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Impact of Aerosols on the Transport of Ruthenium in the primary circuit of nuclear power plant

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Abstract

In the NKS-ATR activity (year 2014) by VTT Technical Research Centre of Finland and Chalmers University of Technology the aim was to study the effect of aerosols and air radiolysis products on the transport of gaseous and particulate ruthenium species through a model primary circuit. The radiotoxicity of ruthenium oxides is near that of iodine in the short term and near that of caesium in the long term. All experiments were conducted using VTT's Ru transport facility at 1227 °C with dry or slightly humid air as the main carrier gas. The results show that the impact of additional NO₂ gas feed (75 ppm volume) to the flow of ruthenium oxides (in humid air) was significant both on the transport of ruthenium through the facility and on the speciation of the transported ruthenium. Transport of gaseous RuO₄ was increased significantly, whereas at the same time the amount of aerosols reaching the filter was decreased. However, the release of ruthenium from the crucible was similar as in an experiment without NO₂ (in air atmosphere). This indicates that the molar ratio of RuO₃/RuO₄ in the gas flow had changed. A proposed explanation is based on the oxidation of RuO₃ to RuO₄ by NO₂.

On the other hand, when only pure silver particles (diameter 0.5-1.0 µm) were fed to the humid air flow, the transport of RuO₄ decreased significantly. Most likely, gaseous RuO₄ had reactively condensed on the surface of silver particles as RuO₂. Addition of both silver particles and NO_x in a form of , NO₃ droplets (which decomposed to silver and NO₃ when heated and further to NO₂, NO and O₂) to the flow of Ru oxides (in humid air) enhanced the transport of gaseous RuO₄ as well, but not as much as in case of NO₂ feed. In these experiments (with NO₂ or AgNO₃), the observed transport of gaseous ruthenium seemed to be several orders of magnitude higher than in the previous experiments with only pure ruthenium oxides in the air atmosphere. These results indicate that the composition of gaseous atmosphere in the primary circuit has a significant effect on the amount and chemical form of ruthenium transported to the containment during a SA.

Key words

Ruthenium, Aerosol, Air radiolysis, Severe Accident, Source Term

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Impact of Aerosols on the Transport of Ruthenium in the primary circuit of nuclear power plant

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Preface

The experiments on the transport of Ru in primary circuit conditions were conducted at VTT Technical Research Centre of Finland (Espoo, Finland) in 2014. The “VTT Ru transport experimental facility” was slightly updated for these new experiments. The samples of gaseous and particulate ruthenium, produced as a result of experiments, were analysed with various techniques at Chalmers University of Technology (Göteborg, Sweden), Aalto University (Espoo, Finland), FOI Swedish Defence Research Agency (Umeå, Sweden) and VTT (Espoo, Finland). The activation of Ru samples for INAA analysis was performed with VTT’s research reactor.

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Authors

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Introduction

During the operation of a nuclear power plant (NPP), a significant amount of ruthenium is build up in the fuel as a product of nuclear fission. The importance of ruthenium from the radiological point of view is mainly due to ^{103}Ru and ^{106}Ru isotopes with half-lives of 39.35 days and 373.5 days, respectively. These highly radiotoxic isotopes cause a risk to the population both in a short and long term, when ruthenium is released from the fuel to the environment in a severe NPP accident.

Previously, ruthenium has been considered as a non-volatile fission product (FP) during a severe nuclear accident [1]. However, the Chernobyl accident and experiments performed during the last decades have shown that ruthenium has an ability to be released from the fuel matrix in a volatile form. The released fraction of ruthenium was up to 65 % in the experiments conducted under VERCORS experimental programme in an oxidizing atmosphere with a steam flow rate of 1.5 g/min [2, 3]. Interestingly, 6 % of ruthenium was released also in a hydrogen rich atmosphere and thus in reducing conditions [3]. In the experiments conducted under PHEBUS FP programme, the release of ruthenium from the fuel matrix was up to 17 % [2]. The release of ruthenium mainly took place in the form of volatile ruthenium oxides. However, oxidation of the nuclear fuel is needed before the release of ruthenium can occur. Oxidation of the fuel causes the formation of cracks in the fuel lattice as UO_2 is oxidized to U_3O_8 , which occupies around 30 % more volume. This step rapidly increase the penetration of oxygen into the fuel pellet [4]. As UO_2 has a higher affinity for oxygen than metallic ruthenium, the oxidation of fuel leads to a higher oxygen pressure in the fuel and thus it favours the oxidation of ruthenium. Both the disintegration of the fuel pellet and the higher oxygen pressure in the fuel catalyse the release of ruthenium from the fuel.

The transport of ruthenium through a reactor coolant system (RCS), after being released from the fuel, has been investigated in several experimental programmes recently, summarized in [5]. VTT Ru transport programme has shown that the release of Ru from RuO_2 powder was dependent on the oxygen partial pressure in air-steam atmospheres at 827, 1027, 1227 and 1427 °C [5, 6]. The highest fraction of gaseous RuO_4 at the outlet of the model primary circuit was observed at 1027 °C oxidation temperature [6]. At higher temperatures, ruthenium transported mainly as RuO_2 aerosol.

In the RUSSET programme the presence of other FPs, e.g. BaO and CeO_2 , in the area where ruthenium oxidation took place (at 1100 °C) decreased the fraction of gaseous RuO_4 in the outlet air over the stainless steel surface compared to the pure Ru oxidation [7]. It was also shown that the transport of RuO_4 was dependent on the surface material in the circuit. In both VTT and RUSSET programmes, the partial pressure of RuO_4 reaching the outlet of model primary circuit was in the range of $10\text{E-}7$ to $10\text{E-}6$ bar, which is significantly higher than what is expected based on thermodynamic equilibrium calculations. The steam content of air was also found to decrease the surface catalysed decomposition of RuO_4 to RuO_2 in those experiments and thus to increase the transport of RuO_4 . It was also observed in the RUSSET programme that molybdenum oxide which was simultaneously present in the vapour phase decreased the surface catalysed decomposition of ruthenium oxides efficiently and increased the transport of gaseous

ruthenium significantly [7]. These experimental programmes have verified that the transport of ruthenium through the primary circuit into the containment is strongly dependent on the temperature and gaseous atmosphere in the primary circuit, as well as, on the chemical composition of the ruthenium to be released and the material of the primary circuit surfaces.

The ATR (Impact of Aerosols on the Transport of Ruthenium) experimental programme was performed in order to focus on the speciation of ruthenium transported through the facility simulating a primary circuit and on the quantification of the amount of ruthenium transported. The study was dedicated to air ingress conditions and thus the collected data provide new information of fission product and air radiolysis species impact on the transport of ruthenium through the primary circuit of nuclear power plant in a severe accident.

Background

Ruthenium forms several volatile oxides depending on the temperature.. RuO, RuO₂, RuO₃ and RuO₄ are known volatile oxides of ruthenium. Both RuO and RuO₃ have not been detected in the solid state and they are presumed to exist only at temperatures above ca. 700 °C (RuO₃) and 1627 °C (RuO) as gaseous compounds [8]. Ruthenium dioxide is volatile at temperatures above 1727 °C [9]. Ruthenium tetroxide is volatile at temperatures above 7 °C [10] and it is the only volatile ruthenium oxide relatively stable at low temperature conditions.

In a severe nuclear accident, RuO₃ and RuO₄ are considered as the most relevant volatile ruthenium species. Based on thermodynamic calculations, the dominating gaseous species of ruthenium at temperatures higher than 1000 °C will be RuO₃ in excess to RuO₄. [11] As the temperature in the primary circuit decreases below 700 °C, RuO₃ decomposes rapidly to the solid RuO₂ (e.g. to RuO₂ aerosol in the gas phase) according to the reaction (1) [8, 11].



Therefore at temperatures below 700 °C, which is expected in the primary circuit of NPP during an accident [9], ruthenium tetroxide becomes the most dominant gaseous species of ruthenium. Additionally, ruthenium will be transported through the primary circuit in form of RuO₂ aerosol originating from the decomposition of RuO₃.

During the transport of ruthenium through the primary circuit other fission and radiolysis products can have an effect on the chemical composition or amount of transported ruthenium. Aerosols originating from the fuel are likely to end up in the primary circuit due to the fuel decomposition 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 to the formation of different oxidizing and reducing species. The most prominent are O₃, NO₂, NO, N₂O and in the case of humid conditions also H₂O₂, hydroxyl radical and solvated electron are formed [12]. Nitrogen oxides are of special interest regarding ruthenium chemistry. Ruthenium tetroxide is known for its ability to form different nitroso and nitrosil compounds after reacting with

nitric acid, NO₂ or NO gasses [10, 13]. RuO₄ can also be readily absorbed into the water phase after reaction with NO₂ or NO gasses [14]. Therefore, nitrogen oxides can have a significant effect on the volatility of ruthenium. Estimations of the amount of NO_x in the containment atmosphere predict that representative concentrations of NO₂ and N₂O will be around 50 ppmV [15]. RuO₄ is also known to have a strong affinity for different metals [16]. In general, RuO₄ is reduced on metal surfaces into solid hydrated RuO₂ in slightly humid conditions. As a result, the transport of gaseous RuO₄ into the containment atmosphere can be strongly reduced due to airborne aerosols (with a high surface area in total) in the gas stream.

Experimental

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 [6],[11] 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 (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.

The furnace tube was made of high purity alumina (Al₂O₃, 99.7 %) and its inner diameter was 22 mm. The alumina crucible with the RuO₂ powder (mass ca. 1 g) was placed over the second heated zone of the furnace, 25 cm from the outlet. The RuO₂ 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 O₂, N₂ and NO₂ gases. The seed particles were generated with an atomizer (TSI 3076) from a solution of ultrapure water (Milli-Q, resistivity of 18.2 MΩ·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 was depended on the flow rate through the atomizer.

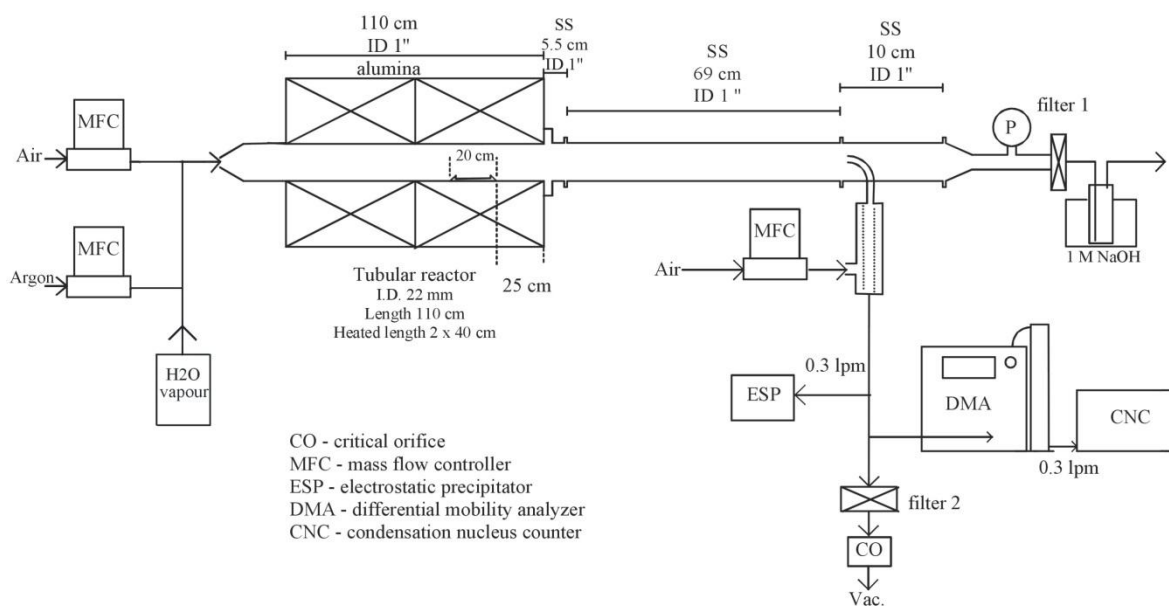


Figure 1. The basic set-up of the experimental facility for ruthenium tests [6].

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 [17] 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 *approx.* 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.

Analysis methods

The release rate of ruthenium from the crucible in the furnace was determined by weighing the mass of the crucible containing RuO₂ before and after the experiments. The mass of released RuO₂ 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 $1 \times 10^{13} \text{ n.cm}^{-2} \cdot \text{s}^{-1}$. 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. All electronics were standard NIM modules (Ortec, Oak Ridge TN, USA). The detector was calibrated according to a semi-empirical approach in order to facilitate calculation of e.g. different correction factors such as corrections for true coincidence summing (TCS) and efficiency transfer (ET) [18]. All measurements in this work were done in a non-standard geometry and therefore corrections for deviation from the calibrated geometry were done using ET. Samples measured in close geometries were corrected for TCS where appropriate.

Physical data (half-lives and photon emission probabilities) were taken from DDEP (Decay Data Evaluation Project) [19]. Correction factors for true coincidence summing were calculated using EFFTRAN [20], which uses physical data from KORDATEN, and VGSL (*Virtual Gamma Spectrometry Laboratory*) [21], which uses data from ENSDF (*Evaluated Nuclear Structure Data File*). In these calculations, the detector, as modelled earlier [18] was implemented in the two codes and used in combination with the geometry of each sample.

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 ^{110m}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) [22] 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).

The total mass concentration of particles was monitored online with a Tapered Element Oscillating Microbalance (TEOM, Rupprecht & Patashnick Co., Inc. Series 1400A) with a time resolution of 10 s. Inside the TEOM the particles are collected on a replaceable filter which is connected to a hollow tube. The particles on the filter shifts the oscillation frequency of the hollow tube from which the deposited mass can be determined. The inlet line, as well as the sampling flow, and the filter in the mass transducer were heated to 30 °C in order to reduce any errors due to condensation of water. The measurement and the function of the instrument were monitored with the RPComm software version 2.1.0.

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).

The particles collected either on an analysis filter or on a glass coupon were analysed with Raman spectroscopy. Raman measurements were performed using a JobinYvon® (LABRAM HR) spectrophotometer, equipped with a Notch filter. The 632.82 nm radiation of a He/Ne gas laser (power less than 2 mW on the sample) was focused through a 50x microscope objective onto the sample surface. The same microscope was used to collect the signal in backscattering geometry. The scattered light, dispersed by the spectrophotometer, was detected by a Peltier cooled charge coupled device (CCD) detection system. The spectral resolution of this instrument is ~4 cm⁻¹.

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 K α 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.

Experimental procedure and matrix

The experiments were started with placing a crucible filled with RuO₂ 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 °C was reached. The duration of the experiments was approx. 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.

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.

Table 1. The 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	-	1512	atomizer with only water
3	1227	Air	RuO ₂	-	1512	atomizer with only water
4	1227	N ₂ /O ₂ / NO ₂ ^d	RuO ₂ +NO ₂	NO ₂ conc. 75 ppmV	1512	atomizer with only water
5	1227	Air	RuO ₂ +Ag	4 wt. % Ag- water solution (atomizer)	1512	-
6	1227	Air	RuO ₂ + AgNO ₃	4 wt. % AgNO ₃ - water solution (atomizer)	1512	-
7	1227	Air	RuO ₂ + AgNO ₃	4 wt. % AgNO ₃ - water solution (atomizer)	1512	-

^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.

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.% AgNO_3 (water soluble AgNO_3 powder, purity >99 %, J. T. Baker) water solution and the droplets were transported to the furnace.

Uncertainty contributors

The uncertainty of the release rates of ruthenium from the crucible was based on the declared uncertainty of the scale given by the manufacturer (Acculab, ALC-150.3, $d=0,001\text{g}$). Standard uncertainty propagation calculation was then performed from the uncertainties of the measured weight before and after each experiment. Afterwards, all uncertainties were increased by one order of magnitude to avoid underestimating the overall uncertainty in the release rates of ruthenium from the crucible.

Uncertainty for the data obtained by gamma spectroscopy consisted of several components. Input components contributing to the combined measurement uncertainty that was considered were: counting statistics, physical data, the calibration standard, the fit of the calibration function, the positioning of the sample on the detector and the procedure of efficiency transfer as well as correction for true coincidence summing where appropriate. However, in the calculation of activity ratios, the activities are correlated since they contain some common input quantities, e.g. the fit of the efficiency function etc. This was taken into consideration in the calculation of the uncertainties in activity ratios.

Results and discussion

Release and transport results

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.

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 [6], 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 RuO_3 at 1227 °C and 8 % as RuO_4 [11]. 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.

Table 2. Release rates 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 NO_2 gas, AgNO_3 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.

Ruthenium transport

The amount of ruthenium transported as aerosol particles on the filter and as gaseous RuO_4 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 different experiments is summarized in Table 3. The corresponding percentage of the total ruthenium released is summarized in Table 4.

Table 3. Mass of ruthenium transported as aerosol particles and gas through the model primary circuit.

Exp. [#]	Ru transported in total (mg)	Ru in form of RuO ₂ aerosol (mg)	Ru in form of RuO ₄ gas (mg)	Ratio of RuO ₂ /RuO ₄	Ru deposited inside the facility (mg)
1	26±3	25±3	0.98±0.10	31.9±1.4	282±3
2	59±6	58±6	0.64±0.06	124±5	230±6
3	a	a	0.61±0.06	a	a
4	29±3	1.8±0.2	27±3	0.082±0.004	256±3
5	29±3	29±3	0.0088±0.0009	4100±2	284±3
6	36±4	31±3	4.9±0.5	7.9±0.3	276±4
7	38±4	36±4	3.3±0.3	16.5±0.8	240±4

^aAerosol filter of experiment 3 was not analysed with INAA.

Table 4. The 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	8.4±0.8	8.1±0.8	0.32±0.03	91.6±0.8
2	20±2	20±2	0.22±0.02	80±2
3	a	a	0.19±0.02	a
4	10.1±1.0	0.61±0.06	9.5±1.0	89.9±1.0
5	9.4±0.9	9.4±0.9	0.0024±0.0002	90.7±0.9
6	11.6±1.2	10.0±1.0	1.6±0.2	88.4±1.2
7	13.7±1.4	12.8±1.3	0.97±0.10	86.3±1.4

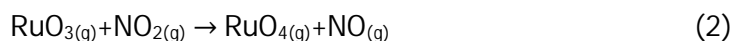
^aAerosol filter of experiment 3 was not analysed with INAA.

From the results it can be concluded that humidity significantly increased 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 decrease the catalytic decomposition of RuO₃ to RuO₂ and the deposition of RuO₂ taking place on the surface when the temperature decreases below 727°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 in the gas flow had a significant effect on the chemical composition of transported ruthenium. The absolute transported amount of ruthenium in these experiments was the same as in the dry air experiment.

A very significant increase in the transport of gaseous RuO₄ was observed in the experiment where NO₂ gas was injected into the system with a concentration of 75

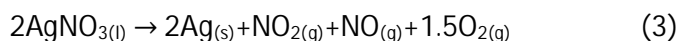
ppmV. This behaviour can be explained by the oxidation of RuO₃ to RuO₄ in the high temperature region of the facility. The proposed reaction occurring is presented as reaction (2).



Thermodynamic calculations assuming equilibrium to be reached gave a stability constant, K, for reaction 2 to be K=16 at 1227 °C, based on calculations with HSC 5.11. software [23]. From the obtained quantities of RuO₄ in the liquid traps and RuO₂ aerosol on the filter, presumably originating from RuO₃ decomposition, RuO₄/RuO₂ ratio in the experiment with additional NO₂ in the gas flow was 15.3±0.7. This value is in a good agreement with the calculated equilibrium value; therefore it is assumed that the reaction (2) reached equilibrium in the hot zone of the facility. This indicates fast kinetics of the reaction. To get deeper insight into the reaction kinetics, further experiments should be performed. In addition, it is noticeable that in case of NO₂ gas feed the RuO₂/RuO₄ ratio was actually reversed when compared to the humid experiments. This observation indicates much higher amounts of gaseous RuO₄ reaching the containment building when compared to the calculations based just on Air/H₂O system in the primary circuit.

The experiments with thusing a feed of pure silver particles into the gas flow showed a significant decrease in gaseous RuO₄ reaching the outlet of the facility. Simultaneously, a noticeable increase of ruthenium in form of RuO₂ trapped on the filter 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 [16, 24]. 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 (3) [25]. 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 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 Tables 3 and 4. 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 RuO_3 into solid ruthenium deposits.

Online monitoring of Ru transport

The online monitoring of the aerosol transport gave a detailed view on the transient behaviour of ruthenium in the facility. The mass concentration of particles transported through the facility was monitored online with TEOM and the corresponding number concentration and number size distribution of particles were monitored with SMPS. Some interference due to technical issues was observed in the online measurements.

The mass concentration of particles ranged from ca. 200 to 850 mg/m^3 when the gas flow was initiated, see Figure 2. At the same time, there seemed to be a peak in the transport of particles. In experiments with pure ruthenium oxides only, the mass concentration was the highest. The transport of aerosol particles decreased in the course of experiments. The transported mass concentration seemed to be similar at both dry (experiment 1) and humid conditions (experiment 2 and 3). However, the transport increased slightly after 500 s in experiment 1 (probably an interference). At the end of experiments the mass concentration of particles had decreased below ca. 150 mg/m^3 . The observed concentration was up to 9 times lower in comparison with the initial concentration in experiments 2 and 3.

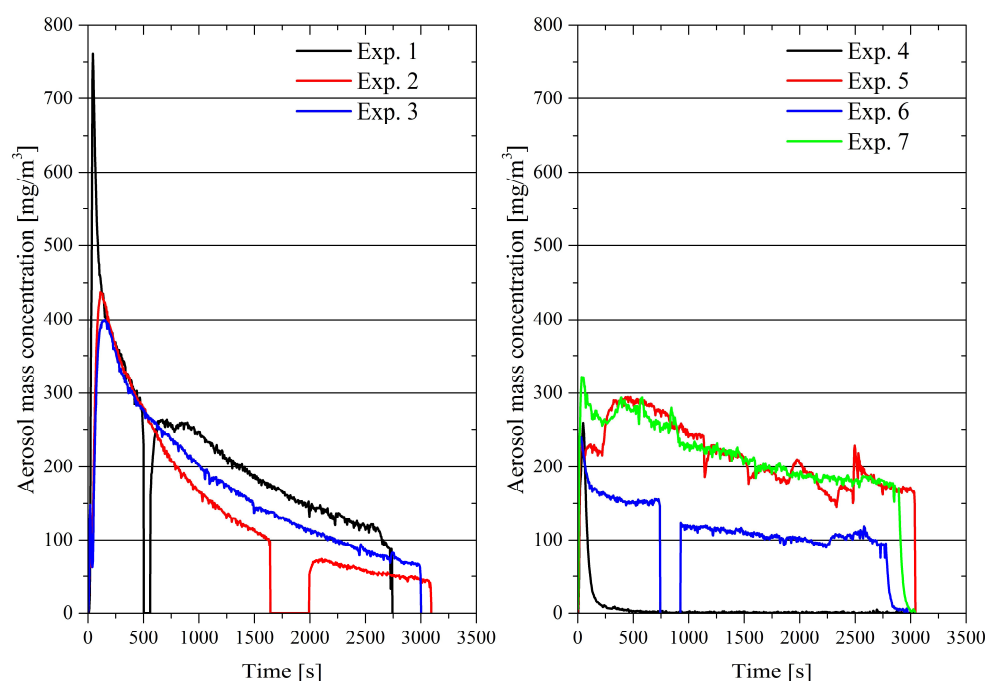


Figure 2. The particle mass concentration [mg/m^3] at the outlet of the facility during experiments (measured with TEOM). In experiments 1, 3 and 6 the measurement was shortly interrupted at ca. 500 s, 1600 s and 700 s respectively. In experiment 5 the gas flow was interfered during 250 s from the beginning of sampling.

The transport of particles was significantly affected by the additional precursors fed to the flow of ruthenium oxides. During experiments 5 to 7 with silver or AgNO_3 additives, the mass concentration of particles in the gas flow decreased with a lower rate when

compared with experiments 1 to 3. Therefore, the transport of particles through the facility was rather stable. In experiment 7 the transport of particles was almost two times higher than in experiment 6, although both experiments were conducted at the same conditions. Most likely the observed variation was due to a difference in the concentration of AgNO_3 in the precursor solution. Thus the concentration of AgNO_3 was lower in experiment 6. At the end of experiments the initial mass concentration of particles had decreased by half. For example in case of experiments 5 and 7, the concentration decreased from ca. 300 mg/m^3 to a level of ca. 170 mg/m^3 .

In experiment 4, the feed of additional NO_2 to the facility decreased the particle mass concentration close to 0.1 mg/m^3 after the conditions inside the facility were stabilized. At the same time, the transport of gaseous ruthenium was very high as described above.

The evolution of particle number concentration in the experiments is presented in Figure 3. The transient behaviour of particle concentration was similar to the behaviour of the mass concentration, as described above. In experiment 1 the measured concentration was lower than in experiments 2 and 3, although the mass concentration seemed to be the highest. The measurement results verified the previous observation on the difference in the transport of particles in experiments 6 and 7. Also, the observed high formation of gaseous ruthenium in experiment 4 was supported by these results.

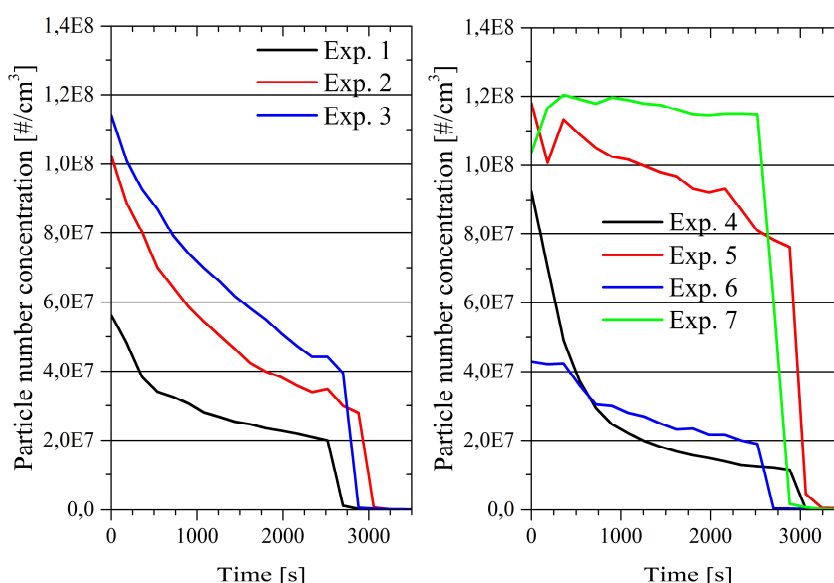


Figure 3. The particle number concentration [# / cm³] at the outlet of the facility during experiments (measured with SMPS). In experiment 5 the gas flow was interfered during 250 s from the beginning of sampling.

The evolution of particle number size distribution is presented in Figure 4. At the beginning of experiments the count median diameter (CMD) of particles was in a range from 100 nm to 150 nm. In experiments 1 to 3, the decrease in the transport of particles by the time was evident, although the CMD remained on the same level. An air flow saturated with water seemed to enhance the particle transport when compared to a dry air flow.

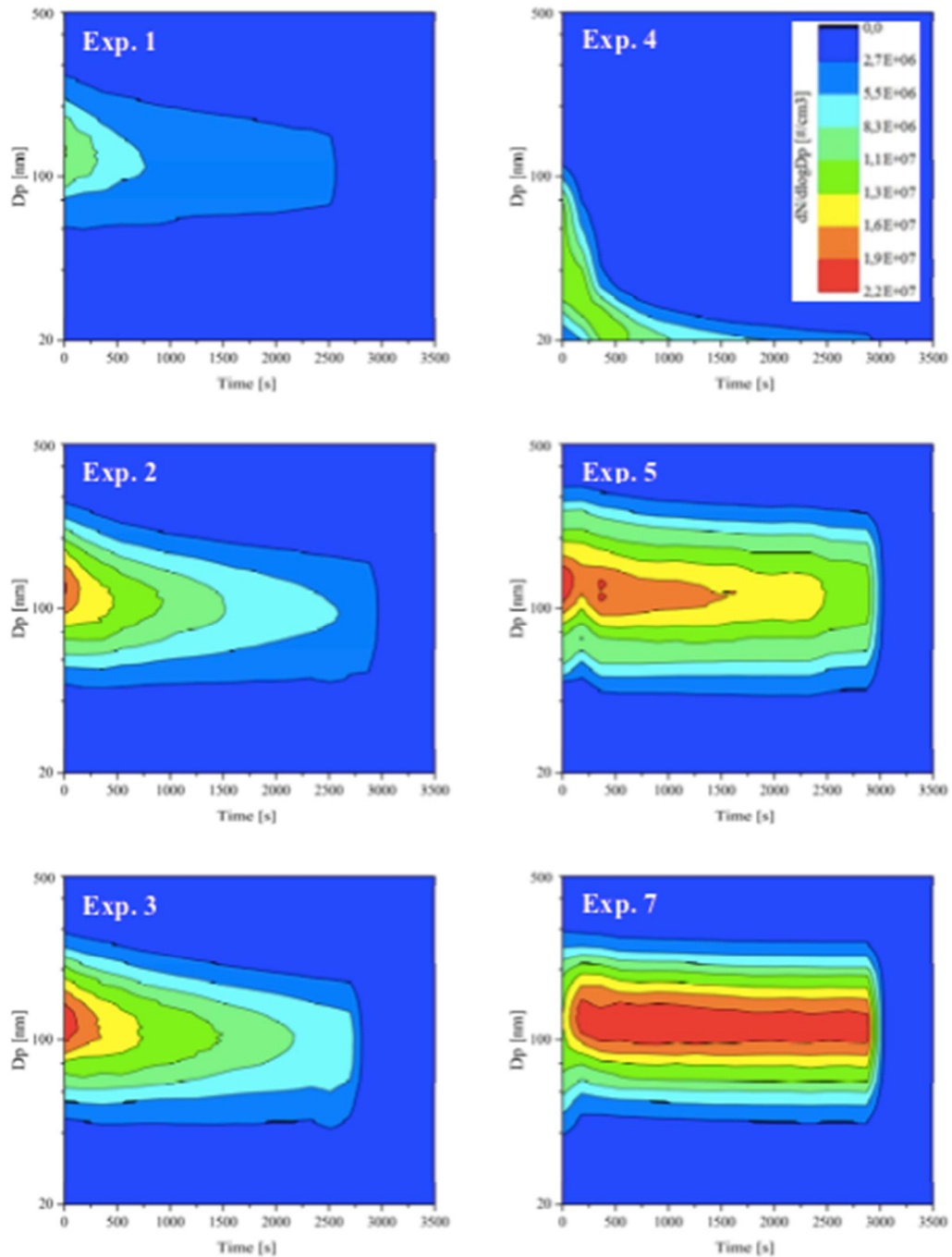


Figure 4. The particle number size distributions at the outlet of the facility during experiments (measured with SMPS). The normalized concentration of particles $dN/d\log D_p$ [$\#/\text{cm}^3$] is presented with colours - see the scale bar in Exp. 4.

The feed of silver particles and AgNO_3 droplets to the flow of ruthenium oxides stabilized the particle transport 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 AgNO_3 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. $1.0\ \mu\text{m}$) to be detected in the SMPS measurement and thus the transported aerosol was mainly of ruthenium compound. The feed of NO_2 gas in experiment 4 decreased the transport of particles significantly. Also the CMD of particles decreased close to the detection limit of SMPS, ca. 20 nm.

SEM-EDX analysis

The ruthenium particle samples were collected on holey carbon coated nickel (400 mesh) grids and analysed with a scanning electron microscope. The SEM micrographs of the collected particles are presented in Figure 5. 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 2 and 5, the typical crystalline needle-shaped form of RuO_2 was clearly evident and it was the dominating form of ruthenium in the samples. Thus this observation supported the previous findings as well [5, 6]. The rather low concentration of silver in experiment 5 did not have a notable effect on the shape of RuO_2 crystals.

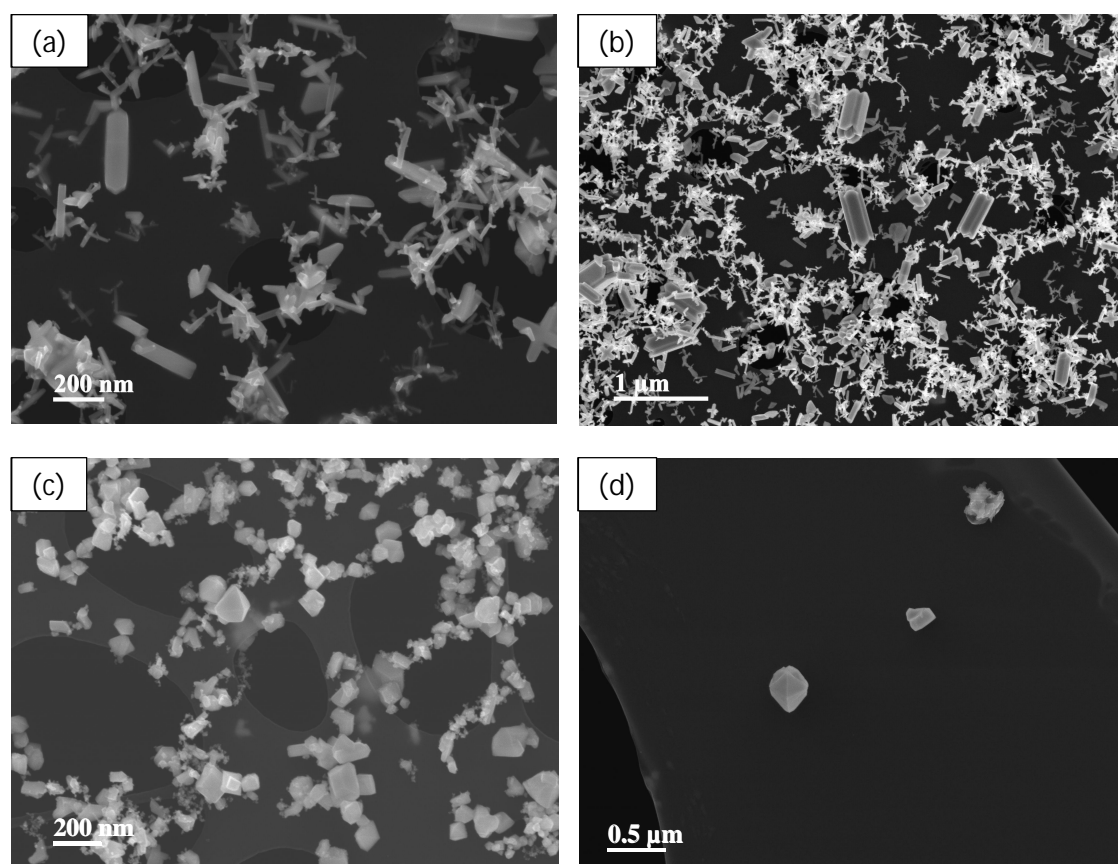


Figure 5. SEM micrographs of ruthenium particles on a nickel/carbon grid in experiments 2 (a), 5 (b), 6 (c) and 4 (d).

The feed of AgNO_3 droplets into the flow of ruthenium oxides in experiment 6 seemed to have an effect on the shape of ruthenium particles. The needle-shaped RuO_2 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 $\text{NO}_2\text{-N}_2\text{-O}_2$ 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 5.

The EDX analysis of spots #1 and #2 on the sample from experiment 1 verified that the formed particles contained ruthenium, see Figure 6. The identified characteristic X-ray line energies for ruthenium were e.g. 2.558 keV ($L_{\alpha 1}$) and 2.683 keV ($L_{\beta 1}$). In both EDX spectra, the total amount of recorded X-ray counts from the sample was the same. In order to separate the spectra from each other, the recorded true counts of spot #2 are multiplied by two in Figure 6. In addition to ruthenium, signals of other elements were also observed at both analysis locations. The nickel originated from the grid and carbon from the foil, whereas the signal of aluminium was from the sample holder. The oxygen originated mainly from the oxidized ruthenium and grid.

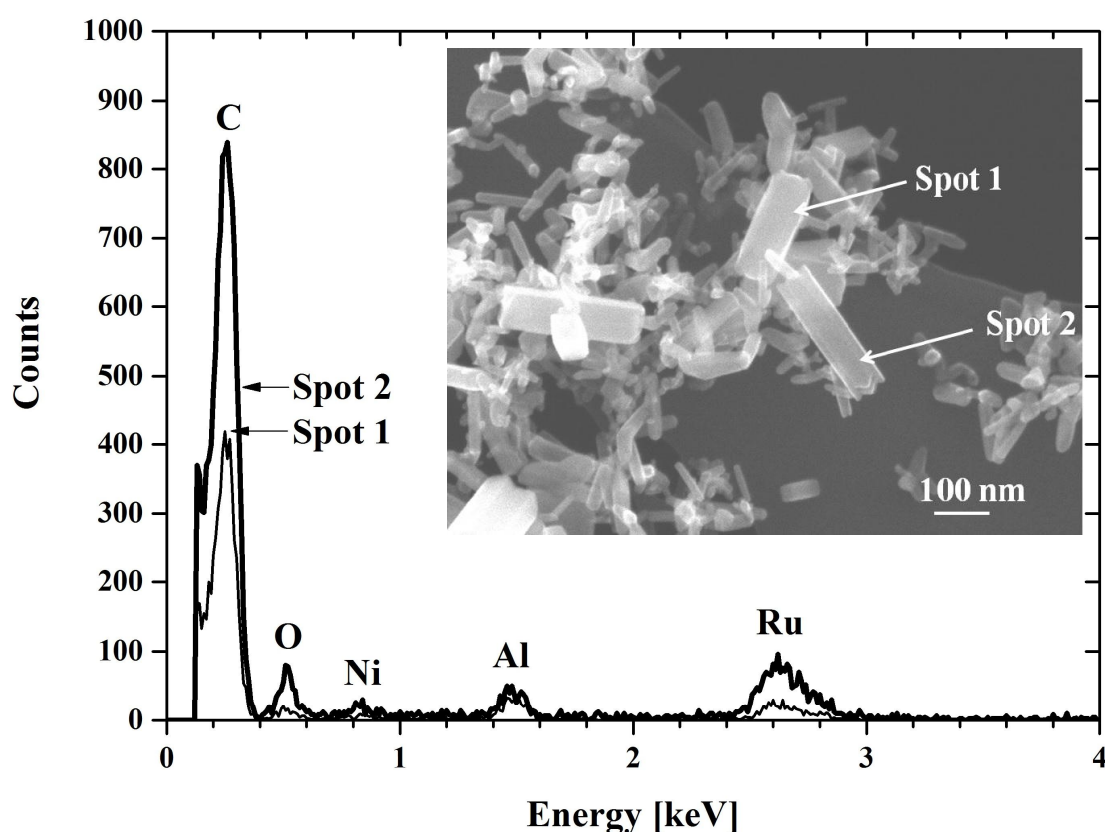


Figure 6. EDX spectra of spots #1 and #2 on ruthenium particles (experiment 1). The recorded true counts of spot #2 are multiplied by two.

Raman analysis

The particle deposits on the surface of furnace tube, which were formed by vapour condensation and by particle diffusion/impaction, as well as, the samples of particles collected directly from the gas phase on a quartz glass surface were analysed using Raman spectroscopy. The selected measured spectra are presented in Figure 7. The deposited sample exhibited typical bands of RuO_2 at 524, 643 and 710 cm^{-1}

corresponding to E_g , A_{1g} and B_{2g} modes. Similar shifts and broadening of the Raman bands are reported in the literature for small crystallites of RuO_2 [26], RuO_2 aerogels [27] and thin films [28]. An additional doublet was observed at about 1390 cm^{-1} and 1420 cm^{-1} in the Raman spectra, which is assigned to Al_2O_3 signal.

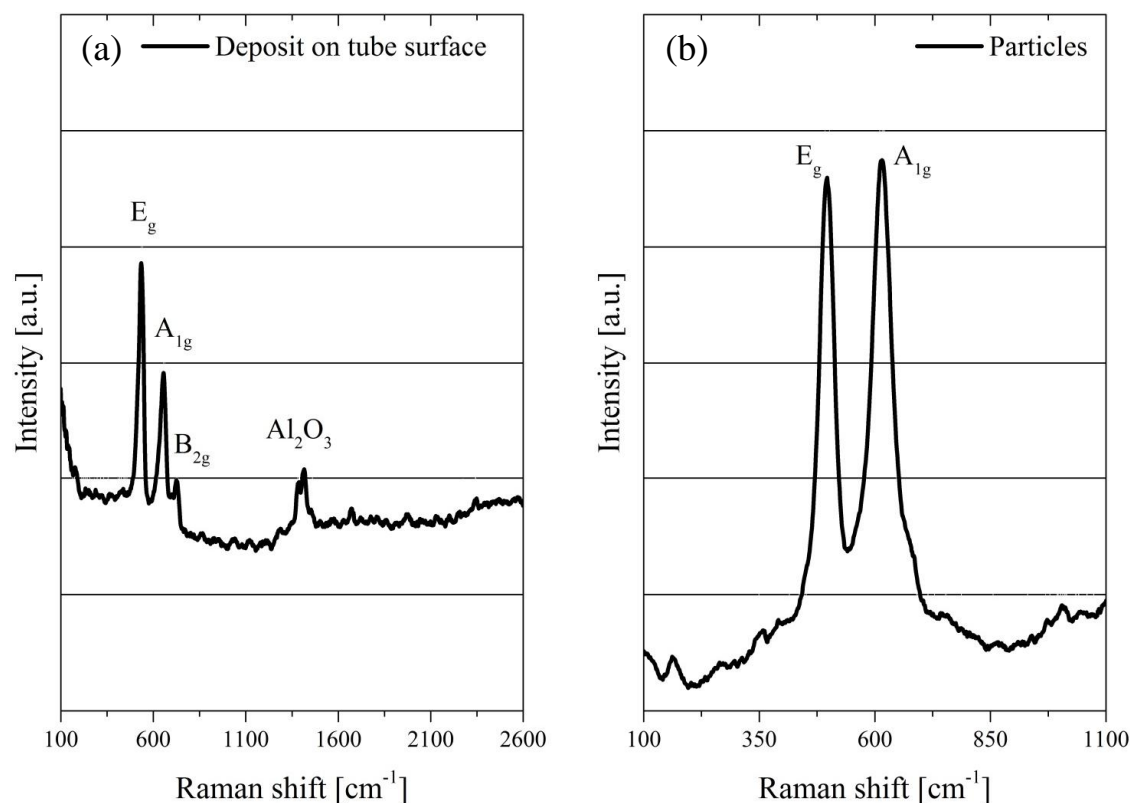


Figure 7. Raman spectra of (a) a particle deposit on the surface of furnace tube and (b) of particles collected from the gas phase on a quartz glass surface.

The particles collected from the gas phase showed identical Raman spectra in every experiment; two distinct vibrational peaks were located at ca. 505 cm^{-1} and 624 cm^{-1} . A typical Raman spectrum is presented in Figure 7. The bands may be assigned to RuO_2 . The observation of $15\text{--}20\text{ cm}^{-1}$ red-shifts in peak position and different intensity ratios have already been noticed [29] and attributed to the nanoscale nature of the oxide, significantly influenced by physical and/or chemical processes. The broadening of the peaks is related to a less-ordered structure.

XPS analysis

The chemical speciation of the transported particles collected from the gas phase in all experiments was analysed also with XPS technique. The samples were prepared with the same way and at the same time as for the Raman analysis, see above.

As a result of the analysis, the binding energies of ruthenium, oxygen, and silver (if used in the experiments) were obtained. The reference values of the binding energies used in the evaluation of the data are presented in Table 5. A summary of the obtained ruthenium binding energies from the samples and also of anhydrous RuO_2 powder can be found in Table 6.

Table 5. Reference values of binding energies for various ruthenium compounds.

Compound	Ru 3d5/2 binding energy (eV)
RuO ₄	283.3 [30]
RuO ₂	280.5 this study
RuO ₂ .xH ₂ O	282.1 [16]
metal Ru	280.0 [30]
RuCl ₃ .3H ₂ O	282.7 [31]
Ru(NO)(NO ₃) ₃	282.3 [32]

Table 6. The measured binding energies of ruthenium 3d5/2 and silver 3d5/2 lines on the aerosol deposit samples.

Exp. [#]	Ru 3d5/2 binding energy (eV)	Ag 3d5/2 binding energy (eV)	Identified compounds
RuO ₂ powder	280.7±0.1	-	
1	280.7±0.1	-	RuO ₂
2	280.7±0.1	-	RuO ₂
3	280.7±0.1	-	RuO ₂
4	280.8±0.1	-	RuO ₂
5	280.7±0.1	-	RuO ₂
6	280.7±0.1	367.5±0.1; 368.3±0.1	RuO ₂ AgO
7	280.7±0.1	367.5±0.1; 368.3±0.1	RuO ₂ AgO

As can be seen in Table 5, the binding energy of Ru 3d 5/2 peak was within the region of 280.7-280.8eV in all experiments. This result is in very good agreement with the binding energy of ruthenium in a pure RuO₂ compound. The measured XPS spectra from ruthenium 3d5/2 region obtained from the commercial anhydrous RuO₂ powder and from the aerosol deposits of experiments are presented in Figure 8. A very good agreement between the samples and reference powder can be seen. Thus, it can be concluded that ruthenium aerosols in the gas flow were consisting of pure RuO₂ regardless of the varying composition of the flow in the experiments. It is notable that in experiments containing NO₂ gas as an additive, the chemical speciation of ruthenium aerosols remained the same as in experiments performed in dry or humid air. Therefore, it seemed that ruthenium oxides did not form ruthenium-nitrogen compounds. Surprisingly, XPS measurements on the sample from experiment 5, in which silver particles were fed into the gas flow, did not reveal formation of any silver compound in

the experiment. This observation is in agreement with the results obtained from INAA analysis on the aerosol samples, where no silver isotopes were detected. Although the number concentration of silver particles was very low due to their initial high mass/large diameter and due to the desired mass concentration of silver in the precursor solution, it still remains unclear why silver particles were not detected on the filter. Further investigations of other deposit samples are being conducted.

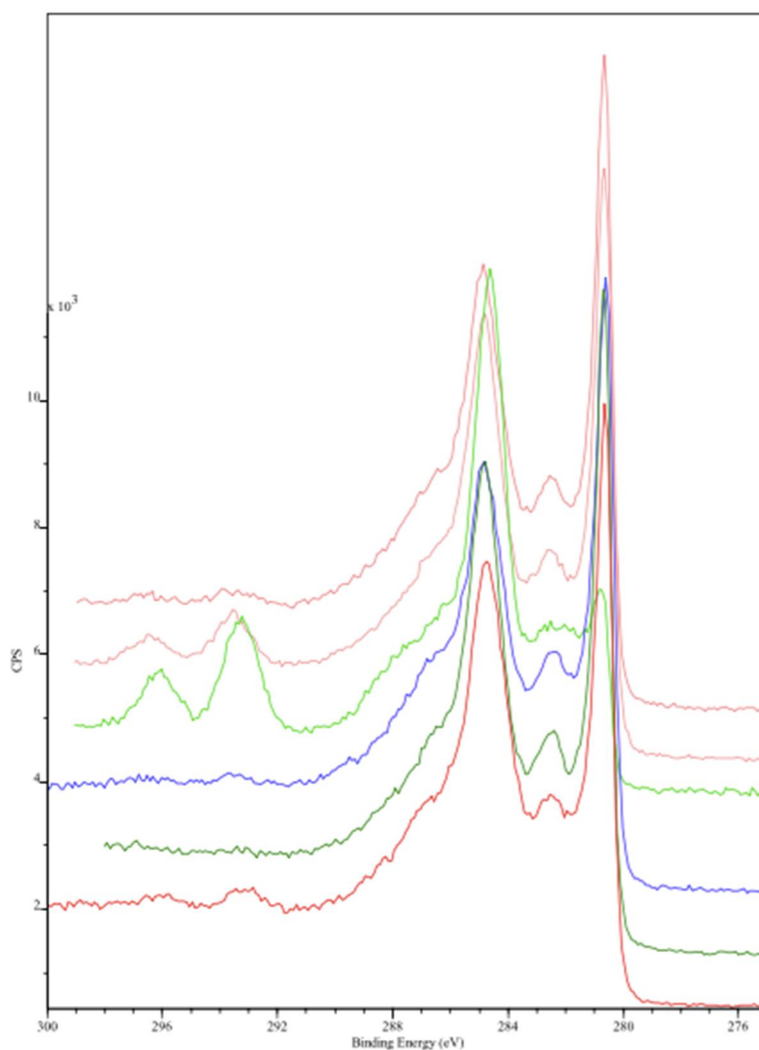


Figure 8. XPS spectra of Ru 3d_{5/2} region obtained from the samples of transported particles and reference anhydrous RuO₂ powder.

Summary and conclusions

The aim in this study was to determine the effect of different atmospheric compositions 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 amount of gaseous and particulate ruthenium transporting through the circuit to the containment conditions. Thus, the outcomes provide

necessary information for the development of SA modelling and ruthenium source term analysis purposes.

A set of performed experiments included investigations on the effect of dry and humid air atmospheres on the transport of ruthenium. In addition, NO_2 gas, AgNO_3 droplets or silver particles were also mixed with the air atmospheres. These additives were representative of particles and air radiolysis products expected in a nuclear accident.

The release rate of ruthenium (not of the oxides) from RuO_2 powder at 1227°C was determined to be ca. 6.1 mg/min in dry conditions. A feed of a low amount of steam (ca. 1512 ppmV) into the system lowered the release to ca. 5.6 mg/min. In other experimental conditions, the release rate of ruthenium was within the range of 5.6-6.1 mg/min. The rather similar release rates of ruthenium from the crucible indicate that except of humidity there was no significant effect by additional particle or gas feed on the release of ruthenium in these experimental conditions.

The trapping of the transported ruthenium was performed separately for gaseous RuO_4 and for ruthenium aerosols originating mainly from the thermal decomposition of RuO_3 to RuO_2 at the outlet of the furnace. During the experiments, the major part of the released ruthenium was deposited on the surfaces of the facility (up to 91.6 %). A significant amount of ruthenium was deposited near the furnace outlet, where the temperature gradient was the highest. At that location, the thermal decomposition of RuO_3 into solid RuO_2 particles took place.

The mass of ruthenium transported through the outlet of facility was quantified and a notable impact of different conditions on the aerosol/gas ratio was observed. Humid conditions increased the fraction of transported aerosols with a lowering transport of gaseous RuO_4 when compared to the dry air conditions. The increase in particle transport was also observed with online measurement devices and the number concentration of particles was doubled at humid conditions. A very significant effect of NO_2 on the ratio between aerosol and gaseous form of ruthenium reaching the outlet of model primary circuit was observed. NO_2 gas in concentration of 75 ppmV increased the fraction of gaseous RuO_4 by two orders of magnitude, which leads to a significantly higher RuO_4 concentration in the containment building when compared to the pure air experiments. It is notable, since NO_2 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 (both on number and mass basis) decreased significantly, which could be detected with online measurement devices. A feed of silver aerosol into the air flow lowered gaseous ruthenium transport by two orders of magnitude when compared to the experiments conducted at humid atmosphere. When both NO_2 gas and silver particles were fed in form of AgNO_3 droplets into the air flow, the fraction of gaseous ruthenium (RuO_4) 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 AgNO_3 to the flow of ruthenium oxides enhanced the transport of particles through the model primary circuit and kept the particle transport on a more stable level when compared with other experiments.

The chemical speciation analysis of the transported aerosol particles with XPS verified the formation of RuO₂, which was also indicated by the typical needle shaped crystals shown in SEM micrographs. Raman analysis supported the conclusion on the formation of RuO₂.

The results obtained within ATR study indicate a very strong effect of the aerosol/radiolysis products in the gas flow through 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 atmosphere. Due to the expectation of aerosols and air radiolysis products occurrence in the atmosphere during a severe nuclear accident, ATR study brings new insight into the behaviour of ruthenium during a severe nuclear accident.

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Title	Impact of Aerosols on the Transport of Ruthenium in the primary circuit of nuclear power plant
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Abstract max. 2000 characters	<p>In the NKS-ATR activity (year 2014) by VTT Technical Research Centre of Finland and Chalmers University of Technology the aim was to study the effect of aerosols and air radiolysis products on the transport of gaseous and particulate ruthenium species through a model primary circuit. The radiotoxicity of ruthenium oxides is near that of iodine in the short term and near that of caesium in the long term. All experiments were conducted using VTT's Ru transport facility at 1227 °C with dry or slightly humid air as the main carrier gas. The results show that the impact of additional NO₂ gas feed (75 ppm volume) to the flow of ruthenium oxides (in humid air) was significant both on the transport of ruthenium through the facility and on the speciation of the transported ruthenium. Transport of gaseous RuO₄ was increased significantly, whereas at the same time the amount of aerosols reaching the filter was decreased. However, the release of ruthenium from the crucible was similar as in an experiment without NO₂ (in air atmosphere). This indicates that the molar ratio of RuO₃/RuO₄ in the gas flow had changed. A proposed explanation is based on the oxidation of RuO₃ to RuO₄ by NO₂.</p> <p>On the other hand, when only pure silver particles (diameter 0.5-1.0 µm) were fed to the humid air flow, the transport of RuO₄ decreased significantly. Most likely, gaseous RuO₄ had reactively condensed on the surface of silver particles as RuO₂. Addition of both silver particles and NO_x in a form of , NO₃ droplets (which decomposed to silver and NO₃ when heated and further to NO₂, NO and O₂) to the flow of Ru oxides (in humid air) enhanced the transport of gaseous RuO₄ as well, but not as much as in case of NO₂ feed. In these experiments (with NO₂ or AgNO₃), the observed transport of gaseous ruthenium seemed to be several orders of magnitude higher than in the previous experiments with only pure ruthenium oxides in the air atmosphere. These results indicate that the composition of gaseous atmosphere in the primary circuit has a significant effect on the amount and chemical form of ruthenium transported to the containment during a SA.</p>
Key words	Ruthenium, Aerosol, Air radiolysis, Severe Accident, Source Term