



Nordic Collaboration: Impact of Ag and NO_x Compounds on the Transport of Ruthenium in the Primary Circuit of NPP in a Severe Accident

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ABSTRACT

When ruthenium is released from the fuel as ruthenium oxides to the environment in a severe NPP accident, ruthenium isotopes ¹⁰³Ru and ¹⁰⁶Ru cause a radiotoxic risk to the population both in a short and long term. As the previous international studies on the transport of ruthenium in the reactor coolant system (RCS) have mainly been conducted in pure air-steam atmospheres, the current study was dedicated to air ingress conditions with representative airborne air radiolysis (NO_x) and control rod (Ag) species which were mixed with vaporized Ru oxides. The aim was to study the impact of these additives on the transport of ruthenium as gas and particles through the primary circuit of nuclear power plant in a severe accident. As a main outcome, the transport of gaseous ruthenium through the facility increased significantly when the oxidizing NO₂ gas was fed into the atmosphere.

1 INTRODUCTION

During the operation of a nuclear power plant (NPP), a significant amount of ruthenium is built up in the fuel as a product of the nuclear fission. The importance of ruthenium from the radiological point of view is mainly due to the isotopes ¹⁰³Ru and ¹⁰⁶Ru with half-lives of 39.35 days and 373.5 days, respectively. When ruthenium is released from the fuel to the environment in a severe NPP accident, these ruthenium isotopes cause a radiotoxic risk to the population both in a short and long term by building-up in the human body and by external exposure to the radiation, thus possibly leading to development of cancer.

Ruthenium forms several volatile oxides depending on the reaction temperature. Based on the thermodynamic equilibrium calculations, the dominating gaseous species of ruthenium in an air atmosphere at temperatures higher than 1000 °C are RuO₃ in excess to RuO₄ [1]. As the temperature decreases below 700 °C, RuO₃ decomposes rapidly to the solid RuO₂ (e.g. to RuO₂ aerosol in the gas phase) [1, 2]. However, RuO₄ is still volatile at temperatures above 7

°C [3] and it is the only volatile ruthenium oxide relatively stable at low temperature conditions.

The transport of ruthenium through a reactor coolant system, after being released from the fuel, has been investigated in several experimental programmes recently. The VTT Ru transport programme [4] has shown that the release of Ru from RuO₂ powder was dependent on the oxygen partial pressure in air-steam atmospheres at 827, 1027, 1227 and 1427 °C. The highest fraction of gaseous RuO₄ at the outlet of the model primary circuit was observed at 1027 °C oxidation temperature. At higher temperatures, ruthenium was transported mainly as RuO₂ aerosol. In the experiments of the RUSSET programme [5] it was observed that the presence of other fission products (FPs), e.g. BaO and CeO₂, as mixed with the metallic Ru precursor when the sample was oxidized at 1100 °C, decreased the fraction of gaseous RuO₄ in the outlet air over the stainless steel surface compared to the pure Ru oxidation. It was also shown that the transport of RuO₄ was dependent on the surface material in the coolant circuit. In both VTT and RUSSET programmes it was noticed, that the partial pressure of RuO₄ reaching the outlet of model primary circuit was in the range of 10⁻⁷ to 10⁻⁶ bar, which is significantly higher than what is expected based on thermodynamic equilibrium calculations.

The previous international studies have mainly been conducted in pure air-steam atmospheres [6], especially the separate effect studies, and thus in relatively simple conditions when considering a severe NPP accident. The gathered experimental data was needed in order to derive and validate the computer models on Ru transport. However, the transport of ruthenium through the primary circuit into the containment atmosphere can be affected by the fission product, control rod, air radiolysis etc. compounds present in the primary circuit. Aerosols originating from the fuel decomposition are likely to end up into the primary circuit in a severe accident. The high radiation field induced by fission and activation products in the fuel will change the composition of the atmosphere. The radiolysis of air results in the formation of different oxidizing and reducing species. Therefore, this study was dedicated to air ingress conditions with representative airborne fission product (CsI), control rod (Ag) and air radiolysis (NO_x) species which were mixed with the vaporized Ru oxides. The aim was to study the impact of these additives on the transport of ruthenium as gas and particles through the primary circuit of nuclear power plant in a severe accident. Another aim was to have a first glimpse into the ruthenium chemistry in more realistic conditions considering a severe accident. The work was performed as a Nordic collaboration between VTT Technical Research Centre of Finland Ltd (Finland), Chalmers University of Technology (Sweden), Aalto University (Finland) and FOI Swedish Defence Research Agency (Sweden). The first results of this collaboration are presented in this paper (based on the reference [7]) and the more advanced experiments are also shortly discussed. The detailed description of the whole study is given in [7, 8, 9]. The background of this study is given in [11, 4, 6].

2 EXPERIMENTAL

2.1 Experimental Facility

The basic set-up of VTT's ruthenium transport facility is schematically described in Figure 1. The set-up was slightly modified in some of these new experiments when compared to the previous experiments [1],[4] using pure Ru oxides. Also some additional online measurement devices were applied, see below. The main component of the facility was the horizontal, tubular flow furnace (Entech, ETF20/18-II-L), which was used to heat the anhydrous RuO₂ powder (purity 99.95 %, Alfa Aesar). The furnace was 110 cm long and it

had two heating sections, each 40 cm long. These zones were separated by a 38 mm layer of insulation. At both ends of the furnace, there was 131 mm of thermal insulation.

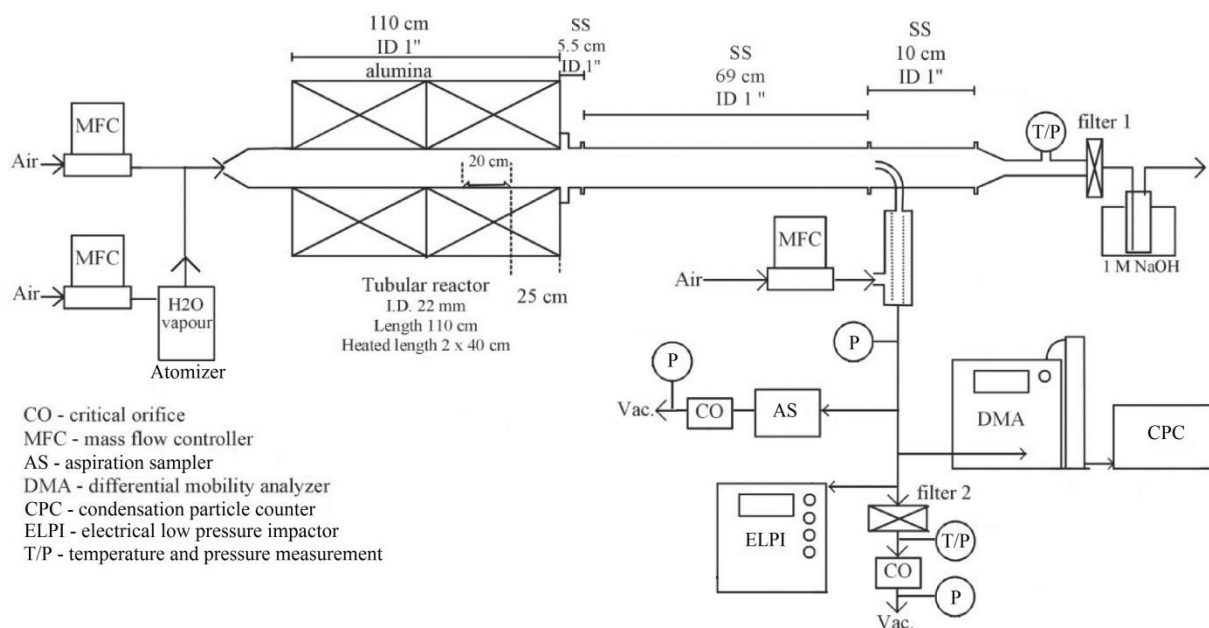


Figure 1: VTT's experimental facility for ruthenium tests.

The furnace tube was made of high purity alumina (Al_2O_3 , 99.7 %) and its inner diameter was 22 mm. The alumina crucible with the RuO_2 powder (mass ca. 1 g) was placed over the second heated zone of the furnace, 25 cm from the outlet. The RuO_2 powder was heated to 1227 °C (1500 K) in an oxidizing flow and the formation of gaseous ruthenium oxides took place.

The total flow rate through the facility was 5 l/min (NTP; NTP conditions 0 °C, 101325 Pa). The gas flow was composed of air or a mixture of O_2 , N_2 and NO_2 gases. The seed particles were generated with an atomizer (TSI 3076) from a solution of ultrapure water (Milli-Q, resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ at 25 °C) and the precursor material. A carrier gas flow through the atomizer transported the produced droplets via the heated line (120 °C) into the inlet of the furnace. Water evaporated when the droplets were heated and the formation of solid particles took place. It also led to an increase in the steam concentration within the furnace. The steam concentration depended on the flow rate through the atomizer.

After the gas flow passed through the outlet of the furnace, it was cooled in a stainless steel (SS; AISI 316L) tube. The aerosol products from the possible reaction of ruthenium oxides with the seed particles or the gaseous medium within the facility were filtered out at point 106 cm downstream of the furnace. The filter used was 90 mm in diameter and it was made of Mitex® (pore size 5 μm , Millipore). The temperature of the gas flow going through the filter was ca. 30 °C. Downstream of the filter, the gaseous ruthenium was trapped in a 1 M NaOH solution of Milli-Q water with two sequential liquid traps (400 ml of solution per trap) at ca. 25 °C. A NaOH solution was previously found as an efficient trap for gaseous RuO_4 [11] in which RuO_4 is reduced into form of ruthenate and per-ruthenate salts. The flow rate through the filter and traps was 4 l/min (NTP).

Aerosol gas-phase sampling was done at a point 74 cm downstream of the furnace using a j-shaped probe (inner diameter 4.6 mm) pointing upstream in the flow. The sample flow (1 l/min, NTP) was diluted and quenched to ca. 25 °C with a porous tube diluter in order to minimize losses. The dilution ratio was ca. 11. The formed particles were collected on a

carbon/nickel grid (400 mesh, Agar Scientific) directly from the gas phase by directing a flow of 0.3 l/min (NTP) through the grid. The sampling flow rate was controlled using a critical orifice connected to a vacuum pump. Particles were also collected on an analysis filter (pore size 5 μm , diameter 47 mm, Mitex®, Millipore). The sampling flow rate (2 l/min, NTP) through the analysis filter was also controlled with a critical orifice.

All gas fed to the facility were controlled with mass flow controllers (Brooks S5851). Pressure (Druck pressure meter, model DPI 145) and temperature (K-type thermocouple with a tip diameter of 1.5 mm) measurements were conducted upstream of the aerosol filter and at locations downstream of both the diluter and the analysis filter.

The experiments were started with placing a crucible filled with RuO_2 powder (1 g) into the furnace and then heating up the system (heating rate of 10 degrees in a minute). The gas flow through the facility was started when the set-point of 1227 $^\circ\text{C}$ was reached. The duration of the experiments was ca. 50 minutes. In the experiments, particulate and gaseous reaction products were collected on a filter and trapped in a 1M NaOH solution respectively. At the same time, particles in the gas phase were analysed online and additional samples of the particles were collected for the analyses to be conducted later. After the experiment, the gas flow was stopped and the facility was cooled down (cooling rate of 10 degrees in a minute) before the collected samples were removed.

2.2 Analysis Methods

The release rate of ruthenium from the crucible in the furnace was determined by weighing the mass of the crucible containing RuO_2 before and after the experiments. The mass of released RuO_2 was converted to the corresponding mass of metallic ruthenium for the evaluation of results.

Ruthenium in the sodium hydroxide liquid traps was quantitatively precipitated with injection of EtOH (96 %, Sigma-Aldrich). Samples were then centrifuged and precipitates of ruthenium were filtered from the solution.

Both filters containing the transported aerosol particles and filters with the precipitates of gaseous ruthenium transported to the liquid traps were analysed with the instrumental neutron activation analysis (INAA) technique. The irradiation of filters was performed in a research reactor at VTT (Triga Mark II reactor in Otaniemi, Espoo) with a thermal neutron flux of $1 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$. Samples were irradiated in the reactor for 1 to 4 hours depending on the amount of ruthenium. The radioactivity of the activation products was measured afterwards using gamma spectrometry. All gamma spectrometric measurements were done using a p-type high purity germanium detector (HPGe, Ortec, Oak Ridge TN, USA) having a relative efficiency of ca. 80 %, and a resolution of ca. 1.9 keV, both at 1332 keV. Ruthenium-103 activity was established from the counts at 497 keV peak, silver activity was measured at the peak of 657.5 keV originating from $^{110\text{m}}\text{Ag}$ isotope. Detection limit for the ruthenium in the samples was established to be 1.0 μg and the uncertainty of the measurements was calculated to be 10 %. This calculation was done according to GUM (the Guide to the Expression of Uncertainties in Measurements) [12] using the software GUM Workbench (GUM Workbench v2.4, Metrodata GmbH, Germany).

The number size distribution of particles was measured online with a combination of a differential mobility analyser (DMA, TSI 3080/3081) and a condensation particle counter (CPC, TSI 3775) with a time resolution of 3 minutes. The particles were size classified according to their electrical mobility by the DMA and the number of particles in each size classes was counted by the CPC. The measurement range was from 15 nm to 670 nm.

However, a pre-impactor removed particles larger than 615 nm at the inlet of the DMA. The measurement system was controlled with the Aerosol Instrument Manager software version 9.0 (TSI).

Particles were also collected on glass coupons, which were attached on each of twelve impaction stages of an Electrical Low Pressure Impactor (ELPI, Dekati Oy model 97 2E). The cascade impactor of the ELPI was used without charging the particles and thus the online measurement information was not produced. The inlet of the impactor was at ca. atmospheric pressure and the outlet of it was at 100 mbar (absolute). The collected particles were differentiated by their aerodynamic diameter on the impaction stages inside the impactor. The measurement range of the ELPI was from ca. 7 nm to 10 μm .

The size, morphology and elemental composition of particles was analysed with a Scanning Electron Microscope (SEM, Merlin® FEG-SEM, Carl Zeiss NTS GmbH) coupled with an Energy Dispersive X-ray analyser (EDX, Noran Pioneer Si(Li) X-ray detector).

A more detailed analysis on the elemental composition and speciation of particle deposits was performed with X-ray photoelectron spectroscopy (XPS). For the analysis a Kratos Axis ultra electron spectrometer with monochromatic Al Ka irradiation at 100W (X-ray tube voltage 12.5 kV, anode current 8mA) and charge neutralization was used. The samples were pre-evacuated in the instrument fore-chamber overnight in order to stabilize the vacuum conditions. The depth of the x-ray reach was less than 10nm of the sample surface and the electron take-off angle was 90°. Sampling was performed from at least two different spots on sample.

2.3 Experimental Matrix

The experimental matrix with the details of the experiments is presented in Table 1. Experiment 1 was a reference experiment, in which RuO₂ powder was oxidized in a dry air atmosphere. The release and transport results of vaporized ruthenium oxides are compared with the other experiments. Experiments 2 and 3 were conducted in a humid air atmosphere. The water content in the gas flow was originated from the atomizer, in which only water was used as a precursor solution. In experiment 4, a mixture of nitrogen (N₂), oxygen (O₂) and nitrogen dioxide (NO₂) gases was injected to the furnace. The fraction of oxygen in the gas flow was kept at 21 % to simulate the air flow, whereas the concentration NO₂ was on the level of 75 ppmV. The nitrogen flow was directed through the atomizer in order to reproduce a similar concentration of water into the gas flow as in the other experiments.

The effect of seed particles on the transport of ruthenium was investigated in experiments 5 to 7. Air was used to transport the droplets containing a mixture of water and precursor material from the atomizer to the furnace. Water evaporated from the droplets inside the heated furnace and solid particles were formed. Thus a low concentration of steam was generated into the air flow. In experiment 5, silver seed particles were produced from a 4 wt.% silver (water insoluble silver powder from J. T. Baker, particle diameter 0.5-1 μm) water solution. In experiments 6 and 7, silver was replaced with silver nitrate to compare the effect of this compound on the transport of ruthenium with the results achieved in experiments 4 and 5. Silver nitrate droplets were generated from a 4 wt.% AgNO₃ (water soluble AgNO₃ powder, purity >99 %, J. T. Baker) water solution and the droplets were transported to the furnace.

Table 1: Detailed experimental matrix. The oxidation temperature of RuO₂ precursor was 1227 °C in all experiments.

Exp [#]	T [°C]	Gas ^a	Precursor ^b	Additive precursor conc.	Humidity ^c [ppmV]	Other
1	1227	Air	RuO ₂	-	dry	-
2	1227	Air	RuO ₂	-	21400	atomizer with only water
3	1227	Air	RuO ₂	-	21400	atomizer with only water
4	1227	N ₂ /O ₂ /NO ₂ ^d	RuO ₂ +NO ₂	NO ₂ conc. 75 ppmV	21400	atomizer with only water
5	1227	Air	RuO ₂ +Ag	4 wt. % Ag-water solution (atomizer)	21400	-
6	1227	Air	RuO ₂ +AgNO ₃	4 wt. % AgNO ₃ -water solution (atomizer)	21400	-
7	1227	Air	RuO ₂ +AgNO ₃	4 wt. % AgNO ₃ -water solution (atomizer)	21400	-

^aThe total flow rate through the furnace was 5 l/min (NTP) in every experiment.

^bThe mass of RuO₂ powder in the crucible was ca. 1 g.

^cThe water content in the gas flow was originated from the water based precursor solution of the atomizer.

^dThe volume fraction of N₂ was approx. 79 % and O₂ 21 %. NO₂ concentration was very low, 75 ppmV.

3 RESULTS

At first, the results of ruthenium release from the crucible and transport into the filter and trapping bottles are summarised below. The mass flow rates are presented as of ruthenium(0), not of the oxides. The results are normalised to a flow rate of 5 l/min (NTP), because the carrier gas flow rate through the main line filter and the trapping bottle was not, due to the online sampling, the same in all experiments. The on-line results of ruthenium aerosol transport through the model primary circuit are given next. Afterwards, the morphology and elemental composition of particles are presented.

3.1 Ruthenium Release

It was assumed that the release rate of ruthenium from the crucible was constant during the course of experiment, as it has been shown in an air atmosphere with pure ruthenium oxides in [4], and that ruthenium was released only when the air was introduced into the gas flow, i.e. furnace was heated up to the set-point temperature (1227 °C) The ruthenium release rate results are presented in Table 2. The release rate was 6.1±0.3 mg/min in dry air conditions. If the system is assumed to be in thermodynamic equilibrium, 91 % of the ruthenium was released as RuO₃ at 1227 °C and 8 % as RuO₄ [1]. It is possible, that a lower oxygen partial pressure due to addition of steam into the system led to a slightly lower release of ruthenium when compared to a dry air atmosphere. However, the observed variation is still within the measurement uncertainty.

Table 2: Release rate of ruthenium from the crucible.

Experiment (with a label)	Ruthenium release rate (mg/min)
1 Dry atmosphere	6.1±0.3
2 Humid atmosphere	5.6±0.3
3 Humid atmosphere	5.8±0.3
4 NO ₂	5.7±0.3
5 Ag	6.1±0.3
6 AgNO ₃	6.0±0.3
7 AgNO ₃	5.6±0.3

The feed of additional NO₂ gas, AgNO₃ droplets or silver particles to the gas flow did not have a significant effect on the ruthenium release. That is probably due to the low concentration of the additives. In general, the release rate of ruthenium was rather similar in all experiments.

3.2 Ruthenium Transport

The amount of ruthenium transported as aerosol particles on the filter and as gaseous RuO₄ to the liquid traps of 1M NaOH solution was quantified with the use of instrumental neutron activation analysis. The amount of transported ruthenium in the experiments is summarized in Table 3. The values are given as percentages of the total amount of ruthenium released. The presented results are preliminary at the moment.

Table 3: Fractions of ruthenium transported as RuO₂ aerosol particles and RuO₄ gas through the model primary circuit, as well as, the fraction of ruthenium deposited inside the circuit.

All values are given as % of the released Ru.

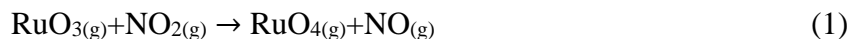
Exp. [#]	Ru transported in total (%)	RuO ₂ transported (%)	RuO ₄ transported (%)	Ru deposited (%)
1 Dry atmosphere	8.4±0.8	8.1±0.8	0.32±0.03	91.6±0.8
2 Humid atmosphere	20±2	20±2	0.22±0.02	80±2
3 Humid atmosphere	^a	^a	0.19±0.02	^a
4 NO ₂	10.1±1.0	0.61±0.06	9.5±1.0	89.9±1.0
5 Ag	9.4±0.9	9.4±0.9	0.0024±0.0002	90.7±0.9
6 AgNO ₃	11.6±1.2	10.0±1.0	1.6±0.2	88.4±1.2
7 AgNO ₃	13.7±1.4	12.8±1.3	0.97±0.10	86.3±1.4

^aThe aerosol filter in experiment 3 was not analysed with INAA.

From the results it can be concluded that humidity increased significantly the transport of ruthenium through the facility. The increased transport mainly took place in the form of RuO₂ aerosol with a decreased RuO₄ fraction when compared to the dry air condition. The proposed explanation is that steam passivates the surfaces of the outlet tube made of stainless steel and thus decreases the catalytic decomposition of RuO₃ to RuO₂ and the deposition of RuO₂ taking place on the surface when the temperature decreases below 800 °C. Therefore, the gas phase formation of RuO₂ particles is increased and the transport of particles is enhanced.

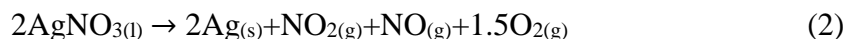
As can be seen from the results, silver particles and NO₂ gas (75 ppmV) in the gas flow had a significant effect on the chemical composition of transported ruthenium. The transported amount of ruthenium in these experiments was the same as in the dry air experiment, but now ruthenium transported mainly as gas. This behaviour can be explained

by the oxidation of RuO₃ to RuO₄ in the high temperature region of the facility. The proposed reaction occurring is presented as a reaction (1).



The experiments with a feed of pure silver particles into the gas flow indicated a significant decrease in the transport of gaseous RuO₄ to the outlet of the facility. Simultaneously, a noticeable increase in the transport of ruthenium in the form of RuO₂ was observed. This behaviour can be explained by the decomposition of RuO₄ to solid RuO₂ on the surface of silver aerosol particles. The explanation is based on the previous observation of the catalytic decomposition of RuO₄ to RuO₂ on various surfaces [13, 14]. Therefore, as the number concentration of particles in the gas flow is increased by the feed of silver particles, the surface area available for RuO₄ reduction increases, leading to a more significant decomposition of RuO₄.

To test the combined effect of both silver particles and NO₂ gas on the transport of ruthenium, AgNO₃ droplets were fed to the gas flow. After the AgNO₃ droplets are transported into the hot zone of the furnace they decompose according to reaction (2) [15]. The occurrence of both silver aerosol particles and NO₂ gas simultaneously in the primary circuit during a severe accident is highly probable if air ingress into the reactor vessel occurs.



The feed of both silver and NO₂ together in the form of AgNO₃ droplets resulted in a significant increase of RuO₄ fraction, although the increase was not as much as in the experiment with NO₂ gas, as the only additive in the gas flow. This was due to the simultaneous decomposition of RuO₄ on the surface of silver particles, which were formed after the drying and decomposition of the AgNO₃ droplets inside the furnace.

In all experiments, the major part of the released ruthenium was deposited inside the facility as can be seen in Table 3. The highest retention of ruthenium in the facility was observed at the outlet of the furnace, where temperature decreased rapidly. This was attributed to the decomposition of RuO₃ into solid ruthenium dioxide deposits.

3.3 On-line monitoring of Ru transport

The evolution of particle number size distribution is presented in Figure 2, measured with SMPS. In experiments 1 to 3, the decrease in the transport of particles by the time was evident. An air flow saturated with water seemed to enhance the particle transport, when compared to a dry air flow. The transport of particles was deduced from the measured number of particles. However, the diameter of particles was slightly higher in experiment 1. The feed of silver particles (experiment 5) and AgNO₃ droplets (experiment 7) to the flow of ruthenium oxides stabilized the transport of particles with all sizes and up to 6 times higher particle concentration was transported through the facility than without additives at the end of experiments. Likely, the silver particles generated from AgNO₃ droplets were also taken into account in the online measurement results. However, silver particles fed to the facility in experiment 5 were too large in diameter (ca. 1.0 μm) to be detected in the SMPS measurement and thus the measured aerosol was mainly of ruthenium compound. The feed of NO₂ gas in experiment 4 decreased the transport of particles significantly. Based on the measurement data, the formation of particles was decreasing continuously as the number size distribution was fading out below the detection limit of SMPS.

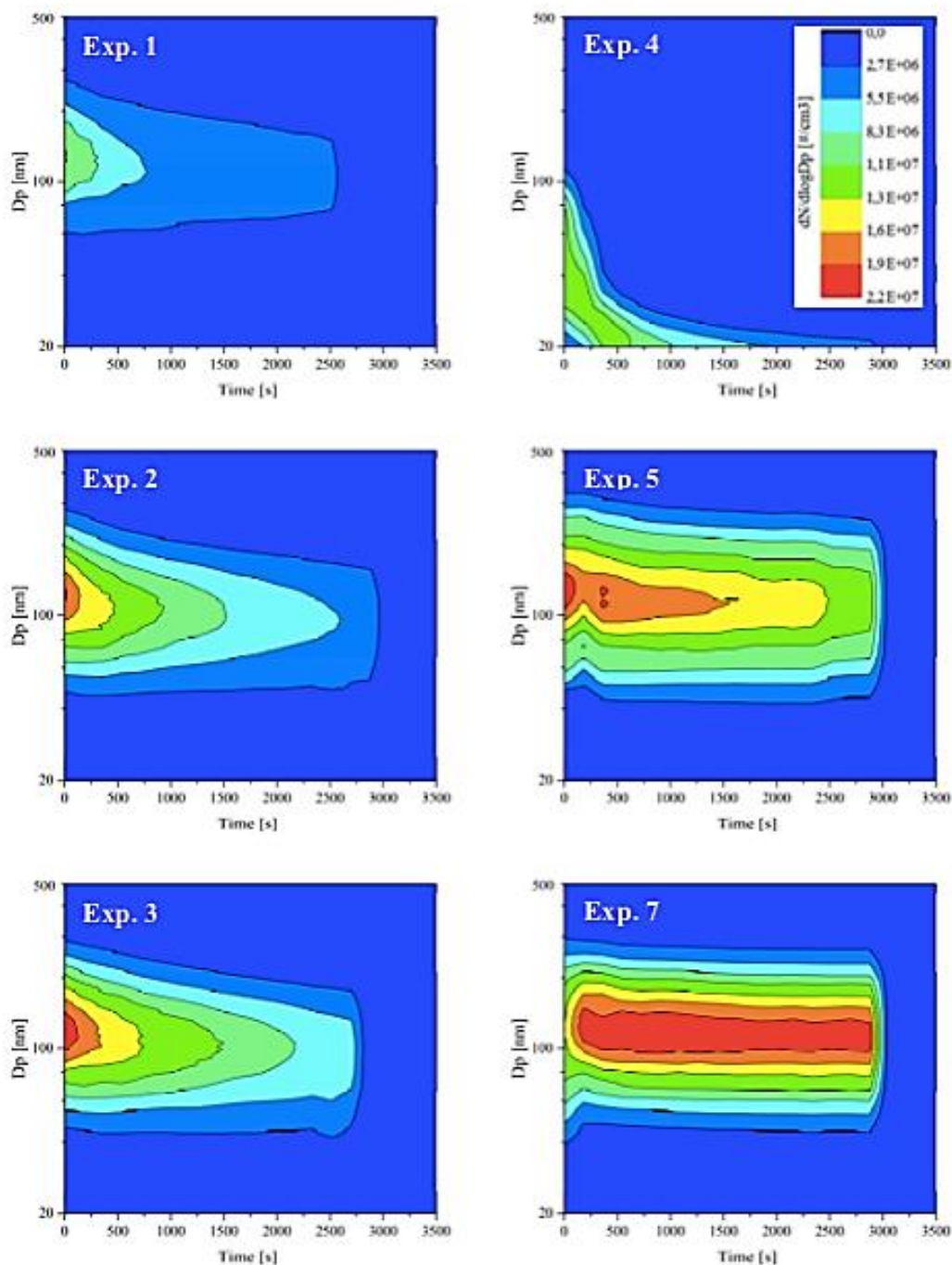


Figure 2: Particle number size distributions at the outlet of the facility during experiments (measured with SMPS). The normalized concentration of particles $dN/d\log D_p$ [# / cm³] is presented with colours - see the scale bar in Exp. 4.

3.4 SEM and XPS Analyses of Aerosols

The SEM micrographs of the collected particles on carbon coated nickel (400 mesh) grids in experiments 2 and 6 are presented in Figure 3. Depending on the reaction conditions, the morphology (particle size and shape) of ruthenium (i.e. ruthenium oxide) particles varied remarkably between the samples. In experiments 1, 2, 3 and 5, the typical crystalline needle-shaped form of RuO₂ was clearly evident and it was the dominating form of ruthenium in the samples. Thus this observation supported the previous findings as well [1, 4]. The rather low

concentration of silver in experiment 5 did not have a notable effect on the shape of RuO₂ crystals.

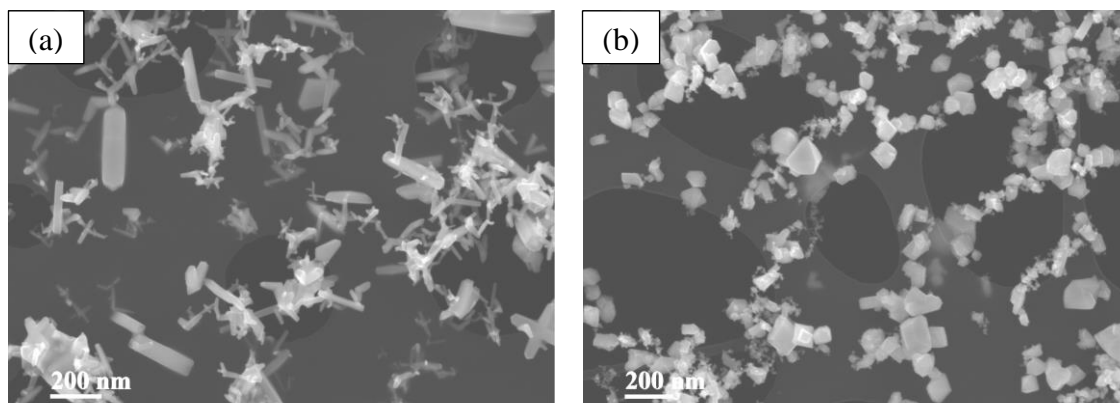


Figure 3: SEM micrographs of ruthenium particles on a nickel/carbon grid in experiments 2 (a) and 6 (b).

The feed of AgNO₃ droplets into the flow of ruthenium oxides in experiment 6 seemed to have an effect on the shape of ruthenium particles. The needle-shaped RuO₂ crystals were not observed anymore. Instead, a variety of different size cubical crystals was formed. Similarly shaped crystals were also observed in experiment 4 in a NO₂-N₂-O₂ atmosphere (composition close to technical air). However, the concentration of the formed particles was very low due to the high formation of gaseous ruthenium and thus only a few particles were observed on the grid for the analysis. In the other experiments, the particle concentration was high inside the ruthenium transport facility and it led to an agglomeration of particles in the gas phase before they were collected on the grid, as can be seen in Figure 3.

The chemical speciation analysis of the transported aerosol particles with XPS verified the formation of RuO₂. No other ruthenium compounds were identified. Silver in the particle samples was observed to be in the form of AgO.

4 DISCUSSION

It has been shown in this study that the prevailing conditions in the primary circuit of a nuclear power plant can have an effect on the partition of ruthenium between gaseous and aerosol compounds and on the transport of ruthenium into the containment atmosphere. The effect of air radiolysis product NO₂ on the increasing formation of gaseous RuO₄ was significant and thus further studies on the effect of representative air radiolysis products N₂O, NO₂ and HNO₃ on the chemistry and transport of ruthenium have been conducted [8]. The experiments verified the importance of these oxidizing compounds on ruthenium speciation, as well as to the formation of gaseous ruthenium.

In this study silver particles seemed to decrease the transport of gaseous ruthenium. In order to understand whether the effect of other aerosols would be similar, the effect of CsI particles, which is an important form of iodine transporting to the containment building in a severe accident, has been studied [9]. Surprisingly, the transport of gaseous ruthenium increased notably due to CsI compound.

These experiments, with an objective to have more realistic experimental conditions, produced new information on the behaviour of ruthenium in accident conditions. Therefore, it is of interest to continue the work on the chemistry of ruthenium (and other fission products) and to study the effect of other possible fission product and air radiolysis species etc. Another important factor playing a role in an accident is radiation. In addition to the formation of

radiolysis products, the effect of radiation on the known reactions and speciation of ruthenium and other fission products could be crucial.

5 CONCLUSIONS

The aim in this study was to determine the effect of representative fission product, control rod and air radiolysis species on the release, transport and chemical speciation of ruthenium in the facility simulating a primary circuit under air ingress conditions in a severe nuclear accident. The main focus was to quantify the transport of gaseous and particulate ruthenium through the circuit to the containment conditions. On one hand, the presented first experiments focused on the effect of pure dry and humid air atmospheres on the transport of ruthenium. On the other hand, NO₂ gas, AgNO₃ droplets and silver particles were also mixed with the air atmospheres.

It was observed that humid air conditions increased the fraction of transported ruthenium dioxide aerosols with a decreased transport of gaseous RuO₄ when compared to dry air conditions. A very significant effect of NO₂ on the ratio between aerosol and gaseous form of ruthenium reaching the outlet of model primary circuit was observed. NO₂ gas in concentration of 75 ppmV increased the fraction of gaseous RuO₄ by two orders of magnitude, which leads to a significantly higher RuO₄ concentration in the containment building when compared to the pure air experiments. It is notable, since NO₂ gas is expected to be formed due to the radiolysis of air by highly radioactive fuel material. On the other hand, the transport of particles decreased significantly, which could be detected with online measurement devices. The feed of silver aerosol into the air-flow decreased the transport of gaseous ruthenium by two orders of magnitude when compared to the experiments conducted at humid atmosphere. When both NO₂ gas and silver particles were fed in form of AgNO₃ droplets into the air flow, the fraction of gaseous ruthenium reaching the facility outlet was increased approximately by one order of magnitude when compared with the experiments conducted at humid air conditions. Based on the online aerosol data, both the feed of silver or AgNO₃ to the flow of ruthenium oxides enhanced the transport of particles through the model primary circuit and they kept the particle transport on a more stable level when compared with other experiments.

The obtained results indicate a very strong effect of the airborne aerosol/radiolysis products in the primary circuit on the speciation of ruthenium reaching the containment building. As a result, the fraction of gaseous ruthenium tetroxide in the containment atmosphere can be significantly higher than what has been expected based on the previous studies in pure air-steam atmospheres. Therefore, it is important to perform representative experiments in more complex atmosphere mixtures in future in order to learn more about the chemistry of ruthenium. And that work should be extended to deal with other fission products as well.

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REFERENCES

- [1] Backman, U., Lipponen, M., Auvinen, A., Tapper, U., Zilliacus, R., Jokiniemi, J.K., On the transport and speciation of ruthenium in high temperature oxidising conditions. *Radiochimica Acta*, 2005. 93(5): p. 297-304.
- [2] Eichler, B., Zude, F., Fan, W., Trautmann, N., Herrmann G., Volatilization and Deposition of Ruthenium Oxides in a Temperature-Gradient Tube. *Radiochimica Acta*, 1992. 56(3): p. 133-140.
- [3] Cotton, F.A., Wilkinson, G., *Advanced inorganic chemistry*. 4th edition ed. 1980: Wiley.
- [4] Kärkelä, T., Backman, U., Auvinen, A., Zilliacus, R., Lipponen, M., Kekki, T., Tapper U., Jokiniemi, J., Experiments on the behaviour of ruthenium in air ingress accidents - Final report. 2007, VTT research report VTT-R-01252-07.
- [5] Vér, N., Matus, L., Pintér, A., Osán, J., Hózer, Z., Effects of different surfaces on the transport and deposition of ruthenium oxides in high temperature air. *Journal of Nuclear Materials*, 2012. 420(1–3): p. 297-306.
- [6] Kärkelä, T., Vér, N., Haste, T., Davidovich, N., Pyykönen, J., Cantrel, L., Transport of ruthenium in primary circuit conditions during a severe NPP accident. *Annals of Nuclear Energy*, 2014. 74(0): p. 173-183.
- [7] Kajan, I., Kärkelä, T., Tapper, U., Johansson, L.-S., Gouëlle, M., Ramebäck, H., Holmgren, S., Auvinen, A., Ekberg, C., Impact of Ag and NO_x compounds on the transport of ruthenium in the primary circuit of nuclear power plant in a severe accident, *Annals of Nuclear Energy*, 2017. 100: p. 9–19.
- [8] Kajan, I., Kärkelä, T., Auvinen, A., Ekberg, C., Ruthenium chemistry and transport in a RCS due to air radiolysis products, Submitted to *Journal of Radioanalytical and Nuclear Chemistry*, 2016.
- [9] Kärkelä, T., Kajan, I., Tapper, U., Auvinen, A., Ekberg, C., Ruthenium transport in an RCS with airborne CsI, Submitted to *Progress in Nuclear Energy*, 2016.
- [10] Kärkelä, T., Pyykönen, J., Auvinen, A., Jokiniemi, J., Analysis of Flow Fields, Temperatures and Ruthenium Transport in the Test Facility. 2008, VTT research report VTT-R-00947-08.
- [11] Backman, U., Lipponen, M., Auvinen, A., Jokiniemi, J., Zilliacus, R., Ruthenium Behaviour in Severe Nuclear Accident Conditions – Final report, VTT research report PRO3/P27/04, 2004.
- [12] Metrology, B.J.C.f.G.i., JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM 100:2008 (GUM 1995 with minor corrections). 2008: Paris
- [13] Kajan, I., Lassesson, H., Persson, I., Ekberg, C., Interaction of ruthenium tetroxide with surfaces of nuclear reactor containment building. *Journal of Nuclear Science and Technology*, 2016. 53(9): p. 1397-1408.

- [14] Holm, J., Glänneskog, H., Ekberg, C., Deposition of RuO₄ on various surfaces in a nuclear reactor containment. *Journal of Nuclear Materials*, 2009. 392(1): p. 55-62.
- [15] Otto, K., Oja Acik, I., Krunks, M., Tõnsuaadu, K., Mere, A., Thermal decomposition study of HAuCl₄·3H₂O and AgNO₃ as precursors for plasmonic metal nanoparticles. *Journal of Thermal Analysis and Calorimetry*, 2014. 118(2): p. 1065-1072.