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Experiments on the behaviour of ruthenium in air ingress accidents

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Abstract

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In a severe accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium may oxidise and form volatile ruthenium species, RuO3 and RuO4, which can be transported into the containment. In order to estimate the amount of gaseous ruthenium species, it is of interest to know, how they are formed and how they behave.

In our experiments the formation and transport of volatile ruthenium oxides was studied by exposing RuO2 powder to diverse oxidising atmospheres at a relatively high temperature. Transport of gaseous RuO4 was further investigated by injecting it into the facility in similar conditions. Upon cooling of the gas flow RuO2 aerosol particles were formed in the system. They were removed from the gas stream with plane filters. Gaseous ruthenium species were trapped in 1M NaOH-water solution, which is capable of trapping RuO4 totally. Ruthenium in the solution was filtered for analysis. The determination of ruthenium both in aerosol and in liquid filters was made using instrumental neutron activation analysis (INAA). In order to close the mass balance and to achieve better time resolution seven experiment were carried out using radioactive tracer.

In this report, the facility for the ruthenium behaviour study and results from experiments are presented. Preliminary conclusions from the experiments are reported as well. Final conclusions will be made after modelling of the facility is completed in a continuation work of this study.

Key words

ruthenium, nuclear safety, fission product, aerosol sampling and transport

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Experiments on the behaviour of ruthenium in air ingress accidents – final report

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Summary

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In a severe accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium may oxidise and form volatile ruthenium species, RuO_3 and RuO_4, which can be transported into the containment. In order to estimate the amount of gaseous ruthenium species, it is of interest to know, how they are formed and how they behave.

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1. Introduction

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. Ruthenium is produced in 15.8% of the fissions of ^{235}U. Approximately 70% of fission product ruthenium is in stable form. The quantity of produced ruthenium increases with fuel burnup and with fuel enrichment in ^{235}U [Seelmann-Eggebert et al. 1974]. The radiotoxicity of ruthenium comes essentially through its isotopes ^{103}Ru ($T_{1/2}$=39.3 days) and ^{106}Ru ($T_{1/2}\cong$1 year). It is important both short- and middle term radiocontaminant. The radiotoxicity of ^{106}Ru is high, comparable to that of ^{131}I. ^{103}Ru is considered to have moderate radiotoxicity as for example ^{137}Cs [Mun et al., 2006].

In a severe accident in a nuclear power plant it is possible that air gets into contact with the overheated reactor core. In this case ruthenium may oxidise and form volatile ruthenium species, RuO_3 and RuO_4, which can be transported in the containment. In contrast to many other fission products the oxide forms of ruthenium are more volatile than the metallic form [Jokiniemi and Zilliacus 2001]. Ruthenium chemistry has been discussed in an earlier study [Backman et al., 2004].

In order to verify, whether radioactive ruthenium would be transported in gaseous form within a nuclear facility, it is of interest to know how its volatile compounds are formed and how they behave. In our experiments the formation and transport of volatile ruthenium oxides was studied by exposing RuO_2 powder to diverse oxidising atmospheres at a relatively high temperature. Transport of gaseous RuO_4 was further investigated by injecting it into the facility in similar conditions. The most important experimental parameters are temperature of the furnace, composition of the humid oxidising atmosphere and material of the tubing.

2. Experimental facility

2.1 Facility for ruthenium release and transport experiments

The system used for the ruthenium experiments is schematically presented in figure 1. The main component of the system was the tubular flow reactor, in which the ruthenium source (RuO_2 powder) was heated. The tubular flow reactor (Entech, ETF20/18-II-L) used was 110 cm long and had two heating zones, each 40 cm long. The tube material in the reactor was high purity alumina. The ceramic crucible with the RuO_2 powder (about one gram per experiment) was placed over the second heating zone of the reactor.

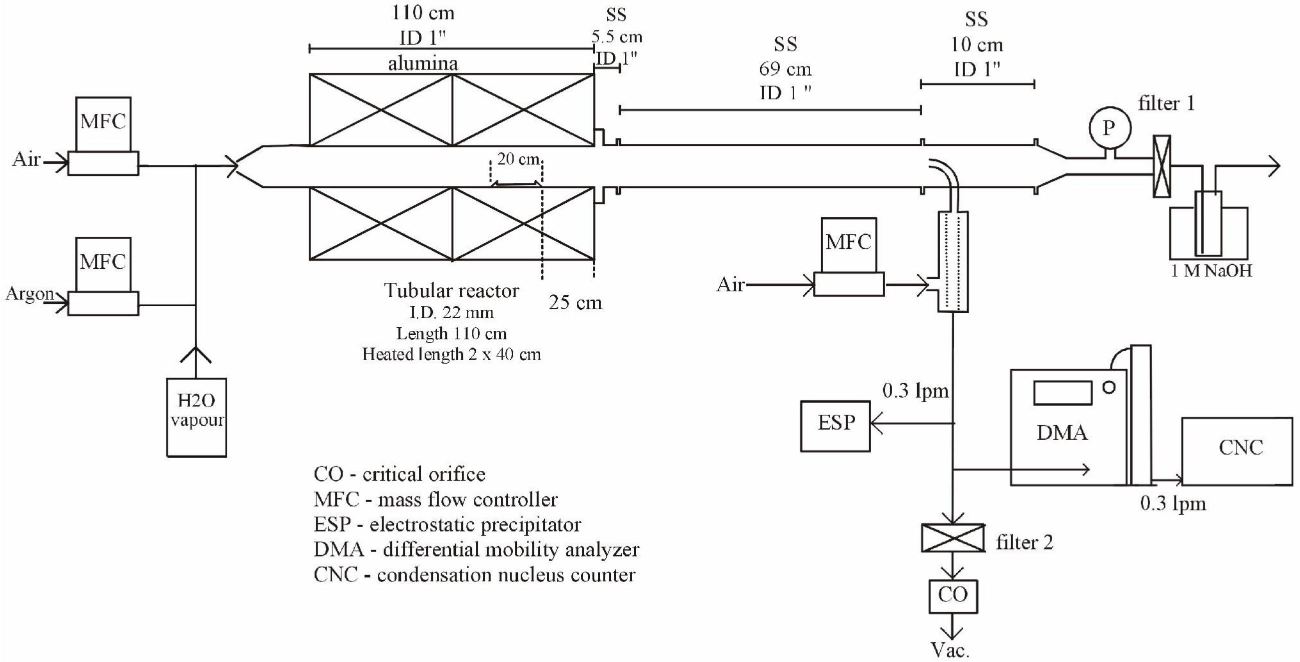

Figure 1. Experimental set-up for ruthenium experiments.

Non-condensable gas flow through the furnace was controlled with mass flow controllers (Tylan FC-2900M and Brooks 5851S). Water was added to the gas stream either by saturating gas flow in a bubbler, placed in temperature controlled water bath (temperature 30°C), or by adding superheated steam directly into the gas stream. Saturated gas flow went into the furnace through an inlet section heated up to 70°C. During steam feed inlet section was heated to 100°C.

As the gas exited the reactor, it cooled in a stainless steel (AISI 316L) tube and the gaseous ruthenium oxides decomposed partly to solid RuO_2. Aerosol particles were filtered out at point 106 cm downstream of the reactor. The filters used were polycarbonate plane filters (Nuclepore). Gaseous ruthenium was trapped downstream of the filter in a 1 M NaOH-water solution. The bubbler containing the trapping solution was placed in an ice-bath.

Gas-phase sampling was done at point 74 cm downstream of the reactor using a j-shaped probe pointing upstream in the flow. The sample was diluted with a porous tube diluter in order to minimise losses during dilution. The number size distribution of the particles was measured with differential mobility analyser (DMA, TSI 3081) and condensation nucleus counter (CNC, TSI 3022). The particles are size classified according to their electrical mobility by the DMA. The CNC counts the number of particles in each size class. The system was controlled with the Aerosol Instrument Manager software version 4.0 (TSI). The gas flow in the sampling line was filtered before being vented to the fume hood, using the same type of filter as in the main line. Transmission electron microscopy (TEM) samples were collected on holey carbon coated copper grids using an electrostatic precipitator (ESP). Aerosol sampling was not conducted in radiotracer experiments.

2.2 Facility for experiments with gaseous RuO_4 injection

The system used for the gaseous RuO_4 injection experiments was almost identical to system in figure 1. The system to feed gas at the inlet was changed, aerosol sampling line was not connected and in some experiments part of the stainless steel tubing was replaced with alumina tubes.

Gaseous RuO_4 was produced in a distillation flask. The procedure was to first dissolve $RuCl_3$ in 5 ml of concentrated HCl-water (1:1) solution. The solution (Ru 27.9 mg / ml) was mixed with 100 ml of concentrated H_2SO_4 in a distillation flask. By heating the flask gently up to approximately 100°C chlorine was distilled out of the solution. RuO_4 gas could then be produced by adding a drop of oxidizing agent, $KMnO_4$ or H_2O_2, from a dropping funnel into the solution. Reaction was vigorous and gas temperature in the distillation bottle rose up to 85°C. Air flow of 1 l/min (NTP) carried the produced RuO_4 gas into the facility. Before entering the furnace carrier gas was mixed with air flow of 4 l/min (NTP) that had been saturated at 30°C with water in a thermo stated bubbling bottle. Both gas flows were controlled using mass flow controllers (Tylan FC-2900M and Brooks 5851S).

In three experiments the first 64 cm of the stainless steel tube was replaced with alumina tube of the same length and diameter.

2.3 Analytical methods

The detection limit for ruthenium with instrumental neutron activation analysis (INAA) using 3 hour irradiation time is 2 μg/sample. The amount of the solution that can be irradiated in the reactor limits the determination of ruthenium from liquid samples. Therefore, the trapping solution was heated on a sand bath and ethanol was added to reduce ruthenates to RuO_2. The solution was filtered and ruthenium on the filter paper was irradiated for 1 minute. Gamma measurements of the irradiated filters were conducted one day after irradiation. Aerosol filters applied in the experiments were analysed similarly using INAA.

Morphology of collected RuO_2 particles was analysed with transmission electron microscope (TEM). Selected area electron diffraction (SAED), which was connected to TEM, was applied in study of the crystal structure of the particles. The lattice structure and spacing, measured from the diffraction image, could be applied in the identification of the studied crystals.

Few RuO_2 samples were analysed with XPS (X-ray Photoelectron Spectroscopy). XPS uses an X-ray source to ionise electrons from the surface of a solid sample. The binding energy of these electrons are measured and are characteristic of the elements and associated chemical bonds (chemical state) in the top few atomic layers of the material.

3. Experimental matrix

Altogether seventeen experiments were carried out during the project. The details of the experiments can be found in table 1. Table contains also details of two experiments done in the previous project [Backman et al., 2004] – experiments A and B. The main parameters varied in the experiments were furnace temperature, composition of the gas flow and source of ruthenium oxides. In order to facilitate comparison between different experiments, flow rate through the facility was mainly kept constant at 5 l/min (NTP). The length and diameter of the tubing after the furnace was also the same in most experiments, although in experiments 14, 15 and 17 the tube material was changed.

Table 1. Details of the experiments during years 2005-2006.

Exp #	Reactor T K	Flow rate lpm	Gas	Tube material (from furnace to filter)	Duration min	Other
A	1500	5	Air	SS (106 cm)	42	Previous project
B	1700	5	Air	SS (106 cm)	20	
1	1300	5	Air sat. w. H_2O	SS (106 cm)	45	-
2	1700	5	Air sat. w. H_2O	SS (106 cm)	40	-
3	1700	5	Air sat. w. H_2O	SS (96 cm)	360	revaporisation
4	1500	10	Steam/Ar/Air 25/45/30	SS (106 cm)	23	higher flow rate
5	1100	5	Steam/Ar/Air 10/60/30	SS (106 cm)	372	-
6	1500	5	Air sat. w. H_2O	SS (106 cm)	41	radiotracer
7	1300	5	Steam/Ar/Air 10/60/30	SS (106 cm)	45	radiotracer
8	1300	5	Steam/Ar/Air 50/20/30	SS (106 cm)	45	radiotracer
9	1300	5	Air	SS (106 cm)	45	radiotracer
10	1700	5	Steam/Ar/Air 10/60/30	SS (106 cm)	40	SS-plate preparation
11	1700	5	Steam/Ar/Air 10/60/30	SS (106 cm)	190	revaporisation
12	1500	5	Steam/Ar/Air 10/60/30	SS (106 cm)	46	SS-plate preparation
13	1500	5	Steam/Ar/Air 10/60/30	SS (106 cm)	190	revaporisation
14	1500	5	Air sat. w. H_2O	AlO_3 (64 cm) SS (42 cm)	45	RuO_4 inject
15	1500	5	Air sat. w. H_2O	AlO_3 (64 cm) SS (42 cm)	210	RuO_4 inject, radiotracer
16	1500	4	Air sat. w. H_2O	SS (106 cm)	35	RuO_4 inject, radiotracer
17	1500	4	Air sat. w. H_2O	AlO_3 (64 cm) SS (42 cm)	50	RuO_4 inject, radiotracer, SS-plates, CsI

Oxidation of RuO_2 sample and subsequent transport of ruthenium oxides in air flow was studied in experiments 1, 2, 6 and 9. In three of these experiments the gas flow was saturated with water vapour at 30°C, while experiment number 9 was conducted in dry air. Reactor set point in these experiments was either 1300 K, 1500 K or 1700 K. Duration of these experiments varied between 40 and 45 minutes. Revaporisation of previously deposited ruthenium in air flow was studied in experiment number 3. In this experiment temperature of the reactor was 1700 K and the duration of the experiment was 360 minutes.

In steam feed experiments 4, 5, 7, 8 and 10-13 the temperature ranged from 1100 K to 1700 K. The gas flow was a combination of steam, argon and air. In these experiments oxygen partial pressure was kept constant even though steam volume fraction was changed. Experiments 11 and 13 were revaporisation experiments without RuO_2 powder sample. In these experiments the furnace tube was the same as used in the previous experiment. The duration of both revaporisation experiments was 190 minutes. Duration of other steam feed experiments varied between 23 and 46 minutes except for experiment number 5. The duration of that experiment was 372 minutes, because the temperature was very low.

In preparation of gaseous RuO_4 transport experiments, four out of eight stainless steel sample plates (SS 316L, size 15 mm x 20 mm) were oxidised in steam-nitrogen atmosphere at 1273 K. Duration of oxidation was 330 minutes. During experiments 10 and 12 two metallic and two oxidised stainless steel sample plates were coated with RuO_2 particles.

Experiments 14-17 were gaseous RuO_4 transport experiments. The gas flow was a combination of air saturated with water and gaseous RuO_4. Carrier gas flow rate for RuO_4 injection should have been 1 l/min (NTP). Mixed with 4 l/min (NTP) nitrogen flow it should have resulted total flow of 5 l/min. Total flow rate in experiments 16 and 17 was only 4 l/min as the valve for carrier gas was not opened. Fortunately oxygen produced in the reaction bottle carried enough gaseous RuO_4 into the facility. Experiment 16 was done with a stainless steel tube after the furnace, whereas ceramic tube was used in experiments 14, 15 and 17. In addition, retention of gaseous RuO_4 on different surfaces was studied in experiment 17. Therefore previously prepared SS-plates were attached on the surface of the ceramic tube at two locations, 30 cm and 55 cm after the outlet of the furnace. For the same reason, a ceramic boat with CsI powder (mass 1 g) was placed inside the ceramic tube at location 65-90 cm after the furnace. Duration of the experiments ranged from 35 to 210 minutes.

In experiments 6-9 and 15-17 radioactive tracer was used in order to close the mass balance and to get on-line data about the behaviour of ruthenium.

4. Results

The results of the experiments are summarised in table 2. Table contains also results of two experiments done in the previous project [Backman et al., 2004] – experiments A and B. The amount of evaporated ruthenium is measured by weighting the crucible before and after the experiment. Mass of ruthenium in bubbler and in filters is determined with INAA. In the estimation of ruthenium release and transport rates it was assumed that the rates were constant throughout the experiment.

In experiments with gaseous RuO_4 injection the release of ruthenium from distillation flask dependent strongly on the amount of oxidizing agent as well as on the rate it was added to the flask. Therefore averaged ruthenium release or transport rates would be misleading and are not calculated.

Table 2. The amount and rate of released and transported ruthenium in various experiments. Values are presented as mass of ruthenium metal. The flow rate is scaled to 5 l/min (NPT) in all experiments.

Exp #	Reactor T K	Ru released mg	Bubbler mg	Filter mg	Release rate mg/min	Transport: gaseous mg/min	Transport: aerosol mg/min
A	1500	463.5	0.46	54.92	11.04	0.011	1.31
B	1700	507.8	0.79	126.0	25.38	0.055	8.82
1 (SS)	1300	88.5	4.80	0.6	1.97	0.17	0.021
2 (SS)	1700	777.0	0.16	> 123.3	19.43	0.0054	> 4.18
3 (SS)	1700		4.53	4.84		0.013	0.013
4 (SS)	1500	223.9	1.01	15.3	9.73	0.052	0.79
5 (SS)	1100	40.3	~ 0	0.26	0.11	~ 0	0.0007
6 (SS)	1500	247.5	0.05	52.0	6.04	0.0012	1.27
7 (SS)	1300	36.8	1.40	2.0	0.82	0.031	0.044
8 (SS)	1300	37.5	0.82	0.5	0.83	0.018	0.011
9 (SS)	1300	45.0	2.33	2.9	1.00	0.052	0.065
10 (SS)	1700	382.5	0.10	98.0	9.56	0.0025	2.45
11 (SS)	1700		1.10	0.6		0.0058	0.0032
12 (SS)	1500	296.3	~ 0.15	37.6	6.44	0.0033	0.82
13 (SS)	1500		0.17	0.33		0.0009	0.0017
14 (AlO_3)	1500	-	0.60	0.0			
15 (AlO_3)	1500	2.0*	0.17	0.06			
16 (SS)	1500	11.1*	0.19	0.74			
17 (AlO_3)	1500	22.7*	1.29	0.71	Ru trapped by CsI 0.74 mg		

* Ruthenium released means ruthenium transported into inlet of furnace.

4.1 Ruthenium release

Ruthenium release from the crucible took place as RuO_2 powder was oxidized to gaseous ruthenium compounds RuO_3 and RuO_4. As presented in earlier work, RuO_3 should be the major compound with RuO_4 comprising less than 10 mol-% of the released ruthenium [Backman et al., 2004]. Ruthenium release rate results are presented in figure 2. A couple of the presented release rates at dry conditions were measured in an earlier study [Backman et al., 2004]. Ruthenium release rate increased from 0.11 to 19.4 mg/min as temperature increased from 1100 K to 1700 K. This indicates that significant vaporisation of ruthenium take place at temperatures above 1100 K. According to the results, the release rate of ruthenium decreases with the decreasing oxygen partial pressure – as expected. Increasing steam partial pressure while keeping the oxygen partial pressure constant seemed to have no effect on release rate. Higher gas flow rate at 1500 K seemed to also increase ruthenium release rate.

The amount of gaseous ruthenium produced in RuO_4 injection experiments was comparable to the amount of RuO_4 released in previous experiments. It ranged from 2 to 23 mg. The amount of RuO_4 produced in experiment 14 could not be determined as the released amount was very small and radiotracer was not applied in the first injection experiment. The rate of gaseous RuO_4 injection depended on oxidation procedure and was generally faster than in the previous experiments.

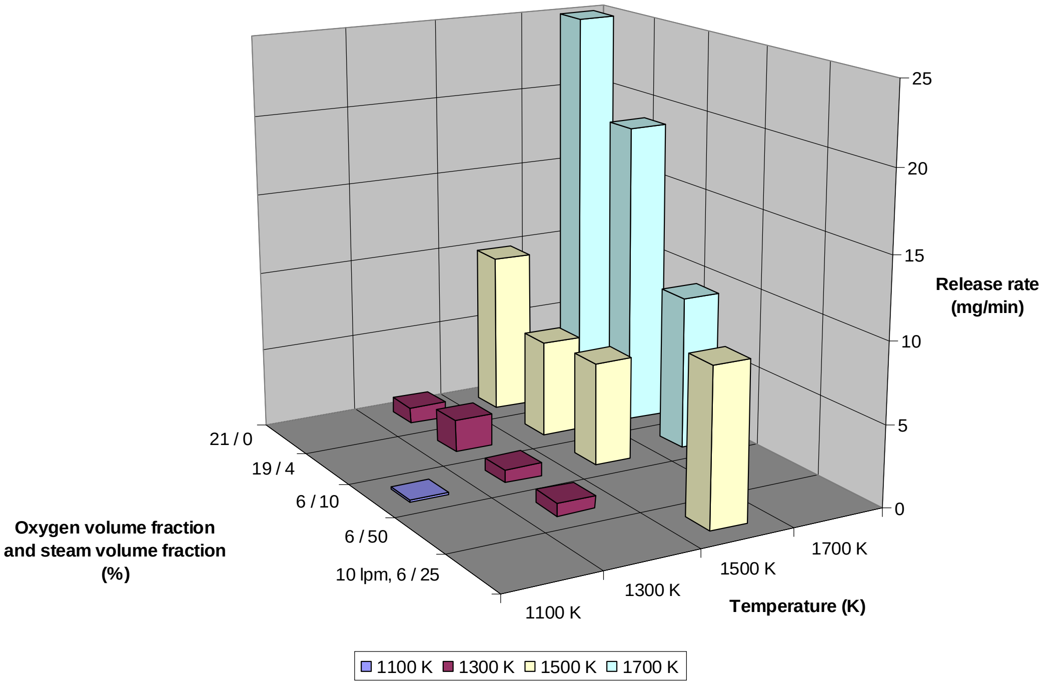

Figure 2. Ruthenium release rate (mg/min). Other axes are temperature (K) and oxygen volume fraction and steam volume fraction (%) in carrier gas flow. There is one experiment with 10 l/min flow rate.

4.2 Transport of ruthenium through the facility

The rate of ruthenium transported through the facility was determined by analysing the amount of ruthenium in the trapping bottle and in the aerosol filter downstream of the facility. When the transport rates were estimated, it was assumed that the rates remained constant throughout the experiment. The results from various experiments are presented in figure 3 for gaseous ruthenium and in figure 4 for particles (values as ruthenium metal). A couple of the presented transport rates at dry conditions were measured in an earlier study [Backman et al., 2004].

Most of the release from the crucible took place as gaseous RuO_3. Because RuO_3 thermally decomposes to solid RuO_2 as temperature decreased below approximately 800°C, a very large fraction of released ruthenium deposited on the surfaces of the facility. The transport of especially ruthenium oxide particles competed with the reaction on the surfaces. As the temperature of the furnace increased also the cooling rate increased. Fast cooling rate favours RuO_2 particle formation in the gas phase and decreases the fraction of RuO_2 deposited on the walls.

The lowest transport rate of ruthenium was measured at 1100 K. At this temperature only about 0.6% of the released ruthenium reached the outlet of the facility. The transport rate of gaseous ruthenium could not be determined at all as the amount of ruthenium in the trapping bottle was below the detection limit. The values are rather uncertain though due to a very low release rate.

At 1300 K the fraction of released ruthenium transported through the facility ranged from 9.2% to 11.7%, when the steam volume fraction was at most 10%. With steam volume fraction of 50% the transported fraction decreased to 3.5%. At this temperature transport rate of gaseous ruthenium was at its highest level although the release rate continued to increase as the temperature of the furnace was increased. Addition of a small amount of water vapour into the air flow increased gaseous ruthenium transport rate by factor of 3.3, when compared to dry air flow. When steam volume fraction was further increased, the transport rate decreased below that measured in dry air. However, it is likely that the observed decrease was more related to heating of the filter and the line at outlet. As the humidity was increased also the temperature of the walls had to be increased in order to avoid condensation. Gaseous ruthenium likely reacted with the metallic surfaces at slightly elevated temperatures as is explained in chapter 4.4. In air saturated with water vapour at 30°C the fraction of gaseous ruthenium of all ruthenium transported through the facility was as high as 89%. In dry air or at higher humidity the gaseous ruthenium fraction varied between 41% – 62%.

As the furnace temperature was increased to 1500 K the fraction of ruthenium transported through the facility increased and ranged from 12% to 21% depending on the experiment. At the same time a significant change in the gaseous ruthenium transport kinetics took place. When compared to experiment conducted at 1300 K the transport rate in dry air decreased by factor of about 3.8. Such change is not explained by changing chemical equilibrium, especially as the release of ruthenium increased substantially. The fraction of gaseous ruthenium of all ruthenium transported through the facility at 1500 K ranged from 0.1% – 0.8%. Moreover, the transport of gaseous ruthenium seemed to be most significant in dry conditions. Decreasing oxygen volume fraction from 19% to 6 % did not essentially change the fraction of ruthenium transported in gaseous form. A most notable exception was experiment 4 done with a higher flow rate. In this experiment the fraction of ruthenium transported through the facility decreased to 8.7%, which suggests that the reaction on the surface became more efficient. At the same time the fraction of ruthenium transported in gaseous form increased significantly to 6.2%. In a revaporisation experiment, conducted at 1500 K without the RuO_2 sample, as much as 34% of the ruthenium was transported in gaseous form. Because revaporisation takes place primarily close to the outlet of the furnace at temperature significantly below 1500 K, it is understandable that also the result is closer to those found at experiments conducted at 1300 K.

Very similar behaviour was observed in experiments conducted at 1700 K. As the temperature was increased, the fraction of ruthenium transported through the facility increased again and ranged from 21% to 35% depending on experiment. The lowest transported fraction was measured in the 2nd experiment, in which all ruthenium trapped in the filter could not be analysed. The values presented in table 2 and in figure 4 thus under-estimate the true transport rate of RuO_2 particles. Due to a much higher release rate the transport rate of gaseous ruthenium increased slightly, when compared to experiment conducted at 1500 K. However, the fraction of ruthenium transported in gaseous form remained very small ranging from 0.1% – 0.6%. In the two revaporisation experiments conducted at 1700 K, the fraction of ruthenium transported in gaseous form was 48% and 65%. The average transport rate of gaseous ruthenium was higher in revaporisation experiments than it had been in the previous experiment conducted at the same temperature. It is thus likely that in all experiments at 1700 K, revaporisation of deposited RuO_2 could have been a significant source of gaseous ruthenium. Again it should be noted that in the revaporisation experiments, oxidation of ruthenium deposits must have taken place at a temperature significantly lower than 1700 K.

In experiments with RuO_4 injection 79% – 93% of produced gaseous ruthenium reached the inlet of the facility. $KMnO_4$ applied as the oxidising agent in experiments 14 and 15 produced a substantial amount of MnO_2 particles, which partially deposited on the tube surfaces. As it was feared that MnO_2 may influence gaseous ruthenium transport, H_2O_2 was used in its stead in the remaining two experiments. Unfortunately, in these two experiments the valve for the carrier gas was not opened and consequently a fraction of produced RuO_4 gas did not reach the facility. In experiments with alumina tube the fraction of ruthenium transported through the facility ranged from 9% –12%. The fraction of ruthenium transported in gaseous form ranged from at least 65% – 100%. The smallest fraction of gaseous ruthenium was measured in an experiment with stainless steel sample plates and a crucible filled with CsI powder placed inside the alumina tube. During the experiment 0.74 mg of ruthenium reacted with CsI most likely to Cs_2RuO_4. It should be noted though that almost 40% of ruthenium injected into the facility was deposited on stainless steel surfaces at the outlet of the facility. It is most likely that the retained ruthenium was transported in gaseous form and reacted with the heated surface. From these results it is obvious that in the previous experiments the main source of both RuO_2 particles and deposition within the facility was gaseous RuO_3 produced during the oxidation of the sample. It is clear as well that in the injection experiments ruthenium oxides did not reach thermo-dynamic equilibrium within the facility at 1500 K.

When the alumina tube was replaced with stainless steel tube in the 16th experiment, the fraction of ruthenium transported through the facility decreased to 8.4% and the fraction of ruthenium transported in gaseous form decreased to 20%. Stainless steel thus catalysed reaction of RuO_4 on its surface to RuO_2. The retention of RuO_4 was however much less significant than in previous experiments conducted with stainless steel tube at 1500 K. It seemed that RuO_2 particles enhanced dissociation of RuO_4 on stainless steel surface.

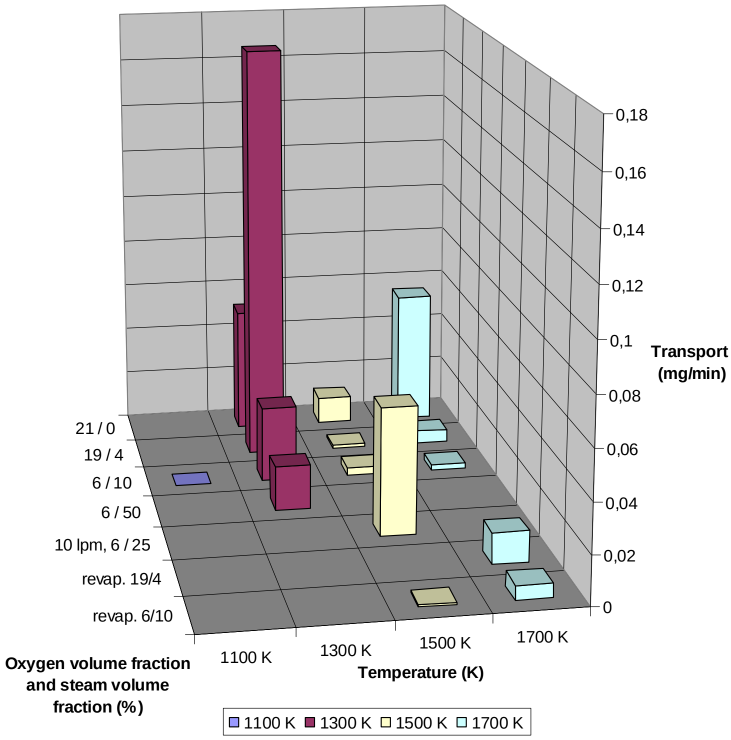

Figure 3. RuO_4 transport rate (mg/min). Other axes are temperature (K), oxygen volume fraction and steam volume fraction (%). The transport rates are also presented for experiments with 10 l/min flow rate and revaporisation.

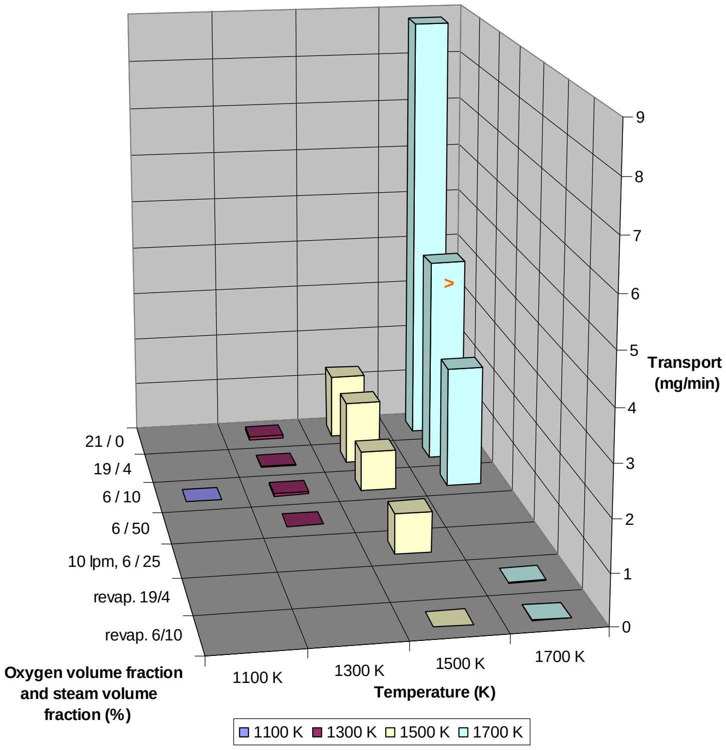

Figure 4. RuO_2 transport rate (mg/min). Other axes are temperature (K), oxygen volume fraction and steam volume fraction (%). The transport rates are also presented for experiments with 10 l/min flow rate and revaporisation.

4.3 On-line measurement of ruthenium transport

Activated RuO_2 powder was used as γ-tracer in experiments 6, 7, 8 and 9. Five detectors measured the activity in the facility on-line during the experiments. The measured locations were the powder sample in the ceramic crucible, ceramic tube at the outlet of the furnace, inlet of the stainless steel tube, aerosol filter and trapping bottle for gaseous ruthenium compounds. An additional detector was applied in experiment 9 to measure the activity of the stainless steel tube at location 25-35 cm downstream of the furnace outlet. Detectors measuring the filter, the bubbling bottle and the downstream location of the stainless steel tube were placed as close as possible to the section they measured. The other detectors were placed at a distance of 20 cm from their measurement location. All data from the online measurements is presented in appendix A.

The cumulative release of ruthenium and its cumulative transport to filter and to trapping bottle in experiment 6 is presented in figure 5. It can be seen, that the release rate of ruthenium at 1500 K was almost constant. It decreased only slightly probably due to the decreasing surface area of the powder sample. Ruthenium transport both as aerosol and as gas closely followed the kinetics of the release. It should be noted though that the transport of gaseous ruthenium to the trapping bottle was three orders of magnitude less than the transport of aerosol particles.

Cumulative release of ruthenium in experiment 9, conducted at 1300 K, is presented in figure 6. As in the previous experiment, the release rate seems to be slightly decreasing. However, scattering of the data is more significant than at 1500 K, because the amount of ruthenium released from the crucible is smaller. Release in experiments 7 and 8, conducted also at 1300 K, was very similar to that presented in figure 6. Results from these experiments are presented in appendix B.

Cumulative transport of ruthenium as aerosol in experiments conducted at 1300 K is presented in figure 7. As can be seen, the transport rate of aerosol particles decreased significantly as the steam volume fraction in the carrier gas increased. It seems that increasing steam partial pressure favours the formation of gaseous ruthenium species in expense of aerosol particles.

Cumulative gaseous ruthenium transport at 1300 K, presented in figure 8, seems to be much more complicated than the aerosol transport. It is likely that in experiments presented in figure 8, most of the ruthenium was transported in gaseous form. Gaseous ruthenium seemed to have mostly reacted with the heated stainless steel components at the outlet of the facility, before it reached the trapping bottle. As the steam partial pressure in the experiments was increased also wall temperature had to be increased in order to avoid condensation. Kinetics of the gaseous ruthenium transport, measured from the trapping bottle, depended mostly on the heating of these components. Therefore, the online measurements can not be applied in estimation of ruthenium transport in the facility.

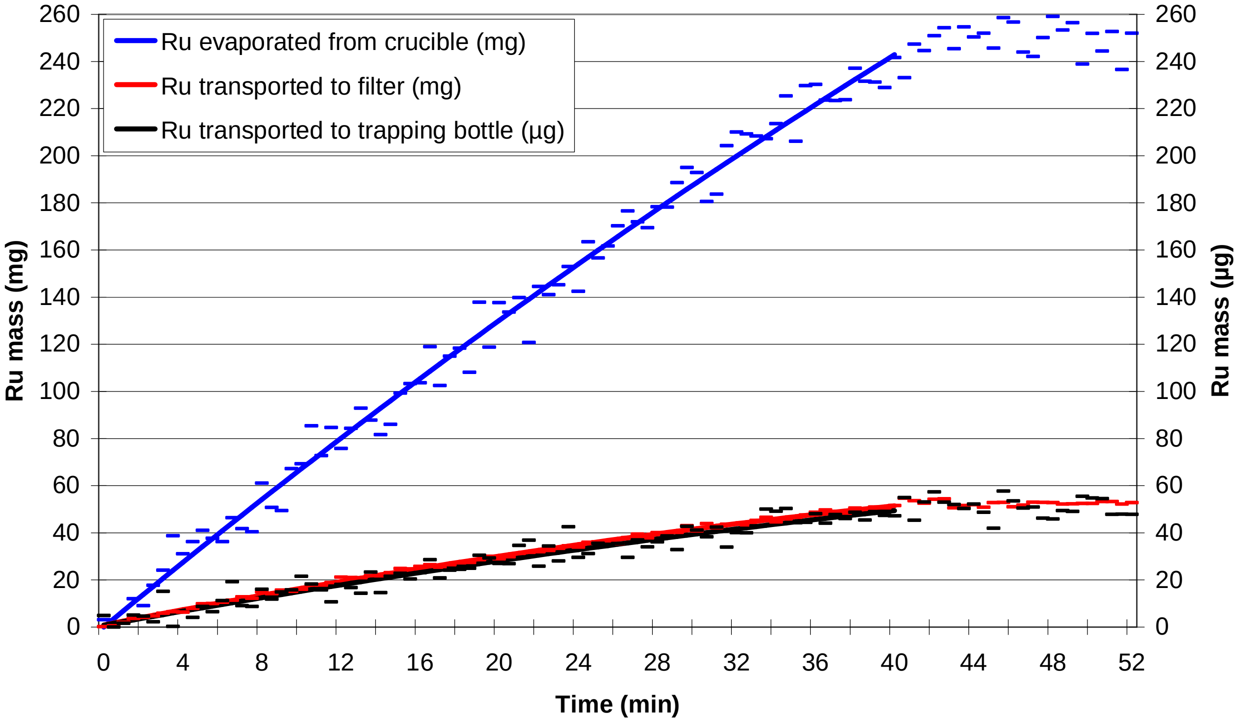

Figure 5. Ruthenium evaporated from crucible (mg), ruthenium transported to filter (mg) and ruthenium transported to trapping bottle (µg) in experiment 6. Furnace temperature was 1500 K and gas flow was air saturated with water.

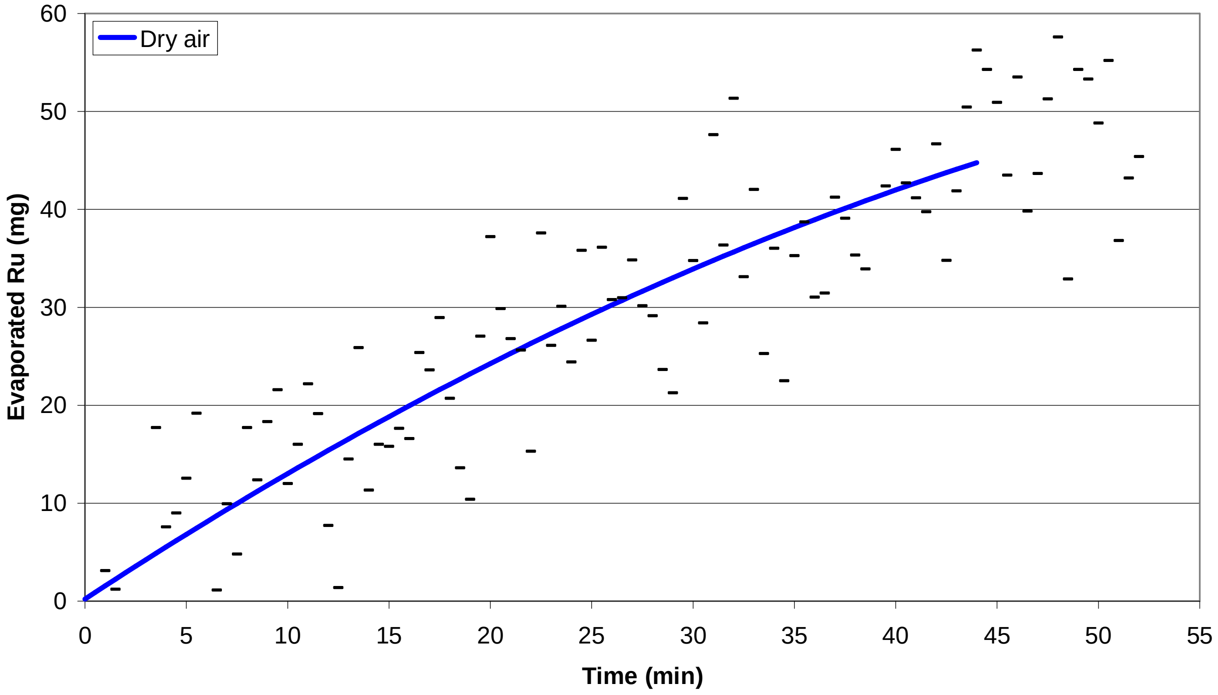

Figure 6. Ruthenium evaporated from crucible (mg) in experiment 9. Furnace temperature was 1300 K and gas flow was dry air.

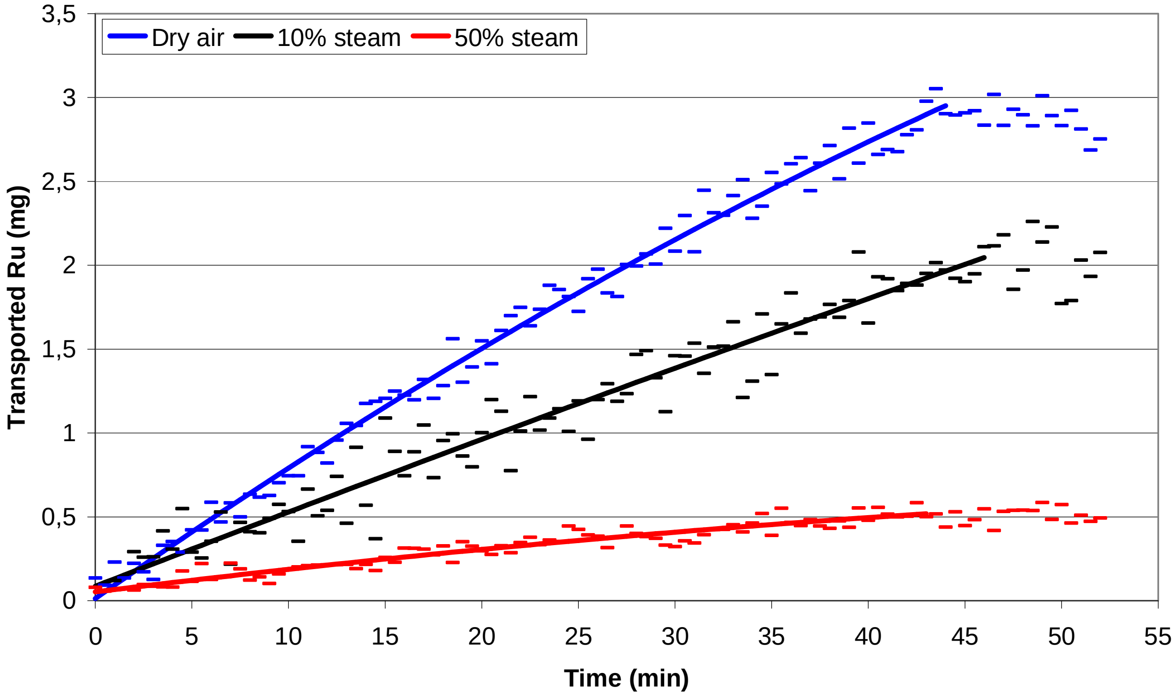

Figure 7. Ruthenium transported to filter (mg) in experiments 7 (black), 8 (red) and 9 (blue). Furnace temperature was 1300 K in experiments.

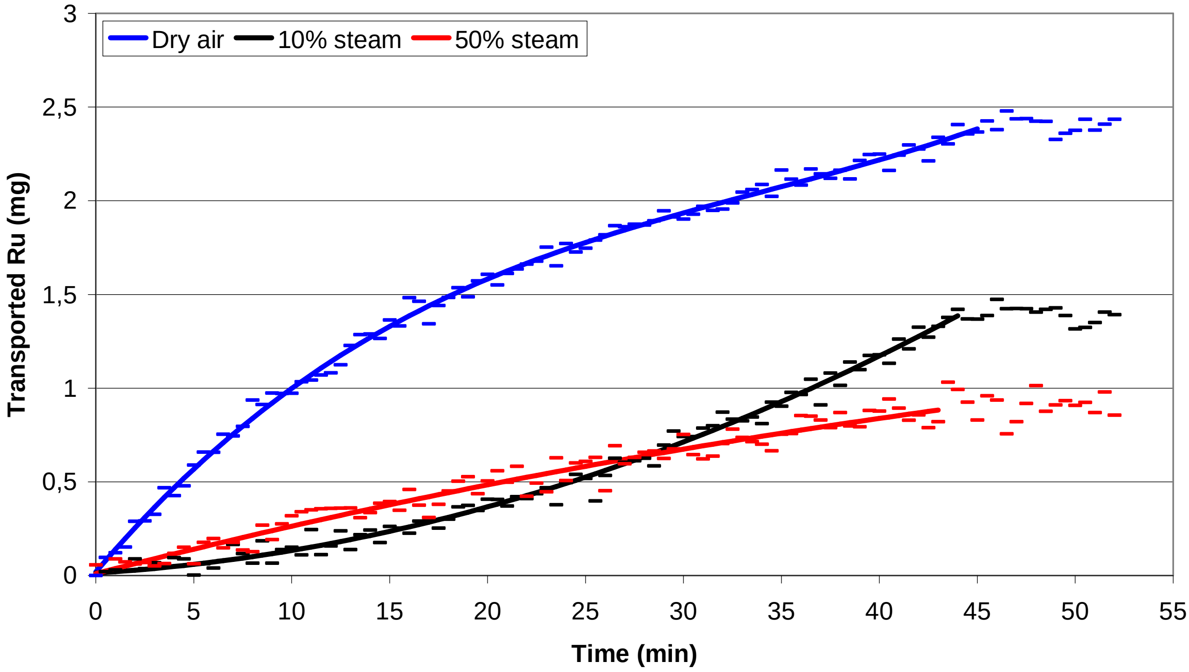

Figure 8. Ruthenium transported to trapping bottle (mg) in experiments 7 (black), 8 (red) and 9 (blue). Furnace temperature was 1300 K in experiments.

Transport rates of ruthenium in aerosol particles and of gaseous ruthenium in experiments 6, 7, 8 and 9 are presented in table 3. In the table the average values can be compared with the values at the beginning and at 40 minutes estimated from the online measurements. As could already be seen from figure 5, the transport rates decreased in experiment 6 conducted at 1500 K. At 1300 K the transport rate of particles was almost constant. Values for gaseous ruthenium transport at 1300 K are unreliable, because of extensive reaction at the outlet of the facility.

Table 3. Ruthenium aerosol and gaseous transport rates from calculated fitting curves (at moments t = 0 min and t = 40 min) and INAA analysis.

Exp.	Temperature (K)	Aerosol transport [mg/min]			Gaseous transport [µg/min]		
		t = 0 min	t = 40 min	INAA	t = 0 min	t = 40 min	INAA
6	1500	1.7	0.9	1.3	1.5	0.9	1.2
7	1300	0.04	0.04	0.04	6.4	52	31
8	1300	0.01	0.01	0.01	27	15	18
9	1300	0.08	0.06	0.07	123	30	52

4.4 Measurement of ruthenium deposition profiles

With the help of radioactive tracer it was possible to measure ruthenium deposition profile and to quantify the amount of ruthenium deposited in the tubes after experiments 6-9 and 16-17. The deposition profiles inside the ceramic furnace tube and stainless steel tube are presented in figure 9. They are given as proportion of ruthenium mass found per centimetre, as RuO_2, to released ruthenium. Ruthenium deposition profile in a previous study [Backman et al., 2004] is presented in figure 10. In that figure the profile is calculated as proportion of ruthenium mass found per four centimetres to released ruthenium. In both figures, furnace outlet is located at 0 cm.

All measured profiles share some common features. At first, it is important to note that there is no ruthenium deposition at the sample location or directly after it. The first deposition peak takes place inside the furnace at the end of the ceramic tube. In experiments 16 and 17 with gaseous RuO_4 feed the first deposition peak starts slightly later than in experiments with RuO_2 powder sample. At the location of the first deposition peak, there is a large temperature gradient, because the outlet of the furnace is insulated. Deposition likely takes place by thermal dissociation of RuO_3 to RuO_2, which is expected to take place as the wall temperature decreases to about 800°C.

The second deposition peak is at furnace outlet and is formed most likely by thermophoresis. Part of RuO_3 does not react on the wall but forms RuO_2 aerosol particles. These particles are driven to the wall by thermophoresis especially at the furnace outlet, where the temperature difference between the gas and the wall is very high.

The last peak is very clear in experiments 6 and 9 (at ca. 35 cm in the figure 9) as well as in RuO_4 injection experiments 16 and 17. It is probably formed as RuO_4 has decomposed to RuO_2 on stainless steel surface at about 100-150°C. As is explained in the next chapter, decomposition seems to be enhanced on metallic surface by deposited RuO_2 particles. Probably therefore the deposition peak was almost absent in experiments 7 and 8, in which formation of RuO_2 aerosol was very limited. In experiment 16, conducted with a stainless steel tube, the reaction seemed to have taken place all along the tube. In that experiment the tube was heated up to 100°C as the amount of water vapour produced in the generation of RuO_4 was not know. In experiment 17, peaks are very visible at locations around the stainless steel sample plates that were attached to the ceramic tube.

The fraction of ruthenium deposited on the tube surfaces and transported through the facility is presented in table 4. In experiments 16 and 17 the fraction of ruthenium deposited after the aerosol filter was measured as well. In experiment 6, conducted with RuO_2 powder sample at 1500 K, most of the ruthenium either deposited on the tube surface or was transported through the facility as aerosol particles. All released ruthenium was found, even though the stainless steel components at the outlet were not measured. In experiments 16 and 17 with RuO_4 feed a significant fraction of ruthenium was transported in gaseous form although the temperature of the furnace was 1500 K. It is likely that ruthenium oxides did not reach thermodynamic equilibrium within the facility. A significant fraction of the gaseous ruthenium reacted on the wall especially in experiment 16 conducted with the stainless steel tube. In both experiments decomposition of gaseous ruthenium within the heated stainless steel components before the trapping bottle was very significant. In both experiments the mass balance was better than 92%. In experiments 7-9, conducted at 1300 K, mass balance ranged only from 32% to 66%. It is very likely that in these experiments ruthenium was primarily transported in gaseous form. Gaseous ruthenium likely reacted before the trapping bottle in sections that were not measured in these experiments. It seemed that increasing steam volume fraction to 10% favoured formation of RuO_4. Further increase in the steam partial pressure seemed to have only a limited effect on ruthenium speciation.

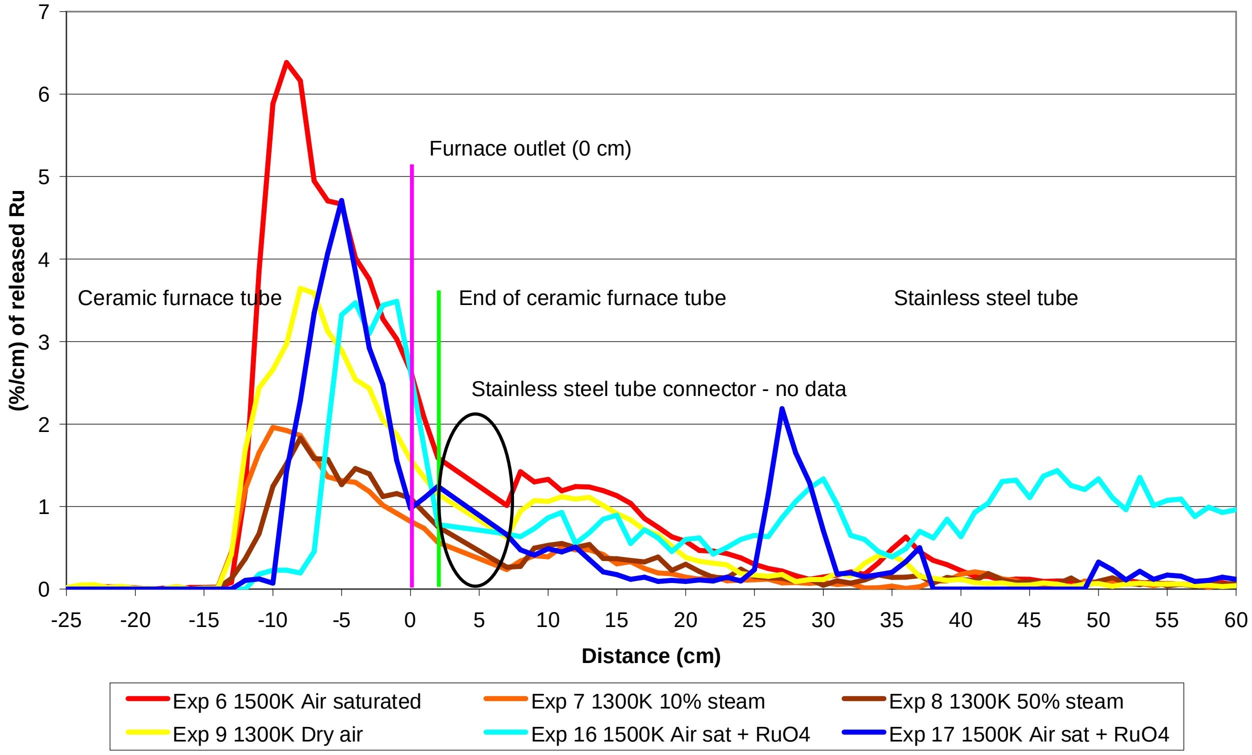

Figure 9. Ruthenium deposition profiles in the experiments 6-9 and 16-17. Deposition is proportion of Ru mass found (as RuO_2) of released Ru mass per one centimetre (%/cm). Furnace outlet is located at 0 cm. There is no deposition data from stainless steel tube connector (2-7 cm).

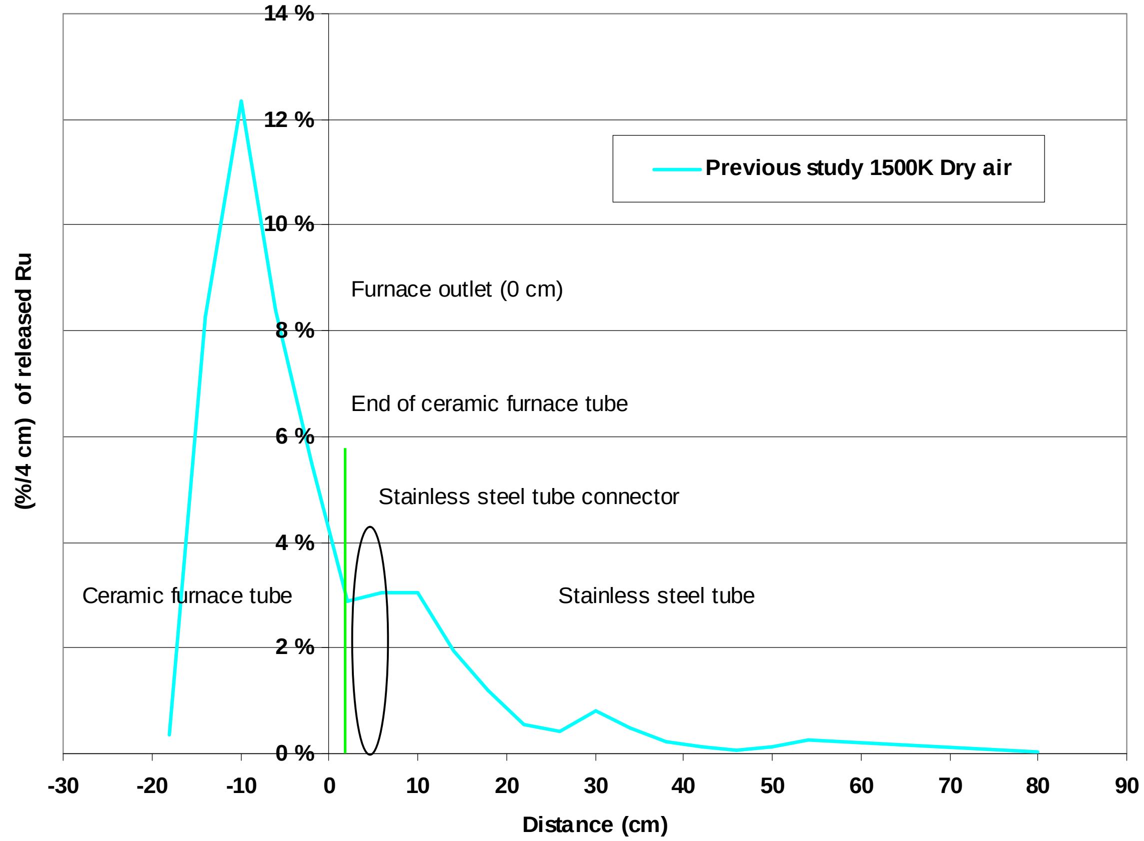

Figure 10. Ruthenium deposition profile in a previous study at 1500 K in dry conditions. Deposition is proportion of Ru mass found (as RuO_2) of released Ru mass per four centimetres (%/4 cm). Furnace outlet is located at 0 cm.

Table 4. Ruthenium deposited and found in experiments 6-9 and 16-17.

Exp.	Temperature [K]	Ru deposited [%]	Ru in tube line [%]	Ru in parts after tube line [%]	Ru transported [%]	Found [%]
6	1500	79.0	81.7	No data	21.0	102.7
7	1300	90.8	28.3	No data	9.3	37.5
8	1300	96.5	28.4	No data	3.5	31.9
9	1300	88.3	54.3	No data	11.7	65.9
16	1500	91.6	77.5	11.3	8.4	97.1
17	1500	91.2	44.6	39.3	8.8	92.6

4.5 Analysis of decomposed RuO_4 on Stainless steel sample plates

In experiment 17 altogether eight stainless steel sample plates were placed within the alumina tube downstream of the furnace. Four of the eight plates were oxidised at 1000°C in steam flow and four had metallic surface. Before the experiment RuO_2 particles were deposited on top of two oxidised plates and two metallic plates. The surface of the sample plates with aerosol deposits was analysed with XPS to confirm that ruthenium layer on plates was in form of RuO_2. XPS analysis was conducted in Surface Science group lead by Docent Jouko Lahtinen in Helsinki University of Technology, Laboratory of Physics. The result of the analysed deposit for one oxidised and one metallic plate is presented in figure 11. The results show that the deposit on both surfaces is indeed RuO_2 with a possible trace of RuO_3. Neither of the samples contained any metallic ruthenium.

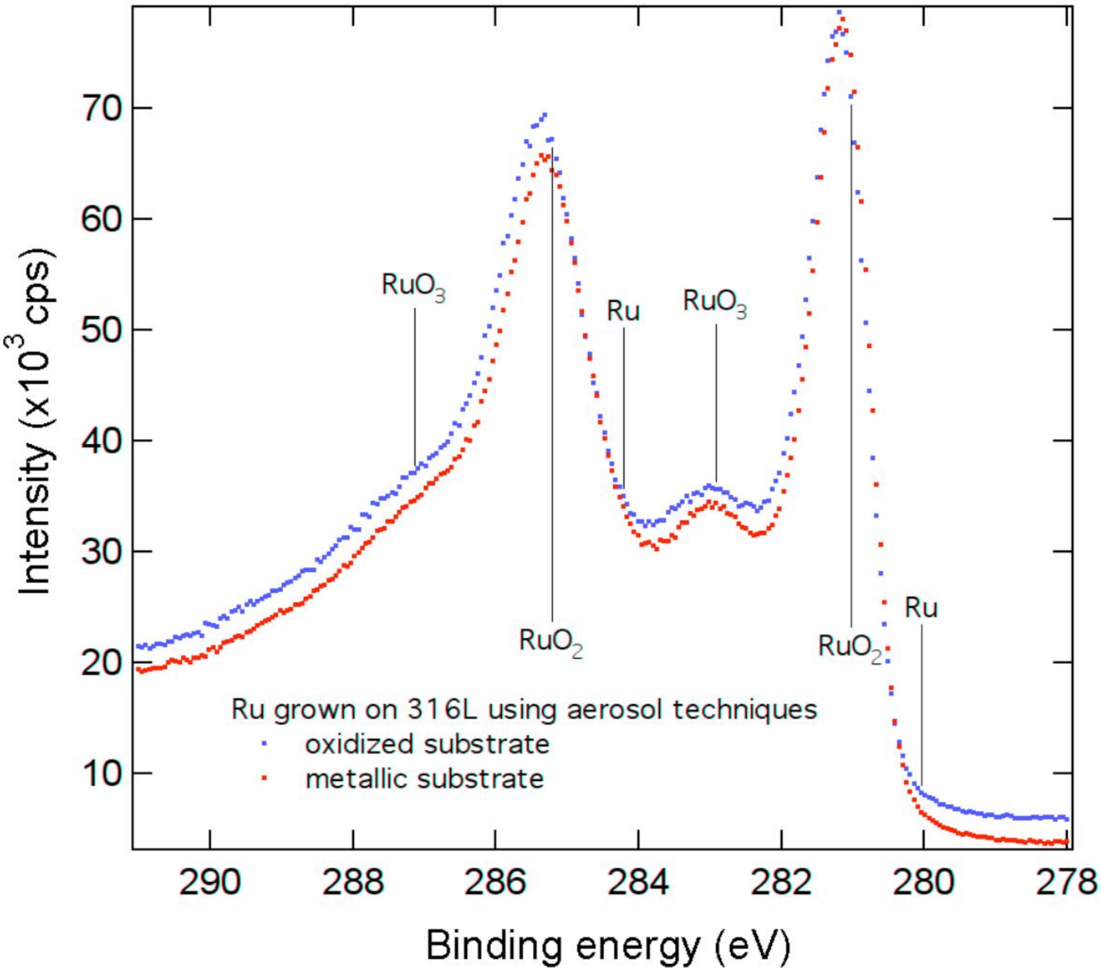

Figure 11. Ruthenium deposit analysed with XPS on oxidised (blue dots) and on metallic (red dots) stainless steel surface. Axes are binding energy (eV) and measured intensity (x 1000 counts per second).

The sample plates were attached on the ceramic tube surface at two locations, 30 cm and 55 cm downstream the furnace. Four differently prepared plates were used at both locations. The placement of the places is presented in figure 12. At 30 cm downstream of the furnace, three of the plates were attached in parallel with each other. The metallic sample plate without RuO_2 deposit was placed immediately downstream of the other plates at the bottom of tube. At 55 cm downstream of the furnace, all plates were attached in parallel with each other. The amount of ruthenium deposited on different sample plates during the experiment could be determined from the activity of the plates, since part of the ruthenium injected into the facility was activated before the experiment. As a result the mass of ruthenium deposited on SS-plates is presented in the table 5.

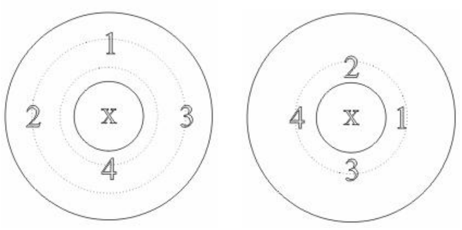

Figure 12. The placement of sample plates inside the tube at 30 cm (on the left) and at 55 cm (on the right) downstream of the furnace. Gas flow direction is towards X. The plates are: 1. oxidised, 2. metallic + RuO_2, 3. oxidised + RuO_2 and 4. metallic. At location 30 cm the plate #4 was attached immediately downstream of the other plates.

Table 5. The amount of ruthenium deposited on stainless steel plates. Values are mass of ruthenium metal [mg] and deposited proportion (%) of released ruthenium.

Plate	Location 30 cm Mass [mg]	Location 30 cm Fraction of released [%]	Location 55 cm Mass [mg]	Location 55 cm Fraction of released [%]
metallic	0,098	0,43	0,140	0,62
metallic + RuO_2	0,016	0,07	0,192	0,85
oxidised	0,147	0,65	0,039	0,17
oxidised + RuO_2	0,385	1,70	0,042	0,18

There was one important difference between the two locations, where the sample plates were placed. At 30 cm downstream of the furnace the wall temperature was approximately 150-250°C, whereas at 55 cm the surface of the ceramic tube was heated up to only 100°C.

According to the results, at higher temperature the oxidised surface was more efficient in trapping ruthenium as the metallic surface. The amount of ruthenium on top of the oxidised surface was 1.5 times greater than on metallic surface. Pre-deposited RuO_2 particles further increased ruthenium retention on oxide surface by factor of 2.6. On metallic surface RuO_2 particles significantly inhibited the retention of ruthenium. Oxidised stainless steel sample plate prepared with RuO_2 deposits trapped 24 times more ruthenium than similarly prepared metallic plate placed on the opposite wall of the tube. Such a great difference is not explained by aerosol deposition processes and therefore has to be a result of difference in RuO_4 reaction on the surface.

At lower temperature the situation was reversed. The amount of trapped ruthenium on metallic surface was greater than on oxidised surface by factor of 3.6. Pre-deposited RuO_2 particles increased retention of ruthenium on metallic surface by 37%. The observed dependence of RuO_4 reaction on the temperature of stainless steel surface agrees very well with the previously measured ruthenium deposition profiles. A deposition peak was formed at 30 cm to 37 cm from the outlet of the furnace as the temperature of the stainless steel tube decreased enough the allow reaction of RuO_4 on its surface.

4.6 Aerosol particles properties

RuO_2 particles were collected with the electrostatic precipitator (ESP) and analysed with the transmission electron microscope (TEM). Representative TEM images of particles are presented in figure 13 together with a selected area electron diffraction (SAED) pattern of a single RuO_2 crystal. The number size distribution of the particles was measured using a DMA/CNC combination. A typical size distribution is presented in the figure 14. The mean particle size was 108 nm and the geometric standard deviation was 1.5. The measured particle size distribution corresponds to the size of agglomerates formed predominantly in gas phase and is therefore larger than the size of primary particles.

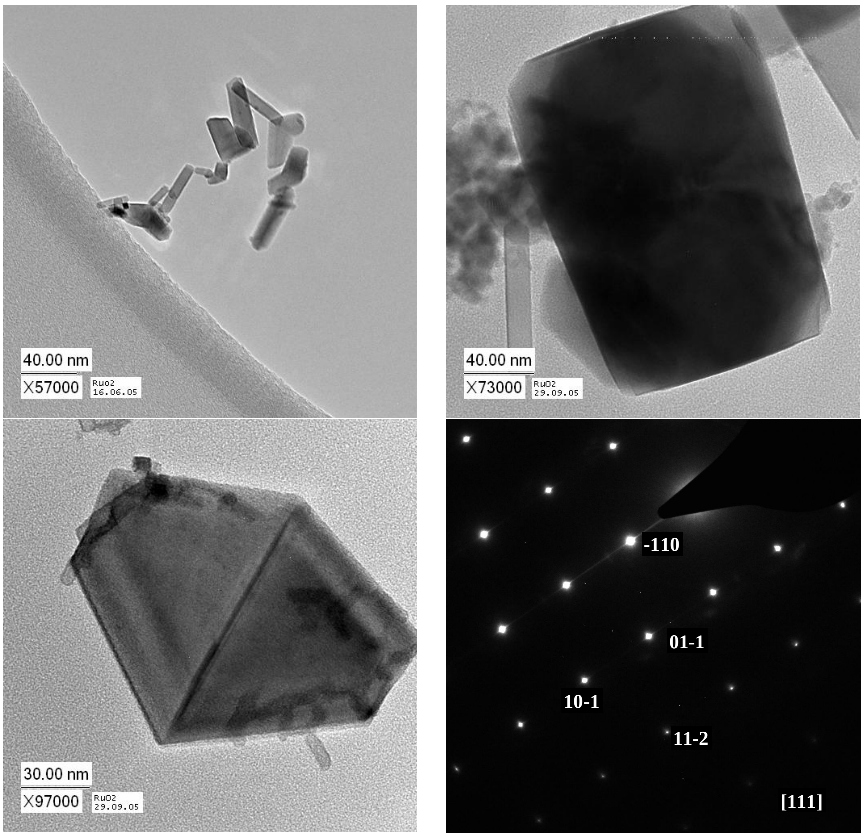

Figure 13. Representative TEM images of RuO_2 particles in the experiments 2 (16.06.05) and 4 (29.09.05) and SAED pattern of a single RuO_2 crystal.

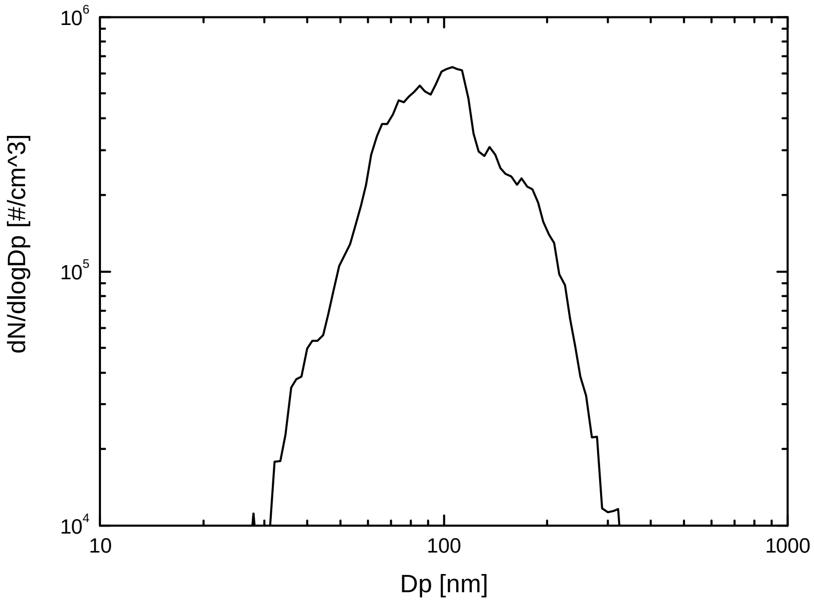

Figure 14. Typical number size distribution of RuO_2 agglomerates (experiment 2).

5. Conclusions

This project is a continuation of ruthenium transport and speciation experiments conducted previously at VTT. In previous experiments it was found out that gaseous ruthenium decomposed on steel surface at dry atmosphere. They also indicated that humid atmosphere may favour gaseous ruthenium transport.

Seventeen experiments, in which the behaviour of ruthenium was studied in oxidizing conditions, were carried out during this project. It was noticed that a very large fraction of ruthenium may be transported in gaseous form. A significant difference in the decomposition rate of gaseous ruthenium depending on the reactor temperature was found. At 1300 K ruthenium was primarily transported in gaseous form and increasing steam partial pressure increased the fraction of gaseous ruthenium. At 1500 K and above, ruthenium transport took place almost entirely as aerosol particles. Gaseous ruthenium seemed to react on the surface of the stainless steel tube, on top of which RuO_2 particles had been deposited. However, revaporisation of deposited RuO_2 particles was also found to be a very significant source of gaseous ruthenium oxides.

Retention of gaseous RuO_4 was found to be very different on oxidized than on metallic stainless steel surface. At higher temperature oxidized surface trapped gaseous ruthenium very efficiently and RuO_2 particles enhanced the retention. At higher temperature RuO_2 particles deposited on metallic surface inhibited decomposition of RuO_4. At about 100-150°C metallic surface was significantly more efficient in trapping gaseous ruthenium. At that temperature deposited RuO_2 also enhanced decomposition of RuO_4 on metallic surface. Further experiments using oxidized stainless steel tubes could prove to be very useful as all experiments in this study were conducted either with fresh steel tubes or with alumina tubes.

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Appendix A. The measured activity of ruthenium in on-line experiments

In figures 15-20 is the measured ruthenium activity at different locations in the facility during experiments 6-9.

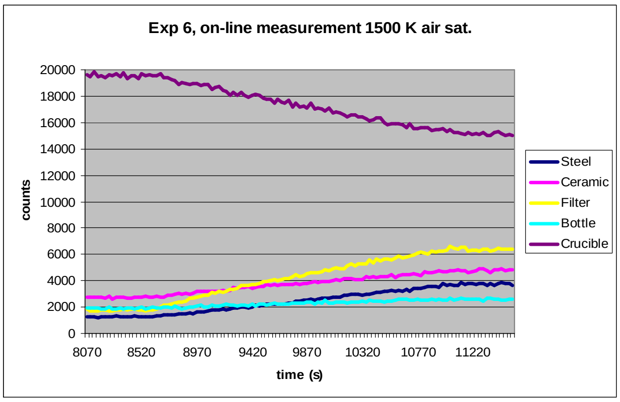

Figure 15. Experiment 6 on-line measurement. Axis units are the measured activity of sample at five location and time.

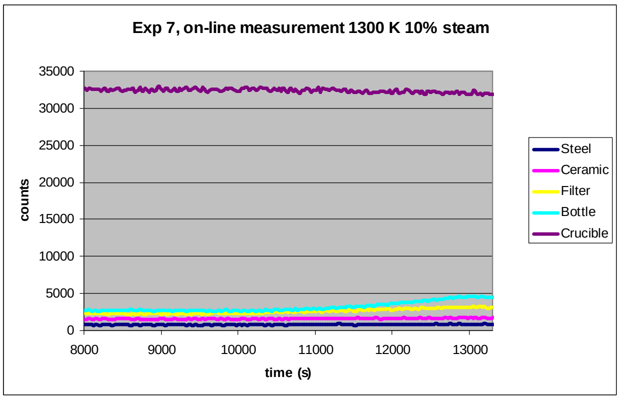

Figure 16. Experiment 7 on-line measurement. Axis units are the measured activity of sample at five location and time.

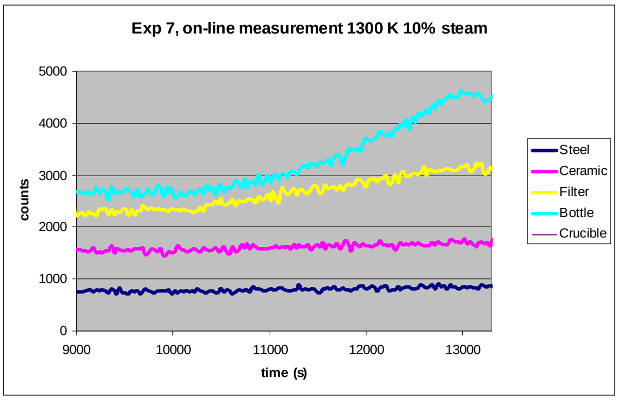

Figure 17. Experiment 7 on-line measurement, without data from the crucible. Axis units are the measured activity of sample at four location and time.

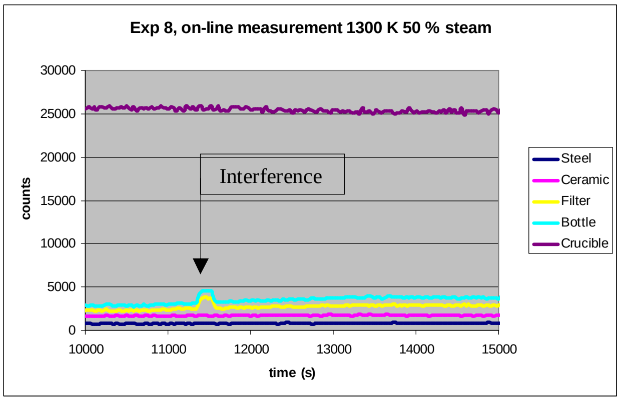

Figure 18. Experiment 8 on-line measurement. Axis units are the measured activity of sample at five location and time.

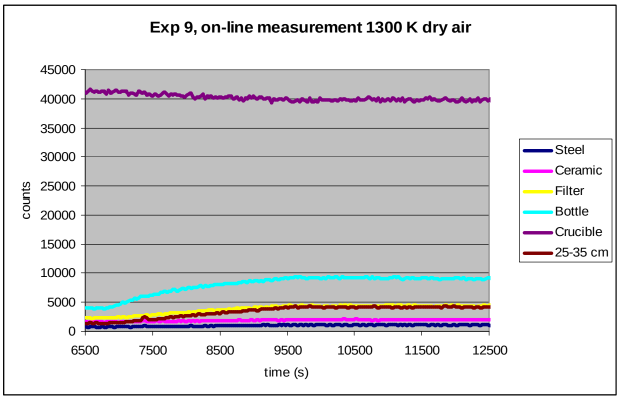

Figure 19. Experiment 9 on-line measurement. Axis units are the measured activity of sample at six location and time.

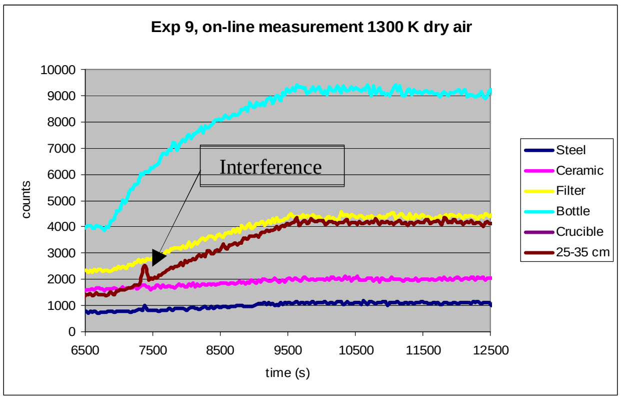

Figure 20. Experiment 9 on-line measurement, without data from the crucible. Axis units are the measured activity of sample at five location and time.

Appendix B. Ruthenium release from crucible in experiments 7 and 8

In figures 21 and 22 is ruthenium evaporated from crucible. Measured data contained quite a lot of noise and therefore curve fitting was difficult.

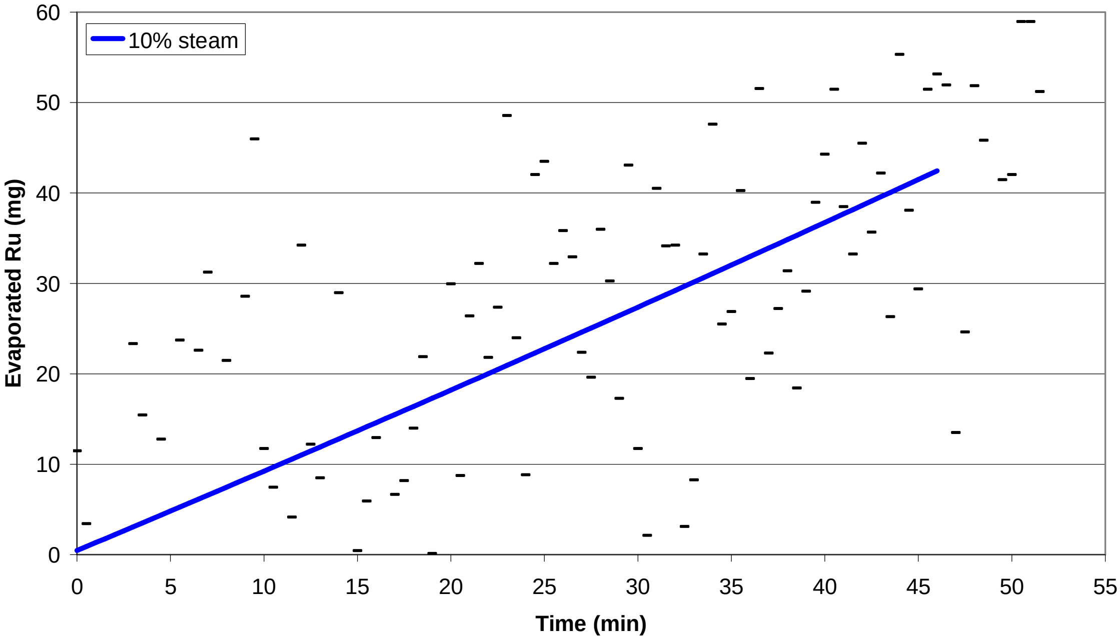

Figure 21. Ruthenium evaporated from crucible (mg) in experiment 7. Furnace temperature was 1300 K and gas flow was containing 10% of steam.

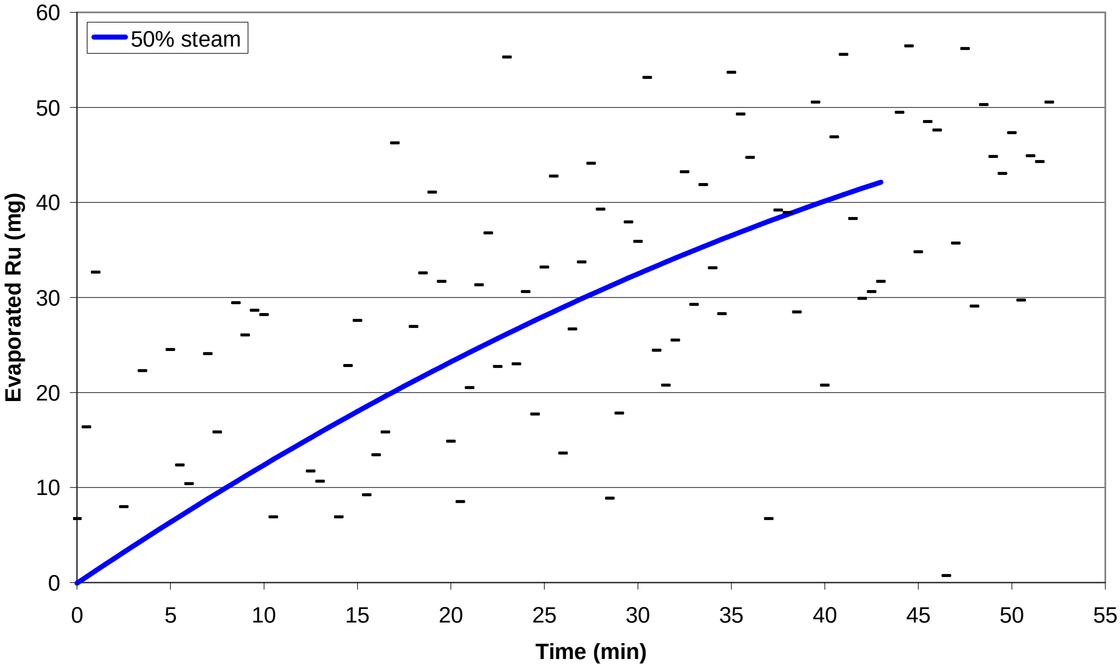

Figure 22. Ruthenium evaporated from crucible (mg) in experiment 8. Furnace temperature was 1300 K and gas flow was containing 50% of steam.

Bibliographic Data Sheet **NKS-151**

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Abstract

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In a severe accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium may oxidise and form volatile ruthenium species, RuO3 and RuO4, which can be transported into the containment. In order to estimate the amount of gaseous ruthenium species, it is of interest to know, how they are formed and how they behave.

In our experiments the formation and transport of volatile ruthenium oxides was studied by exposing RuO2 powder to diverse oxidising atmospheres at a relatively high temperature. Transport of gaseous RuO4 was further investigated by injecting it into the facility in similar conditions. Upon cooling of the gas flow RuO2 aerosol particles were formed in the system. They were removed from the gas stream with plane filters. Gaseous ruthenium species were trapped in 1M NaOH-water solution, which is capable of trapping RuO4 totally. Ruthenium in the solution was filtered for analysis. The determination of ruthenium both in aerosol and in liquid filters was made using instrumental neutron activation analysis (INAA). In order to close the mass balance and to achieve better time resolution seven experiment were carried out using radioactive tracer.

In this report, the facility for the ruthenium behaviour study and results from experiments are presented. Preliminary conclusions from the experiments are reported as well. Final conclusions will be made after modelling of the facility is completed in a continuation work of this study.

Key words ruthenium, nuclear safety, fission product, aerosol sampling and transport

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