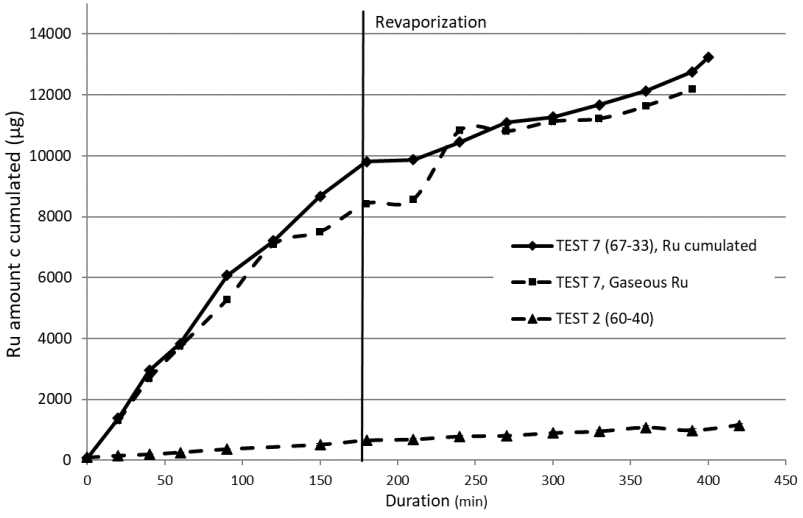


Fig. 6 Evolution of the gaseous Ru (dotted line) and the raw Ru mass in the first liquid trap of test 7, under (67%-33%) H_2O-air mixture and a higher flow rate (4.65 NL/min) and of test 2 under (60%-40%) H_2O-air mixture

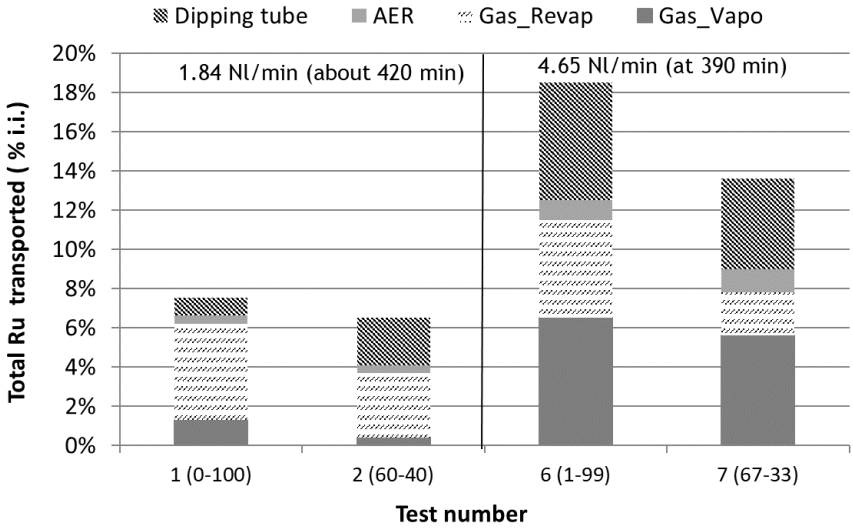


Fig. 7 Ru gas, Ru aerosol particles AER (from first liquid trap and filter) and Ru deposits in the dipping tube at about 420 min (% i.i.). The Ru transport was not finished at the end of test 7

NO_x potential effect

The START2 tests performed with a NO_x (NO_2 or N_2O) feed allowed completing information on the potential impact of more-oxidizing conditions, like those induced by air radiolysis products.

In our test conditions with 1.84 NL/min, the addition of NO_2 (50 ppm) in the carrier gas has a weak effect on the Ru transport at the tube outlet whatever the gaseous composition (dry air or steam in excess in air), as shown in Fig. 8. In presence of NO_2, there is no significant break of the slope between vaporization and revaporization phases with a similar Ru transport kinetics (~20 µg/min with dry air and ~2 µg/min with steam, tests 4 and 5 respectively), but the revaporization phase was less efficient and shorter, leading to smaller formation of volatile ruthenium. It can be due to $RuO_3(g)$ oxidation by NO_2 ($RuO_3(g) + NO_2 \leftrightarrows RuO_4(g) + NO$ with $\Delta G_R°(1000°C) < 0$), leading to less Ru deposits at high temperature. The results obtained with the NO_2 feed at the furnace exit allow deducing that there is no NO_2 effect on the Ru deposits at temperature below 900°C in agreement with the thermodynamic view: $RuO_2(s) + 2\ NO_2 \leftrightarrows RuO_4(g) + 2\ NO$ with $\Delta G_R° > 0$ for T < 1000 °C. With dry air (test 4), after 1h of experiment, there was an evolution of the gaseous/aerosol partition with an increase of Ru aerosols amount. At the end of the test, and for the first time in the START program, some black deposits were observed on the glass wall of the first liquid trap (estimated at 0.9% i.i.). This observation agrees well with Igarashi's H. study [8] where the authors concluded that "NO or NO_2 can react with RuO_4 to form nitro complex of nitrosyl ruthenium $Ru(NO)(NO_2)_2(OH).2H_2O$ which was more soluble into water and less volatile" and "This transformation was proved by the black deposits in the glass tube". In the same way, Klein et al. [15] observed that "the gas phase reaction of RuO_4 and nitrogen oxides formed fewer volatile compounds of Ru".

With a flow rate of 4.65 NL/min, a steam rich H_2O/air mixture more representative of severe accident with oxidizing condition (67/33 $\%_w$ H_2O/air mixture, test 9), most of the vaporized Ru was deposited in the thermal gradient tube (> 80% of "crucible" vaporized Ru mass, i.i.) as observed without nitrogen dioxide. At the end of the experiment, the total Ru

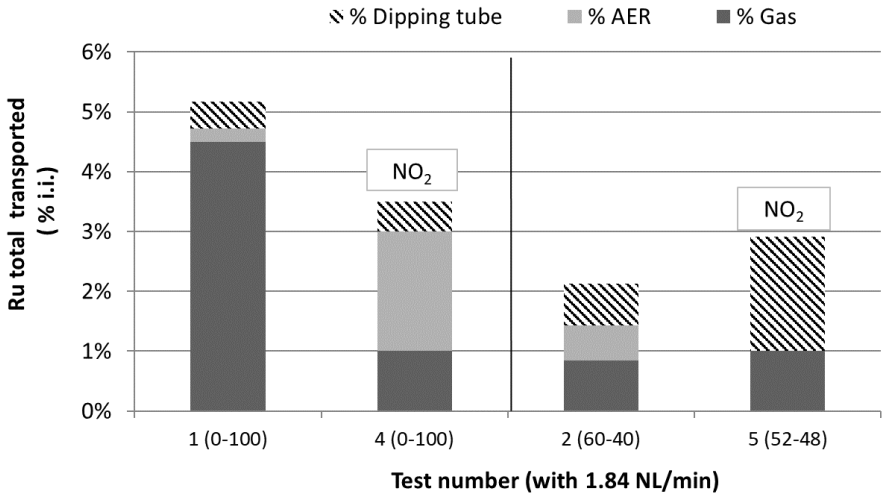
amount (gaseous and aerosols) transported to the tube outlet with NO_2 feed represented up to 10.5% i.i., in the same order of magnitude than in the reference test without NO_2 (13.5% i.i., test 7). But the gaseous fraction of volatile ruthenium was significantly lower, 1.8% with NO_2 versus 7.7% without NO_2 (Fig. 8). Kinetics of Ru transport was linear for the two phases with about 21 µg/min for the vaporization phase (0-170 min) and 2.5 µg/min for the revaporization phase (210-360 min). Contrary to test 7, the Ru transport was finished at the end of the test 9. So, with NO_2 feed, the Ru transport kinetics are really lower for vaporization and revaporization phases. With almost dry air (1%$_w$ H_2O, test 8), no impact of NO_2 feed (50 ppm) was observed on the gaseous Ru amount transported at the tube outlet (about 10% ii) and on the RuO_4/RuO_2 partition, similar to the results obtained with the lower flow rate (1.84 NL/min). Kinetics of Ru transport during the vaporization phase (111 µg/min) is similar to the one observed in test 6 (117 µg/min). No effect of NO_2 was observed on the revaporization. Similar to test 6, the contribution of gaseous Ru amount transported to the outlet is similar during the vaporization (6-7 % i.i.) and the revaporization process (5 % i.i.).

With steam in excess and the higher flow rate, the total Ru amount (gaseous and aerosols) transported to the tube outlet with N_2O feed represents a maximum value of 13.6% i.i. (test 10), similar to the reference test 7 without NO_2 (13.5% i.i.). But the revaporization phase was not finished at the end of these two tests. Kinetics of Ru transport was linear for the two phases with about 23 µg/min for the vaporization phase (0-170 min) and revaporization phase (210-390 min). This trend is different than in test 7 with respectively 54 µg/min and 16 µg/min. Finally, the contribution of gaseous Ru amount transported to the outlet is similar during the vaporization (2.4 % i.i.) and the revaporization process (3 % i.i.). So, concerning the N_2O feed (test 10), no noticeable effect was observed on the total Ru amount transported at the tube outlet similarly to [12] even if the partition gas/aerosol is a bit different. The gaseous Ru amount was lower, but the Ru deposited into the dipping tube was higher.

Without considering the Ru deposits into the dipping tube of the first liquid trap, the Ru amount transported at the outlet under gaseous form tends to decrease with NO_x feed and steam mixture condition.

To conclude, with a pre-oxidized SS tube, a flow rate of 4.65 NL/min, a furnace temperature at 1200 °C, abrupt thermal profile, and a fluid TGT exit temperature at about 410 °C, the addition of NO_2 or N_2O tends to slightly decrease the gaseous Ru transport at the tube outlet whatever the carrier gas composition (dry air or steam in excess in air).

a/



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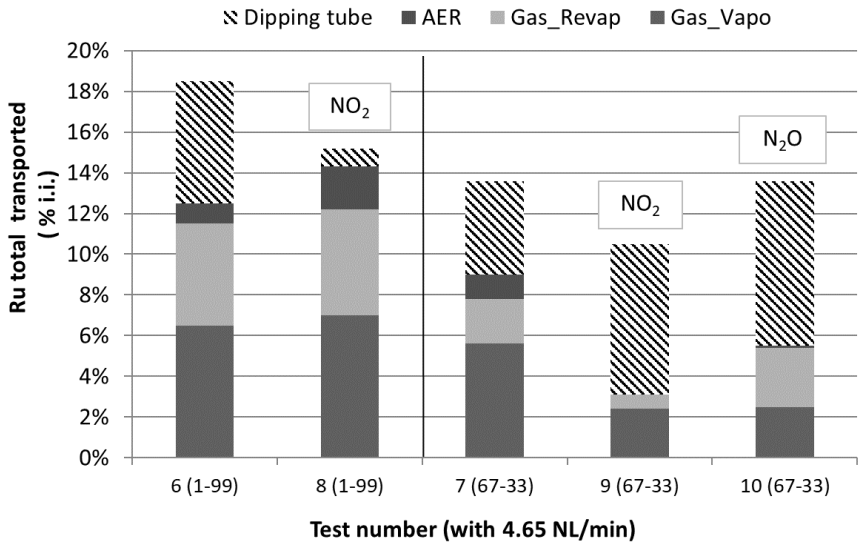


Fig. 8 : Ru gas, aerosols, and deposits in the dipping tube (% i.i.) at 420 min with 1.84 NL/min (a) and at 390 min with 4.65 NL/min (b). The Ru transport was not finished for tests 1, 2, 7 and 10

For revaporization phase, it has been shown [3] that only Ru high temperature deposits (> 900°C) are concerned, temperature where NO_2 was not thermally stable and thus cannot affect revaporization process.

Discussion

a/ Thermal stability of NO_2

We have studied the thermal stability of NO/NO_2, with measurements of NO_x at the exit tube with NO_x feed at the entry or exit of furnace.

The measurements of NO_x/NO at the outlet tube in our thermal-hydraulic conditions (pre-oxidized SS tube, dry air and 4.65 NL/min) led to a thermal decomposition of NO_2 and N_2O gas, estimated taken place near 400 °C and 1010 °C, respectively. With NO_2 feed (50 ± 5 ppm).,

only NO was measured at the exit (46 ppm) with 800 °C or 500 °C all along the tube. When the furnace temperature decreased to 370 °C, 55 ppm of NO_2 was measured again at the exit. The measurements of NO_2 with SS tube before and after the pre-oxidation of the tube (tube without Ru deposits), and with a quartz tube, showed that there was no effect of the surface state. So, the thermal decomposition of NO_2 in our conditions was estimated beyond 400 °C, in accordance with thermodynamic data. N_2O was irreversibly decomposed ($N_2O \rightarrow N_2 + ½\ O_2$), no N_2O and no NO were measured at the outlet tube with furnace at 1200 °C and abrupt profile. This result agrees with literature [16]. Even if N_2O could exist at high temperature due to kinetic limitations, it has been shown from ab-initio calculations [17, 18] that the kinetics of the reactions between ruthenium oxides and nitrogen oxides are low.

Thermodynamic equilibrium calculations with a steam/air mixture and 50 ppm of NO_2 show that beyond 400/500°C NO is preponderant with respect to NO_2 which is partially decomposed as reported in Fig. 9. Even if NO_2 is not stable at elevated temperatures, it could be continuously formed by air radiolysis induced by the radiation from the fuel or from fission products deposited onto the RCS walls and thus exist resulting from competitive processes between formation and destruction pathways according to some kinetic effects. So, it was decided to inject NO_2 into the START tube at the furnace exit (tests 4 and 5), near 900°C (corresponding to the Ru deposit zone at high temperature), to limit the decomposition of NO_2 in the furnace zone at 1200°C.

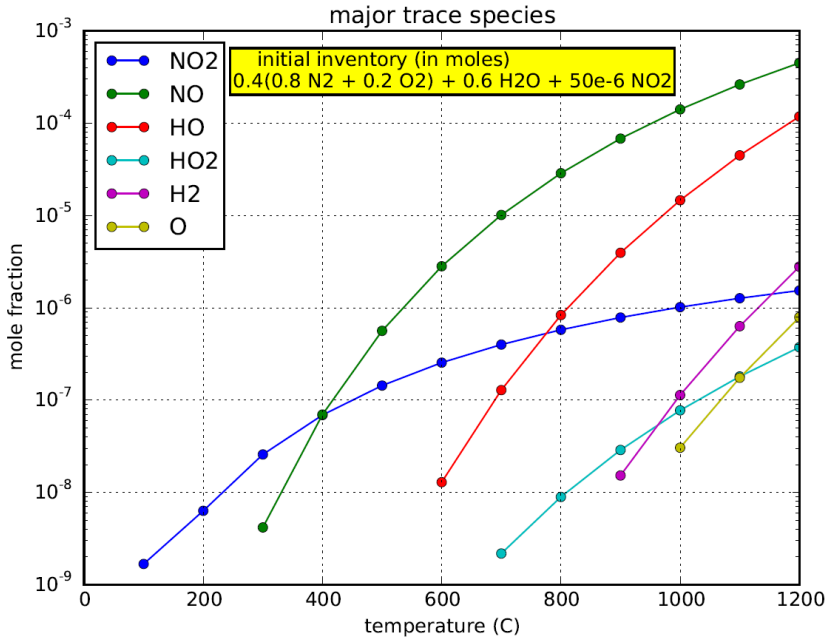


Fig. 9. Thermodynamic calculation with NO_2

So, with a furnace temperature at 1200°C, an abrupt profile, and a fluid temperature at the exit flange near 400°C, it seems that NO_2 and N_2O could not reach the crucible zone with Ru and NO_2 could not be formed again in the part of the tube near the exit flange to react with RuO_x gaseous form or the small amount of Ru deposits, respectively. Effectively, in START2 tests performed with a pre-oxidized SS tube, no noticeable increase of the gaseous Ru amount

transported at the outlet was observed with NO_x feed (50 ppm) whatever the total flow rate and the gaseous composition (low or excess of steam amount), **Table 4**.

b/ Consistency with NKS-VTT results

This paragraph details the characteristics of the two experimental set ups (VTT and START2), as reported in Table 5. VTT's facility is schematically described in [13].

Table 5 Parameters for the two devices.

Device	VTT	START2 (test 9)
Tube geometry:		
Length from crucible to exit	130 cm	70 cm
Internal diameter	22 mm	32.7 mm (23 mm in the furnace)
Material tube	Alumina + pure SS (316L) (not pre-oxidized)	Inconel 600 + pre-oxidized SS 316L
Alumina Crucible	20 x 2 cm	8 x 0.8 cm
Reagent mass (RuO_2)	1 g (or 2 g)	200 mg
Furnace temp.(°C), profile	1227 °C, abrupt	1200 °C, abrupt
Temperature at the exit	~40 °C (inner)	~410 °C (fluid)
Flow rate (NL/min)	5 (2.5 + 2.5)	4.65 (4.15 + 0.5) « laminar flow »
NO_2 feed	Injected to the furnace using an inner tube (through the entry flange), which opening was downstream the crucible location inside the furnace	Injected by the entry flange
H_2O-air mixture	$2.1x10^4$ ppmV H_2O (2%mol H_2O)	67%$_w$ H_2O -33%$_w$ air (77%mol H_2O)
Test duration (min)	20 min with NOx, such as NO_2 60 min for other tests	390
Experimental protocol	Oxidative gas injection when 1227 °C was reached (T0)	Oxidative injection after 1h at 1200 °C (T0+1h) with a low argon flow before (5h)

Filter position	before liquid traps (Mitex® 5µm PTFE)	after liquid traps (quartz paper 0.3µm)

The results of the main tests (gaseous and aerosol particle partitioning) are presented in Fig. 10.

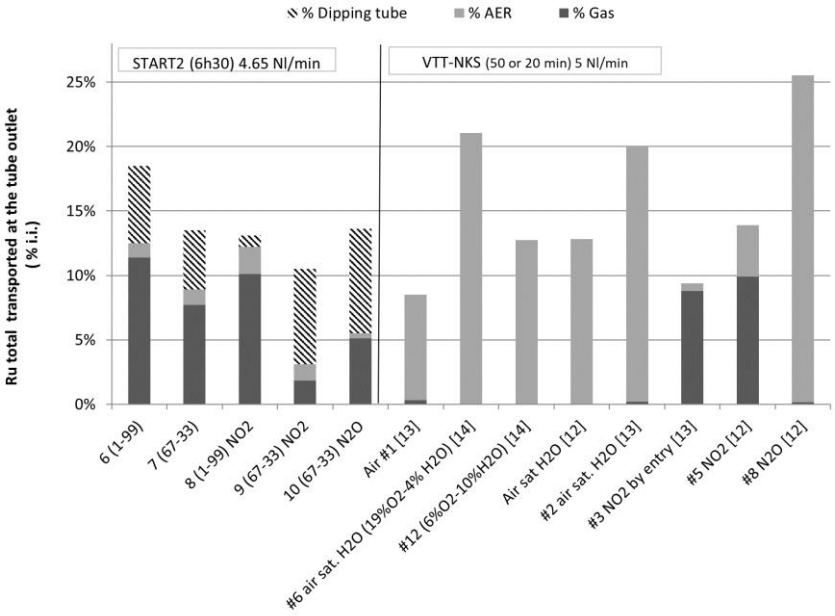
NKS (Nordic nuclear safety research) study on transport of ruthenium in the primary circuit [13] concluded that humidity (saturated at room temperature) significantly increased the Ru transport through the facility, mainly in the form of RuO_2 aerosol (19.8% of Ru released) compared to dry air condition (8.2%). This trend was not observed with our results, with principally gaseous phase without particles at the outlet, with the different thermal-hydraulic conditions from those in VTT facility.

If we focus on gas composition effect, Test 7 and VTT test #12 [14] are quite similar in term of O_2 content (67%H_2O-7%O_2 and 10%H_2O-6%O_2, respectively). If we compared the total Ru amount transported at the outlet, the results are similar (~13% i.i.). The main difference is the Ru composition at the TGT outlet with a mix between aerosol and gaseous forms for IRSN, whereas the aerosol form was largely dominant in the VTT test. The formation of aerosols can be promoted by a strongest gradient tube in VTT conditions.

Test 6 can be compared with VTT test #6 [14] and Kajan test #2 [13], these tests being performed with a very large proportion of air. The VTT and Kajan's results concerning total Ru amount transported at the outlet (~20% i.i.) are close to our test 6 result, see **Table 4**. As for IRSN test 7 with steam, the main difference comes from the nature of the species transported, mainly in aerosols form at the opposite of IRSN result, it is consistent with that VTT facility seems to promote nucleation processes (higher source of Ru and lower outlet temperature).

I. Kajan *et al.* [12] observed a decrease of the formation and transport of particles significantly when NO_2 gas (75 ppm) was fed. At the same time, the transport of gaseous ruthenium increases by about two orders of magnitude (8.8% of Ru released, test #3) compared to pure air experiment (0.2%, test #2) and total Ru amount transported at the outlet remains similar. This trend was not observed with START2 conditions; the major species transported being in gaseous form.

With N_2O feed, the results obtained with the two studies (IRSN test 10 and test #8 [12], Fig. 10) showed the same tendency, with no influence on the Ru transport at the outlet. This result agrees with the irreversible decomposition temperature estimated near 1000°C. By the way even if some N_2O persists due to some kinetic limitations, the kinetics of ($RuO_3 + N_2O \rightarrow RuO_4 + N_2$) is very low as shown by Miradji *et al.* [18] with an Arrhenius energy computed at 106 kJ/mol.



552

553 Fig. 10 : Ru amount partition (Gas, Aerosol particles and Ru deposit into the Dipping Tube of the first
554 liquid trap) in START2 (vaporization and revaporization) and VTT-NKS studies [12-14] with the higher
555 flow rate

556

557 NO_2 influence differs between VTT and IRSN results. In a first approach, it was supposed
558 that it could be due to the different flow rates, but the START complementary tests performed
559 with 4.65 NL/min (tests 8 to 10) do not confirm this assumption even if there is a slight
560 difference in inner diameter. The residence times are quite close in VTT and IRSN studies (4s
561 and 2s respectively). Main differences result from the tube geometry, the Ru source mass
562 flowrate, the gradient profile with the temperature at the exit flange and the tube materials.

563 Firstly, the ratio S/V of VTT set-up (182) is higher than the IRSN's one (Table **5**), favoring
564 the decomposition of gaseous Ru into aerosols by a process occurring on the SS surface, the
565 first stage being adsorption of RuO_3 and/or RuO_4 on surface before being reduced into RuO_2.

566 Concerning the Ru vaporization rate from the crucible, in VTT-NKS studies [12-14], at
567 1227 °C with a low amount of steam and a flow rate of 5 NL/min, a Ru vaporization rate of
568 6.4 mg/min was obtained. With a decrease of the flow rate to 2.5 NL/min and the same gaseous
569 composition [12], the vaporization rate was of 3.2 mg/min. In START tests [3], it was
570 demonstrated that the Ru vaporization rate, due to a much smaller interface area of the RuO_2
571 crucible, is lower, close to 1.8 mg Ru/min. Higher Ru vaporization rate may favor the Ru
572 aerosol formation in the tube.

573 The tube in VTT device was longer with an exit temperature lower than in START2. The
574 fluid temperature at the outlet tube (location of gaseous and particles samples) is sampling at
575 40 °C for VTT (tube exit) and at 410 °C for IRSN with a thermal gradient into the dipping tube
576 of the first liquid trap cooled. This point influences the Ru speciation (gas/particle partition and
577 deposition). IRSN sampling at 410° C (tube exit) can be favorable to a higher gaseous fraction
578 in the sample (RuO_4 and RuO_3) and favor the deposits in DT (RuO_2).

The reactivity at the surfaces could also influence the formation and transport of Ru aerosols. It is worth noticing that the nature of the tube may change the results on account of the reactions at the tube surface with pre-oxidized SS versus quartz. The Ru aerosols formation and transport only exists with SS tube compared with quartz material in START experiments [3]. In VTT the TGT is first an alumina tube in the high temperature furnace zone (1200° to about 650°C) and next a pure SS tube (650°C to the exit of the tube) without pre-oxidized treatment. Authors observed that the transport of RuO4(g) was promoted by alumina tube rather SS tube. So, the pre-oxidized treatment of SS tube has been done during the test with short duration (< 60 min).

The experiments are consistent on the global Ru amount transported at the TGT outlet but with a different gaseous and aerosol partition. In VTT tests, gaseous RuO_3-RuO_4 may form RuO_2 particles between 410 °C and 40 °C as RuO_2 is much more thermochemically stable than RuO_3.

About the NO_2 influence, in VTT experiments, NO_2 was fed at 1227 °C and it resulted in the decomposition of NO_2 to NO and O allowing possible oxidation of RuO_3 to RuO_4. Another assumption is that NO_2 enhance RuO_4 existence at low temperatures, below 410 °C, preventing RuO_3 decomposition into RuO_2. In our test conditions (sampling at 410°C), the influence of NO_2 was not observed.

To get further, VTT and IRSN decided to make an experimental benchmark (Kärkelä T., OECD/NEA STEM2 Joint Project Meeting, personal communication, 2018, 27th June, Boulogne-Billancourt France) with quite common conditions: a flow rate of 2.2 NL/min and duration of 5h, changing of soda liquid traps every 30 to 70 minutes (7 samplings), NO_2 feed of 50 ppm in air saturated with water (20°C), a RuO_2 source of 200 mg with a crucible heated at 1227 °C (area: 8 cm x 2 cm). The main difference is the thermal gradient with the outlet temperature much higher in IRSN device. Aerosol on-line measurements were performed with combination of a differential mobility analyzer (DMA, particle size: 2 nm to 1 µm) and a condensation particle counter (CPC, particles number) [12]. With a Ru vaporization rate estimated at (3.0 ± 0.4) mg/min, the duration to consume all the reagent was about 55 min. The Ru amount transported at the outlet at 40 °C (Fig. 11) was 3.8% i.i RuO_4(g), very similar to the IRSN test 4 results (~3.5% i.i. at 150 min with outlet at 240 °C). Both results are consistent. No aerosols were transported to the filter after 60 minutes of sampling (confirmed by on-line measurements), contrary to previous experiments with 5 l/min (1.8 - 2.6 mg Ru metal). Possibly NO_2 oxidized all RuO_3 into RuO_4. Therefore, RuO_2 formation was decreased. Some black deposits inside the dipping tube of the soda trap were also observed as in START tests. As VTT results are similar to START2 one (test 4), we can conclude that with « lower » flow rate (~2 l/min) no noticeable effect of NO_2 on RuO_4 transport at the outlet tube was observed whatever the experimental device used. It can tend to suspect high influence of Ru flow inlet on nucleation processes.

The measurement bias observed in START2, resulting from reactivity between dissolved Ru and NO_2 in alkaline soda solution (evolution of the gaseous/aerosol partition in the first trapping solution during the test and some black deposits on the glass wall observed at the end of the test), was not observed in VTT test with the changing of liquid traps each 30 min. The NO_2 dissolved in alkaline solution forms nitrite and nitrate ions which may later react to form some ruthenium nitrosyl complexes with a certain kinetics. This observation confirms that there

was a formation of chemical reaction products in the first liquid trap in IRSN test 4 (perhaps, nitrosyl ruthenium complex).

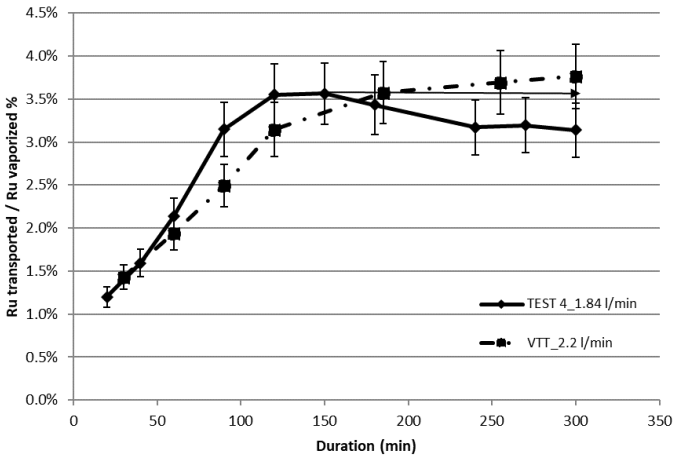


Fig. 11 Evolution of the Ru amount in the first liquid trap during the VTT and START2 tests

CONCLUSIONS

START2 experiments have investigated the ruthenium behavior along the RCS with oxidative conditions. This point was identified as a main source of uncertainties to better evaluate ruthenium source term. During a 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 considered to calculate the ruthenium source terms as it is the most impacting due to delayed releases.

For reminder, the STEM project has shown that the Ru amount transported, under a gaseous form, up to the tube outlet can reach about 4% of initial inventory. The Ru releases come from about a similar contribution of the direct vaporization phase from the crucible (direct phase) complemented by a revaporization phase from the Ru deposits (delayed releases). This 4% cannot be considered as a conservative value because nuclear accident conditions are much more complex than our test conditions and revaporization phase was not achieved.

The START2 ruthenium results allowed gaining knowledge on the key parameters impacting the transport kinetics, the partition between gaseous and aerosols at the outlet of the TGT and the extent of the revaporization process of deposited species. The experiments were performed at 1200°C, with an abrupt profile and a pre-oxidized Stainless-Steel tube to be more representative. The impact of the steam amount in carrier gas, the flow rate and NO_2/N_2O feed (50 ppm) was studied.

The experimental data on Ru transport in the RCS support these conclusions:

- The long duration tests (7 hours) have evidenced the existence of transient phenomena during the first hour (vaporisation phase), confirming the necessity to study the ruthenium chemistry for several hours to catch the precise phenomenology.

- The Ru vaporization kinetics from the crucible (anhydrous RuO_2) in the furnace at 1200°C was characterized, with a good reproducibility, for different carrier gas mixtures (H_2O/air) and was linearly steam mixture dependent. The dry air condition was the most favorable condition for Ru vaporization. At a given temperature, Ru vaporization rate from the crucible depended on the crucible geometry, the flow rate and the gaseous composition of carrier gas (O_2 %).
- Whatever the gaseous composition (mixture of H_2O/air), most of the vaporized Ru was deposited in the transport tube (> 80% of the released initial inventory i.i.).
- The higher the air amount in the carrier gas is, the higher the total Ru amount transported at the outlet is, whatever the flow rate tested.
- For the tests performed with steam/air mixture and a flow rate of 1.84 NL/min during 7h, the Ru gaseous fraction at the outlet remains below to 3-4 % of the Ru mass vaporized (i.i.) whatever the steam fraction (with Ru vaporization rate lower than 1.5 mg/min).
- The effect of flow rate is important: with a flow rate of 4.65 NL/min (factor x 2.5 compared to "standard" conditions of 1.84 NL/min), Ru gaseous fraction at the outlet increased but remained below to 10% i.i. with excess of steam (SA condition).
- The Ru gaseous fraction comes from a direct transport (vaporization) and longer revaporization from the Ru deposits (for T > 900 °C). With a higher flow rate, the revaporization phase is less efficient and shorter, due to lower deposit build-up in the TGT tube during the vaporization phase, leading to smaller formation of gaseous ruthenium on the long term.
- Nitrogen oxides (NO_2 or N_2O feed, 50 ppm) do not increase the outlet gaseous Ru fraction with our thermal-hydraulic conditions (T > 400°C). Indeed, $NO/NO_2/N_2O$ measurements at the outlet have shown a total decomposition of NOx with a furnace temperature at 1200°C and a flow rate lower than 5 Nl/min.
- The Ru gaseous fraction at the tube outlet (~410 °C with 4.65 NL/min and ~290 °C with 1.84 NL/min) could be part of RuO_3 (consistent with remobilization of high temperature deposits and thermal decomposition of RuO_4) which may be converted into RuO_4, sampling at lower temperature in liquid traps.

At the end of this experimental study on Ru transport, some recommendations for Source Term applications can be suggested:

i) There is a good representativeness of START device concerning the gas composition ($RuO_{3(g)}$ and $RuO_{4(g)}$ species) and surface effects (pre-oxidized SS). But, the higher surface/volume ratio in START device favors the surface effect (Ru deposits amount). So, that trend tends to increase the gaseous fraction in the Pressurised Water Reactor case. In return, the presence of aerosols inside the RCS tends to decrease the gaseous fraction at the tube outlet due to sites of heterogeneous nucleation. Data obtained are consistent with the transport of gaseous RuO_3.

ii) If we attribute the persistence of gaseous ruthenium during the direct phase to persistence of $RuO_{3(g)}$, the increase of flow rate decreased the decomposition extent due to kinetic limitation. For future models, it should be needed to consider a kinetic

of decomposition of $RuO_{3(g)}$ into RuO_2 in bulk phase and, also on steel oxidized surface. So, severe accident modelling should consider kinetics concerning the conversion of RuO_3 into RuO_4 and non-congruent condensation processes.

START experimental data allow a better understanding of Ru transport inside the RCS with oxidizing conditions. They also provide guidelines to develop/validate the models and constitute a validation database for SA modelling. These experimental results are used to improve the models currently implemented in the ASTEC IRSN software package (Accident Source Term Evaluation Code) [19] and to reassess ruthenium source term in considering potential gaseous ruthenium outside releases because current Ru ST only consider aerosol releases. Depending on the level of confidence of the models of Ru behaviour in SA simulations software for air-ingress scenarios, these reassessments will be performed either on modelling simulations or based on quite reasonable conservatism approaches. The last step should be to update PSA2 studies and according to potential radiological consequences try to define mitigate means for the involved category of severe accident.

Acknowledgments

The authors acknowledge the OECD/NEA/CSNI hosting the STEM2 project and the STEM project partners: Electricité De France, Canadian National Laboratories (Canada), VTT Technical Research Centre of Finland Ltd (Finland), Nuclear Research Institute (Czech Republic), Gesellschaft für Anlagen - und Reaktorsicherheit (Germany), Korea Atomic Energy Research Institute, Korea Institute for Nuclear Safety, Nuclear Regulatory Commission (USA), Swedish Radiation Safety Authority, National Nuclear Laboratory (England), Japan Atomic Energy Agency and Nuclear Regulation Authority (Japan).

The authors also thank the CNRS Villeurbanne (CREALINS) for the measurements of Ru deposit with the alkaline fusion method (L. Ayouni), K. Boucault, C. Gomez and S. Souvi from IRSN for their technical contribution and fruitful discussion.

Conflict of interest statement

- The authors have no relevant financial or non-financial interests to disclose.
- The authors have no competing interests to declare that are relevant to the content of this article.
- All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.
- The authors have no financial or proprietary interests in any material discussed in this article.

List of abbreviations

Abbreviation	Definition
SA	Severe accident
NPP	Nuclear power plant
STEM	Source Term Evaluation and Mitigation
START	Study of the TrAnsport of RuThenium in the primary circuit
RCS	Reactor cooling system
PWR	Pressurized water reactor
TGT	Thermal gradient tube
SS	Stainless steel
DT	Dipping tube
DMA	Differential mobility analyzer
CPC	Condensation particle counter
ASTEC	Accident Source Term Evaluation Code

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