Ruthenium Behaviour in Severe Nuclear Accident Conditions Final Report

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Abstract

During routine nuclear reactor operations, ruthenium will accumulate in the fuel in relatively high concentrations. In a steam atmosphere, ruthenium is not volatile, and it is not likely to be released from the fuel. However, in an air ingress accident during reactor power operation or during maintenance, ruthenium may form volatile species, which may be released into the containment. Oxide forms of ruthenium are more volatile than the metallic form. Radiotoxicity of ruthenium is high both in the short and the long term.

The results of this project imply that in oxidising conditions during nuclear reactor core degradation, ruthenium release increases as oxidised gaseous species RuO_3 and RuO_4 are formed. A significant part of the released ruthenium is then deposited on reactor coolant system piping. However, in the presence of steam and aerosol particles, a substantial amount of ruthenium may be released as gaseous RuO_4 into the containment atmosphere.

Key words

Ruthenium, releases, severe accidents, experiments.

RUTHENIUM BEHAVIOUR IN SEVERE NUCLEAR ACCIDENT CONDITIONS - FINAL REPORT

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Summary

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In steam atmosphere ruthenium is not volatile and it is not likely to be released from the fuel. However, in an air ingress accident during reactor power operation or during maintenance ruthenium may form volatile species, which may be released to the containment. In contrast to other fission products the oxide forms of ruthenium are more volatile than the metallic form. As the radiotoxicity of ruthenium is high in both short and long term, the understanding of the release and the subsequent transport is of primary importance. However, these phenomena are not very well understood. The aim of this project was to gain a deeper understanding of the behaviour of ruthenium during a severe accident. This was done using a laboratory scale facility simulating accident conditions.

The amount of gaseous ruthenium reaching the bubbler was in dry atmosphere with stainless steel tube 0.1 - 0.2 % of the released ruthenium. Using alumina tube or having water vapour in the system increased the gaseous ruthenium reaching the bubbler to 4 % of the released. This is close to the fraction of RuO_4 released if the system is in thermodynamic equilibrium. This leads to the conclusion that RuO_4 does not decompose at all in these two cases. A major part of the released ruthenium was deposited in the piping, most of it inside the tube furnace, due to RuO_3 decomposition. In the decomposition of gaseous ruthenium needle-shaped RuO_2 particles formed.

The results of this study imply that in oxidising conditions in a nuclear reactor core degradation, ruthenium release increases as oxidised gaseous species RuO_3 and RuO_4 are formed. Significant part of the released ruthenium is then deposited on RCS (reactor coolant system) piping. However, in the presence of steam and aerosol particles substantial amount of ruthenium may be released as gaseous RuO_4 into the containment atmosphere.

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1. INTRODUCTION

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In steam atmosphere ruthenium is not volatile and it is not likely to be released from the fuel. However, in an air ingress accident during reactor power operation or during maintenance ruthenium may form volatile species, which may be released to the containment. In contrast to other fission products the oxide forms of ruthenium are more volatile than the metallic form. As the radiotoxicity of ruthenium is high in both short and long term, the understanding of the release and the subsequent transport is of primary importance. However, these phenomena are not very well understood.

The aim of this project was to gain a deeper understanding of the behaviour of ruthenium during a severe accident. This was done using a laboratory scale facility simulating accident conditions.

2. BACKGROUND

Ruthenium is an element that has the interesting property that its oxides are more volatile than the metal. Some physical and chemical properties of ruthenium and ruthenium oxides are presented in Table 1. Generally, it can be noted that the reaction rates of ruthenium compounds usually are slow [Eichholz 1978].

Table 1: Data on some physical and chemical properties of ruthenium and its oxides

Ru species	Physical form	Melting point [°C]	Boiling point [°C]	Density [g/cm³]	Note
Ru	silver-white metal	2334	4150	12.1	
RuO	gas - no solid form observed*				exists only >1600 °C *
RuO_2	grey-black crystal			7.05	Dissociates to metallic ruthenium at 1540°C in oxygen at 1 bar pressure**
RuO_3	gas - no solid form observed*				Neglectable amounts at < 700°C, decomposes to RuO_2
RuO_4	yellow prisms	25.4	40	3.29	RuO_4 vapours are yellow, toxic and have an odour of ozone.

Source: Lide 2003, except *Eichler et al. 1992 and **Bell and Tagami 1963.

In the Ru-O system the species RuO, RuO_2, RuO_3 and RuO_4 are volatile. However, RuO_2 is unstable in the gas phase, whereas RuO_3 has been identified only in gas phase. Solid phases are known only of RuO_2 and RuO_4. When exposing RuO_2 to oxygen at high temperature, it reacts to form RuO_3 and RuO_4 according to the following reactions [Eichler et al. 1992]:

$$RuO_2(s) + 0.5\ O_2 \leftrightarrow RuO_3\ (g)$$

and

$$RuO_2(s) + O_2 \leftrightarrow RuO_4\ (g).$$
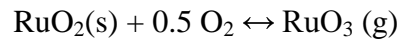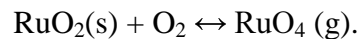
Upon cooling gaseous RuO_3 it becomes thermodynamically unstable and decomposes to RuO_2. As RuO_4 is metastable, it does not necessarily decompose but it can exist in appreciable amount at ambient temperature.

Schäfer et al. (1961) studied the effect of oxygen pressure on the vapour pressure of ruthenium species at 800°C and in the range 1465 - 2090 °C using glowing-filament and transpiration methods. In their work they found evidence for the vapour species RuO_3 and RuO_4. RuO_2 was reported to be in equilibrium with RuO_3 at low oxygen partial pressure and high temperature, whereas at high oxygen partial pressure and lower temperature RuO_4 dominated [Schäfer et al. 1963].

Bell and Tagami (1963) studied the behaviour of ruthenium at temperatures from 800°C to 1500°C at oxygen partial pressures of 0.01 to 1.0 atmosphere. The only stable condensed phase in their experiments was RuO_2. They also noted that the effect of oxygen pressure on vapour pressure indicated that the vapour species are RuO_3 and RuO_4. They found no evidence of gaseous RuO or RuO_2 in their experiments.

Eichler et al. (1992) investigated the volatilisation and deposition of ruthenium oxides in a temperature gradient tube. The highest temperatures in their quartz tubes were between 900 and 1190 °C. They used carrier gas flow rates between 0.2 and 1.2 l/min of oxygen, nitrogen and various mixtures thereof. They found that the gaseous ruthenium deposited in two places, the first zone was at 500°C and the second zone in the charcoal trap, where RuO_4 was filtered. They explained their results using transport reactions and dissociative adsorption.

In experiments carried out in a nitrogen atmosphere in the presence of water vapour, gaseous ruthenium species preferentially deposited at a temperature between 450°C and 500°C and also at a temperature around 150°C. The experiments were carried out in a stainless steel tube. It was also claimed that the decomposition reaction of RuO_4 is catalysed by RuO_2 [Ortins de Bettencourt and Jouan 1969].

Cains et al. (1991) deposited volatile ruthenium on steel surfaces. They found that the deposition took place at temperatures of 150°C and above. The deposit was crystalline RuO_2 and no bonding to the surface was observed [Cains et al. 1991]. There are also studies claming that the deposit is RuO_4 itself and not RuO_2 [Sakurai et al. 1983]. However, our findings do not support this.

Thermodynamic equilibrium calculations for ruthenium species in air and in 50 wt-% air-steam mixture were carried out using ChemSage5.0 software [Bale and Pelton 1999]. The result of the calculation for air is presented in figure 1. From the figure we can see that the most important vapour species are RuO_3 and RuO_4. At temperatures above 1300°C also gaseous RuO_2 is formed in larger quantities. In figure 2 the results from the calculations for an atmosphere of 50 wt-% air-steam mixture are presented. Not very much difference as compared to the air atmosphere case can be observed, other than that $RuO_3OH(g)$ is formed.
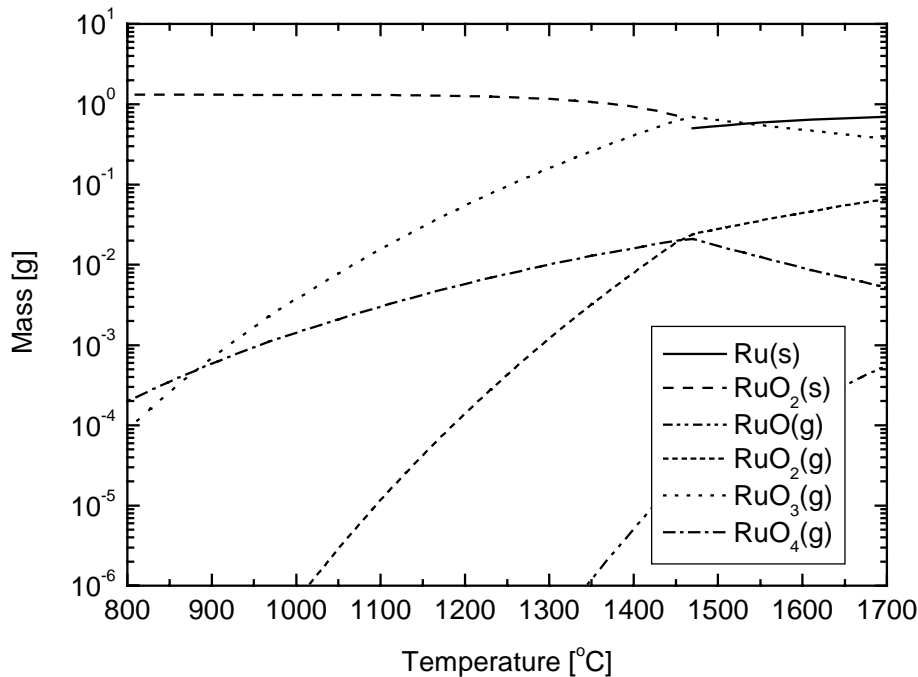

Figure 1: Ruthenium species at thermodynamic equilibrium in air at 1 bar pressure.

2.1. RUTHENIUM AND NUCLEAR POWER PLANTS

In the fission of ^{235}U, ruthenium is produced in 15.8 % of the fissions. 70 % of the ruthenium is in stable form. The two most important isotopes are ^{103}Ru and ^{106}Ru. They have half-lives of 39.6 days and 1 year, respectively. The other isotopes have too short half-lives to be of interest [Seelmann-Eggebert et al. 1974].

The oxidation and release of ruthenium from the nuclear fuel has been studied in different atmospheres: in air and in a mixture of hydrogen and steam. Most experiments are performed using a UO_2 matrix in which also other fission products are mixed, simulating the reactor fuel. It has been found that the UO_2 needs to become sufficiently oxidised before the release of ruthenium takes place [Hunt et al. 1994]. When UO_2 is oxidised to U_3O_8 expansion and cracking of the lattice occurs, which promotes further oxidation [Eichholz 1978].
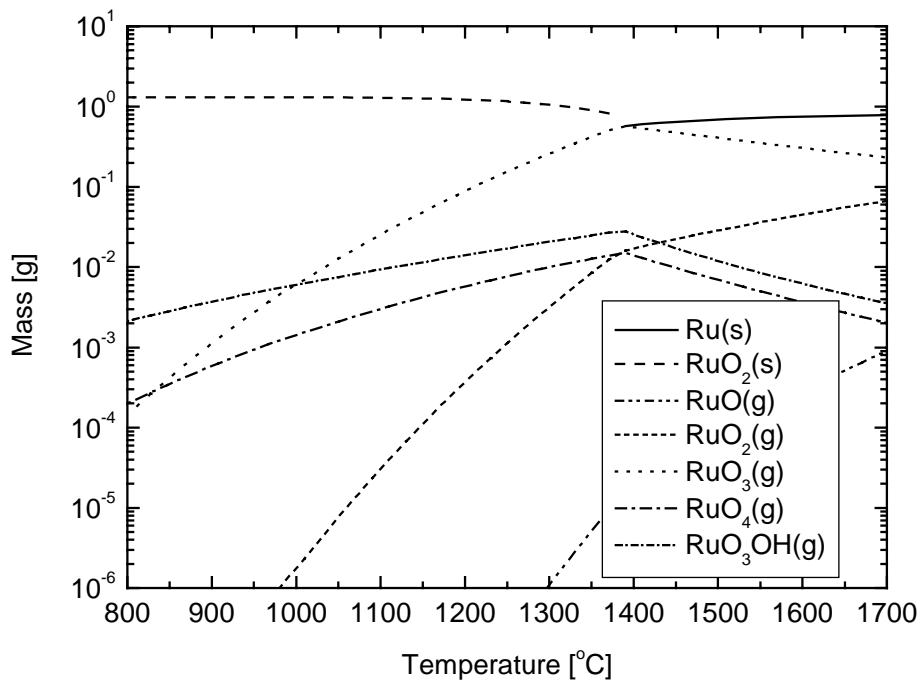
Figure 2: Ruthenium species at thermodynamic equilibrium in 50wt% air-steam mixture.

Under air atmosphere an almost complete evaporation of Ru has been found to occur at temperatures around 1200°C [Ronneau et al. 1995]. However, the emission of ruthenium oxides from overheated nuclear fuel is a complex phenomenon, which depends on the fuel matrix and burn-up, the temperature, the oxygen potential of the atmosphere in contact and on the emission sequence [Froment et al. 2001]. It was observed that ruthenium was released during the accident in the Chernobyl nuclear power plant [Fry et al. 1986, Ronneau et al 1995]. In Finland it was the second most important radionuclide after caesium.

Also in the reprocessing of spent nuclear fuel volatile ruthenium species can cause problems. Volatile RuO_4 is sometimes evolved from boiling nitric acid when reactor fuels are dissolved and when fission-product wastes are concentrated [Eichholz 1978].

3. DEVELOPMENT OF METHODS FOR TRAPPING AND ANALYSING RuO4

The experimental study of Ru behaviour in oxidising environments calls for the quantitative trapping of volatile RuO_4 and an analytical method for Ru in the trapping solution. These were studied experimentally by generating RuO_4 by distillation in sulphuric acid solution and trapping volatile oxide into NaOH solution. The experiments were performed using [103]Ru as radioactive tracer.

3.1. DISTILLATION OF RUTHENIUM

Ruthenium tetroxide, RuO_4, is formed in acidic solutions by strong oxidants. It begins to volatilise at 45°C and the volatilisation is nearly complete at 110°C. In distillates, where RuO_4 is trapped in caustic solution, ruthenates and perruthenates are formed. These decompose slowly to RuO_2 or to the hydrous oxide form, $RuO(OH)_2$. The reduction is accelerated by addition of mild reductants like ethyl alcohol. RuO_2 is soluble in warm hydrocloric acid [Wyatt and Rickard 1961].

3.2. EXPERIMENTAL

Ru tracer

The experiments were performed using a ruthenium solution of 1000 mg/l (Accu Trace[TM] Reference Standard, Ru in dilute HCl). An amount of 5 ml was irradiated for three hours in the Triga Mark II reactor in Otaniemi, Espoo. The neutron flux was 1.2×10^{12} $cm^{-2}s^{-1}$. Ruthenium has several radioisotopes of which [103]Ru was used as the tracer in these experiments. The half-life of the isotope is 39.6 days and the measured γ-energy 498 keV.

Distillation of Ru from H_2SO_4

The first experiment was to distil 0.5 mg of Ru from a solution of 12 M H_2SO_4. Ru was supposed to distil with water. The distillate was collected into 15 ml of 6M NaOH solution in a water bath with ice. The gamma measurements of the distillate and the distillation residue showed that, all ruthenium was still in the residue. This showed that H_2SO_4 alone was not strong enough to oxidise Ru to RuO_4. $KMnO_4$ solution was added into the distilling flask and now the brownish colour of Ru was noticed in the distillate. The reaction was quite violent though it was only gently heated in the beginning of the reaction. Bubbling air through the system and using a higher tube from the flask to the delivery arm was needed to prevent the suckbacks. The Ru yield was 83% in this experiment because of the leak through loosened glass joints caused by the violent reaction. The distillation apparatus is shown in figure 3.

Most of the RuO_2 was precipitated in the tube but the colour of the NaOH solution was still brownish. Ethanol was added and the tube was warmed in a water bath. The solution cleared up. The precipitate was centrifuged, washed with water and ethanol and centrifuged again. Then it was dissolved in 1 ml of warm concentrated HCl. The Ru concentration in this solution can be analysed with ICP-MS (inductively coupled plasma mass spectrometry) or INAA (instrumental neutron activation analysis).

The part of Ru that was lost in the separation was tested afterwards by measuring the [103]Ru activity in the precipitate before separation and after its dissolution in HCl. Less than 3% was lost in the procedure.

Figure 3: The distillation apparatus.

If the amount of Ru is small and it is analysed soon after the distillation so that there has been no precipitation, the analysis can be done from the NaOH solution diluted with 1% HNO_3. To avoid the large dilution of the analytical solution in experiments containing very small amounts of volatile Ru, it would be better to use a more dilute NaOH solution than 6M NaOH.

Therefore the next experiments were done using 1M NaOH solution in the receiver. The double experiments were done with 0.5 mg Ru in concentrated H_2SO_4 and by adding 2 ml of 0.04M $KMnO_4$ as oxidising agent. The receiver contained 15 ml of 1M NaOH. Both experiments gave 100% yield of Ru showing that 1M NaOH is capable of trapping RuO_4 totally.

4. ANALYSIS OF RUTHENIUM

4.1. ICP-MS

Using ICP-MS (inductively coupled plasma mass spectrometry) Ru determination can be done either from 1M NaOH or from HCl solution. In the case of 1M NaOH the solution has to be diluted at least 1/40 because the total concentration of Na may not exceed 1000 mg/l. Na suppresses the Ru sensitivity in this concentration about 15%, which is still acceptable when using indium as an internal tracer. When Ru is analysed from HCl solution it has to be diluted at least 1/20 to get 5% HCl solution, which can be used in ICP-MS.

The detection limit was tested with 1M NaOH solution diluted 1/40. The detection limit for Ru was 0.05 µg/l.

4.2. INAA

The detection limit for Ru with INAA (instrumental neutron activation analysis) is 2 µg/sample. This was calculated for ^{103}Ru with 3 hours irradiation time. The amount of the solution that can be irradiated in the reactor limits the determination of the 1M NaOH. If the NaOH solution is irradiated the gamma measurement of Ru can be done only after a week when ^{24}Na does not have a disturbing effect on the background any more. The determination of Ru from the dissolved precipitate needs smaller irradiation capsules and is therefore more practical to perform.

5. EXPERIMENTAL

5.1. EXPERIMENTAL SET-UP

The laboratory facility used for the experiments with ruthenium is schematically presented in figure 4. The main component of the system was the tubular flow furnace, in which the ruthenium source (RuO$_2$ powder, Sigma-Aldrich) was heated. The tubular flow furnace (Entech, ETF20/18-II-L) used was 110 cm long and had two heating zones, each 40 cm long. The alumina furnace tube has an inner diameter of 22 mm. The alumina crucible with the RuO$_2$ powder (about one gram per experiment) was placed in the second heating zone of the furnace. During an experiment the gas flow rate through the furnace was 5 l/min. The flow rate was controlled with a mass flow controller (Tylan General FC-2900M).

The oxygen in air oxidised the ruthenium dioxide and gaseous RuO$_3$ and RuO$_4$ were released. As the gas exited the furnace it cooled and the gaseous ruthenium oxides decomposed partly to RuO$_2$. The RuO$_2$ particles were filtered out at a point 106 cm downstream of the furnace. At this point the temperature of the gas was approximately 50 °C. In the first experiment quartz-fibre filters were used. The analysing of this filter however turned out to be difficult. In experiment #2 and #3 47 mm Nuclepore filters were used. In the rest of the experiments 90 mm PTFE-filters were used in the main line in order to increase the filtering capacity. The gaseous ruthenium was trapped downstream of the filter in a 1 M NaOH solution. The bubbler containing the trapping solution was placed in an ice-bath.

Gas-phase sampling was done at a point 74 cm downstream of the furnace using a j-shaped probe pointing upstream in the flow. The sample was diluted with a porous tube diluter in order to minimise the losses during dilution. The number size distribution of the particles was measured with a differential mobility analyser (DMA, TSI 3081) and a condensation nucleus counter (CNC, TSI 3022). The particles are size classified according to their electrical mobility by the DMA and 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 in the sampling line was filtered before being vented to the

fumed hood. Transmission electron microscope (TEM) samples were collected on holey carbon coated copper grids using an electrostatic precipitator (ESP). In the TEM analysis the size and morphology of the RuO_2 were studied. The microscope used in these studies was a Philips CM-200 FEG/STEM operated at 200 kV. The walls of the ceramic furnace tube were analysed using a Leo Gemini 982 scanning electron microscope (SEM).

The experimental procedure was essentially as follows: first the ceramic crucible was filled with about one gram of RuO_2. The crucible was loaded into the furnace, the system was assembled and heated. As the furnace reached its setpoint the gas flow was turned on. The duration of the experiments was 20 min - 60 min. At the end of the experiment the flow was turned off and the system was allowed to cool before dismantling. After the experiments the pipes were washed with 1 M NaOH solution or ethanol. The filters, the tube washing solutions and the trapping solution were analysed. The crucible with ruthenium was weighed.

The details of the experiments can be found in table 2. Experiment #1 was the base case, in which the release temperature was set to 1500 K (1227°C) and a 5 l/min (NTP, NTP conditions 0°C, 101325 Pa) air-flow was passed over the crucible containing RuO_2. The tubes downstream of the furnace were made of stainless steel. In experiment #2 the alumina furnace tube was extended downstream for 69 cm. The sampling and the filtering parts were made of stainless steel. The distance between the end of the alumina to the bubbler was 40 cm. The experimental parameters were as in experiment #1. This experiment was carried out to see the effect of the tube material, as stainless steel was believed to catalyse the dissociation of RuO_4 to RuO_2.
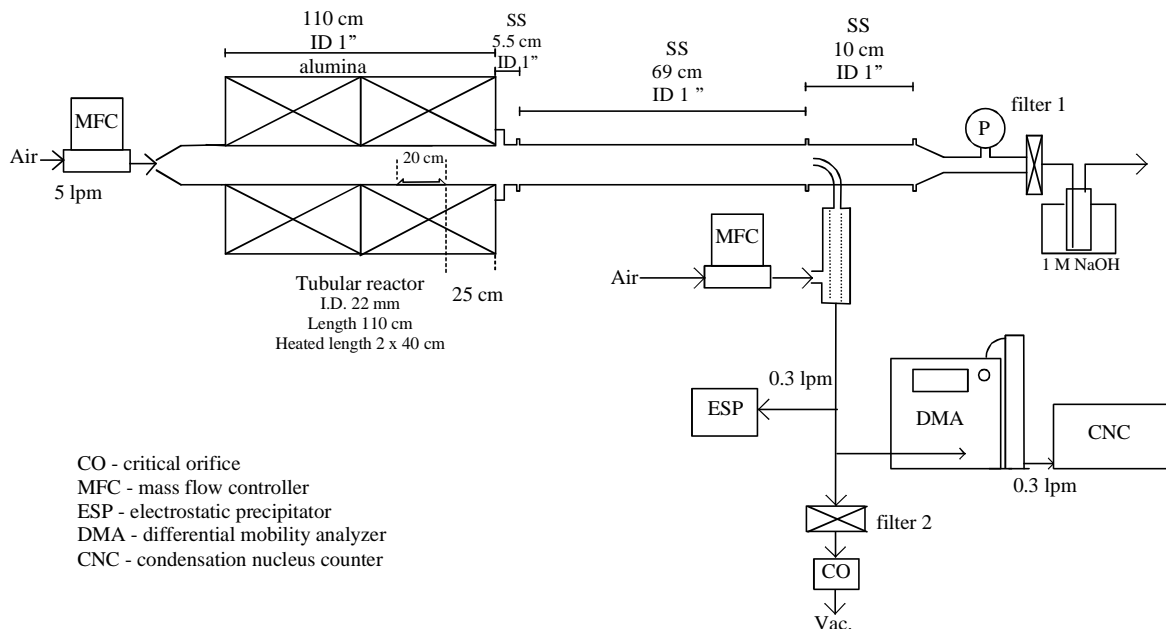

Figure 4: Schematics of experimental set-up used in Ru-experiments.

Table 2: Details on experiments carried out with ruthenium.

Exp #	T release [°C]	Gas	Pipe material	Other	Main line filter	Sample line filter	Duration of experiment [min]
1	1227	Air, 5 l/min	Stainless steel		Balston quartz fibre	Balston quartz fibre	60
2	1227	Air, 5 l/min	Alumina		Nuclepore 47 mm, 0.4 µm	Nuclepore 47 mm, 0.4 µm	45
3	1227	Air, 5 l/min	Stainless steel	Tracer used	Nuclepore 47 mm, 0.4 µm		42
4	1427	Air, 5 l/min	Stainless steel		PTFE 90 mm, 0.5 µm	Nuclepore 47 mm, 0.4 µm	20
5	1227	N_2 + 10 % O_2, 5 l/min	Stainless steel		PTFE 90 mm, 0.5 µm	Nuclepore 47 mm, 0.4 µm	60
6	1227	Air, 5 l/min	Stainless steel	Add seed particles	PTFE 90 mm, 0.5 µm	Nuclepore 47 mm, 0.4 µm	38

In the first two experiments only 44-47 % of the ruthenium in the system was located. After washing the tubes it could be visually observed that ruthenium still remained on the walls. In order to determine the amount of ruthenium an experiment (#3) was carried out using ^{103}Ru as radioactive tracer ($\tau_{\frac{1}{2}}$ = 39.6 days). The experimental parameters were identical to those in experiment #1. However, no sampling of the particles was done.

In experiment #4 a higher release temperature of 1700 K (1427°C) was used. In experiment #5 the effect of lower oxygen concentration (10%) was studied and the effect of seed particles was investigated in experiment #6. The silver seed particles were produced from a 4wt-% AgNO$_3$ solution using an ultrasonic aerosol generator. This method also produced some water vapour into the system. In figure 5 photographs of the experimental set-up are shown.

Figure 5: Photographs of experimental setup used. On the left no particle sampling is done, on the right the particle sampling set-up is shown.

5.2. ANALYSIS OF THE SAMPLES

In the first experiment the two filters were crushed and 100 ml of concentrated HCl was added. This was heated on a sand bath and acid was added. The precipitate was separated from the solution and the solution was almost dried. The remaining solution was diluted with water and analysed with ICP-MS. However, using this method all ruthenium could not be analysed as some ruthenium remained in the precipitate, as was observed visually. In later experiments the filters were analysed with INAA.

The trapping and the tube washing solutions were heated on a sand bath and ethanol was added to reduce ruthenates to RuO$_2$. In the first two experiments the precipitate from the trapping solution was centrifuged and washed twice with water before dissolving it in hot concentrated HCl. After dilution with deionised water the Ru-concentration was analysed with ICP-MS. The precipitate that was lost with the solution in centrifugation was filtered and the filter paper was analysed with INAA. The precipitation from the tube washing solution was so small that the solution was filtered through a filter paper and the filter paper was analysed with INAA. The success of the precipitation was proved by analysing

the filtered solutions by ICP-MS. In later experiments the precipitate from the trapping and tube washing solutions were filtered and the filters were analysed with INAA.

5.3. TEMPERATURE MEASUREMENTS

Before carrying out the experiments temperature measurements were done. The temperature of the gas was measured at 7 different locations downstream of the furnace: at 10, 22, 34.5, 43, 53, 63 and 71 cm from the outlet. The wall temperature was measured at 5 locations downstream of the furnace: at 4.5, 43, 53, 63 and 71 cm from the outlet. The measurements were carried out on the inside wall of the tube through drilled holes. The temperature measurements were carried out using K-type thermocouples at a furnace setpoint of 1500 K (1227°C) and an air flow rate of 5 l/min. The measured gas and wall temperatures as a function of distance from the outlet of the furnace are shown in figure 6.

We also know that the temperature of the tube wall inside the furnace is 1500K at two points, - 33 cm and at - 77 cm. The furnace outlet is located at 0 cm. The furnace is radiation heated and at the outlet there is 8 cm of thermal isolation. In this part of the furnace the temperature decreases rapidly.
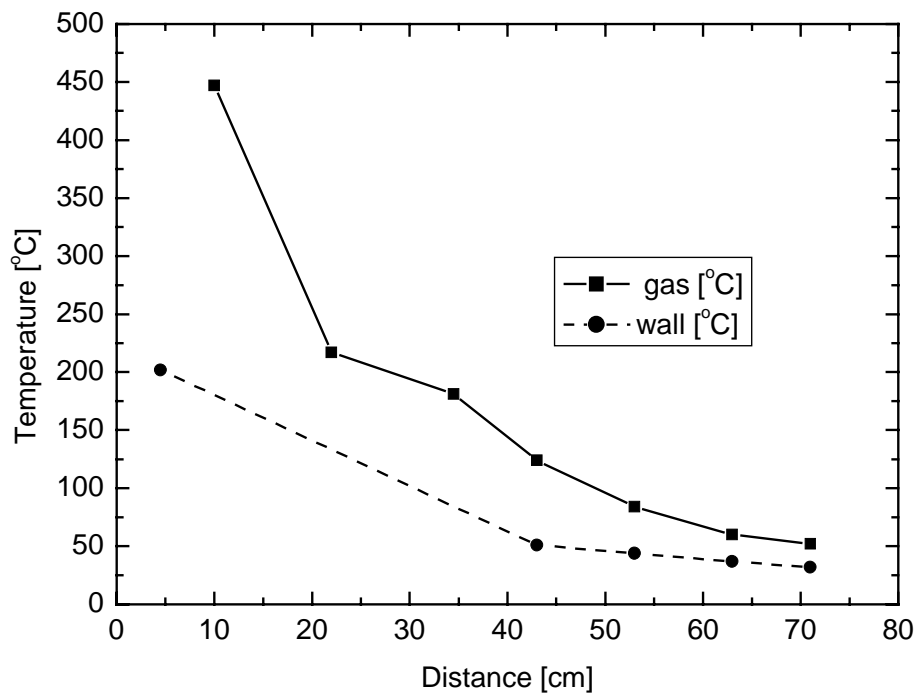

Figure 6: Gas and wall temperature as a function of distance from outlet of the furnace for an air flow rate of 5 l/min.

6. RESULTS

The results from the experiments are summarised in table 3. The release rate was determined gravimetrically from the mass loss of ruthenium from the crucible during the experiment. The mass flow rate for RuO_4 and RuO_2 in the bubbler and the filter, respectively, is the mass of ruthenium, not of the oxides. The results are also normalised to a flow rate of 5 l/min (NTP), because the carrier gas flow rate through the main line filter and the bubbler was not, due to sampling, the same in all experiments. It was assumed that the release rate is constant. The measured masses, flow rates etc are presented in Appendix A. As explained in section 5.2 the result for the RuO_2 aerosol mass in experiment #1 is not correct.

Table 3: Summary of results from ruthenium experiments.

	Release rate [mg/min]	RuO_4 In bubbler [mg/min]	RuO_2 In filter [mg/min]	RuO_4/RuO_2
#1 1227°C 5 l/min air Stainless steel pipe	9.5	0.016	0.40 ?	0.04 ?
#2 1227°C 5 l/min air Alumina pipe	8.9	0.437	1.04	0.42
#3 1227°C 5 l/min air Tracer	11.0	0.011	1.31	0.01
#4 1427°C 5 l/min air	25.4	0.055	8.82	0.01
#5 1227°C 10 % O_2 + N_2 5 l/min	6.6	0.016	1.69	0.01
#6 1227°C $AgNO_3$ -feed 5 l/min air	10.1	0.579	2.61	0.22

6.1 RUTHENIUM RELEASE

From the table we can see that the release rate of ruthenium was almost constant (9 - 11 mg/min), when the release temperature and the gas composition was constant. If the system is assumed to be in thermodynamic equilibrium, 91 % of the ruthenium was released as RuO_3 at this temperature and 8 % as RuO_4. Higher furnace temperature increased the release rate to 25 mg/min. At this temperature 94 % of the released ruthenium was RuO_3 and 3 % RuO_4 according to thermodynamic equilibrium. Lower oxygen concentration (10 %) slightly decreased the release rate to 6.6 mg/min.

Part of the observed variations in the release rate could be explained by time dependence in the release rate. A longer experiment would decrease the release rate, whereas a shorter would increase it. The time dependence of the release rate could be investigated using on-line measurement with radioactive tracer.

6.2 TRANSPORT OF GASEOUS RUTHENIUM (RuO_4)

In dry experiments with stainless steel tube only 0.1 - 0.2 % of the release ruthenium reached the trapping bottle. The ratio seemed to be independent of the release temperature, the oxygen partial pressure and the concentration of ruthenium. This was probably due to the catalytic decomposition of RuO_4 to RuO_2 on the stainless steel surface.

Using alumina tube, 4% of the released ruthenium was transported as gaseous RuO_4 to the trapping bottle. This is comparable to the amount (8 %) of ruthenium released as RuO_4 given by the thermodynamic equilibrium calculations. It seems that the RuO_4 does not decompose to RuO_2 in the experiment using alumina tube. This result also indicates that RuO_2 does not have a strong catalysing effect on the decomposition of RuO_4 as was claimed by Ortins de Bettencourt and Jouan (1969).

In the seed particle experiment, where water vapour was present in the system 4 % of the released ruthenium was transported as gaseous RuO_4 to the trapping bottle. This is 50 times more than at dry conditions. The result is very similar to the result from the alumina tube experiment. The water vapour most likely decomposes on the surface leaving a layer of hydrogen atoms, which in turn prevent other reactions.

In figure 7 a photograph is shown where two trapping bottles can be seen. Two bottles were used in order to verify that the ruthenium really is trapped in just one bottle. In the figure we can see that the trapping solution in the first bottle has turned yellow, whereas the solution in the second bottle is still colourless. In analysis of the solution no ruthenium was detected in the second bottle.

A continuation of this series of experiments would be needed in order to gain a more thorough understanding of these phenomena. In order to investigate the effect of water vapour on gaseous ruthenium, experiments using different concentrations of water vapour should be carried out. In order to investigate if RuO_2 catalyses the RuO_4 decomposition more alumina tube experiments should be carried out, where the catalysing effect of stainless steel does not affect the results.

Figure 7: Two trapping bottles are shown. The solution in the first bottle has turned yellow when ruthenium has been trapped, whereas the solution in the second bottle is still uncoloured.

6.3 TRANSPORT OF RUTHENIUM AEROSOL

Most of the released ruthenium was deposited into the piping (65-88 %). The deposition mostly took place in the alumina tube inside the furnace. Because RuO_3 exists at neglectable amounts at temperatures below 700°C, the deposition is most likely caused by thermal dissociation of RuO_3 to RuO_2. Less deposition (65 %) at high release temperature is due to the fact that the gas flow cooled much faster, which led to more RuO_2 particles in the gas phase. The particles deposit slower than the RuO_3 gas due to the difference in diffusion velocity. Low oxygen concentration also decreased ruthenium deposition (74 %), probably because the gas phase concentration of RuO_3 was lower.

In the experiment using seed particles, Ag particles where produced from 4 w% $AgNO_3$ solution using an ultrasonic generator. The number size distribution of the produced Ag particles is presented in figure 8. Producing silver particles by this method also generated water in the system. Feeding seed particles to the system, the ruthenium aerosol mass flow rate collected on the filter increased to roughly twice as compared to other similar (#3) experiments.
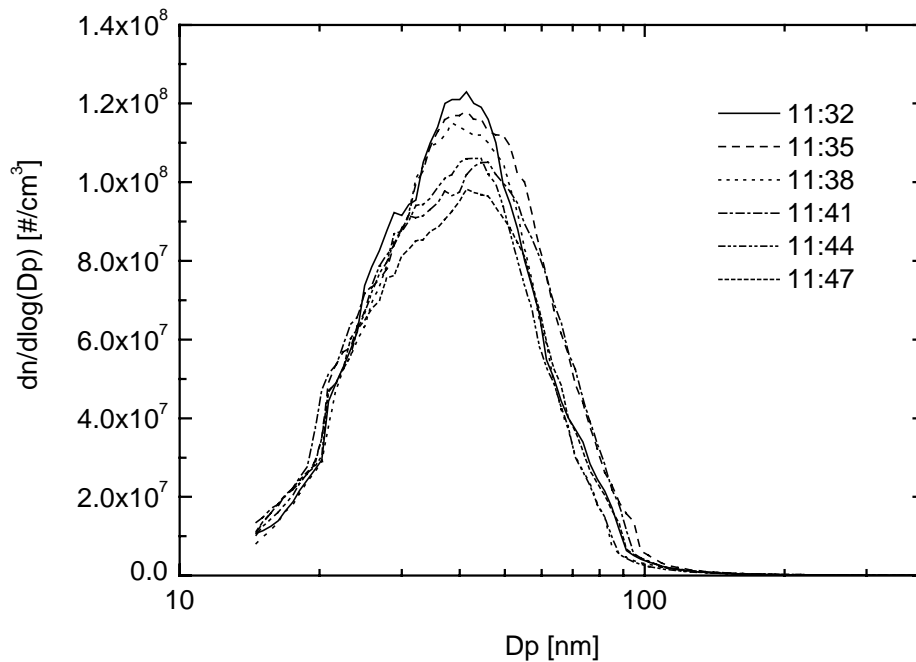
Figure 8: Number size distribution of Ag particles used as seeds in the ruthenium experiment.

Particles produced in the system were collected on carbon coated copper grids for transmission electron microscope (TEM) analysis. Representative TEM images are presented in figure 9. From the figures we can see that the particles are needle-shaped and crystalline. Diffraction patterns are also presented. From them we can see that the particles are RuO_2. Scanning electron microscopy (SEM) was performed on the walls of the ceramic tube in experiment #2. In figure 10 SEM images are shown. It can be seen that crystalline RuO_2 particles also are present on the walls of the tube.

In the first two experiments only about 40 % of the ruthenium in the system was located. It was assumed that the rest of the ruthenium remained on the walls of the system. In order to verify this experiment #3, using radioactive tracer, was carried out. After the experiment the tube was scanned in pieces of 4 cm.

In figure 11 the distribution of Ru downstream of the evaporation crucible is shown. The release crucible was located at - 45 - - 25 cm and the furnace ended at 0 cm. No deposition can be seen at the location of the release crucible or immediately downstream of it. In the distribution three peaks can be observed. The first peak is probably due to the decomposition of RuO_3, as explained earlier. The second peak located just downstream of the outlet is caused by thermophoretic deposition of particles. The third peak may be due to decomposition of RuO_4. The gas temperature distribution is also shown in figure 11. However, it is not known if it is the gas or the wall temperature that is the more important for the processes in the system.
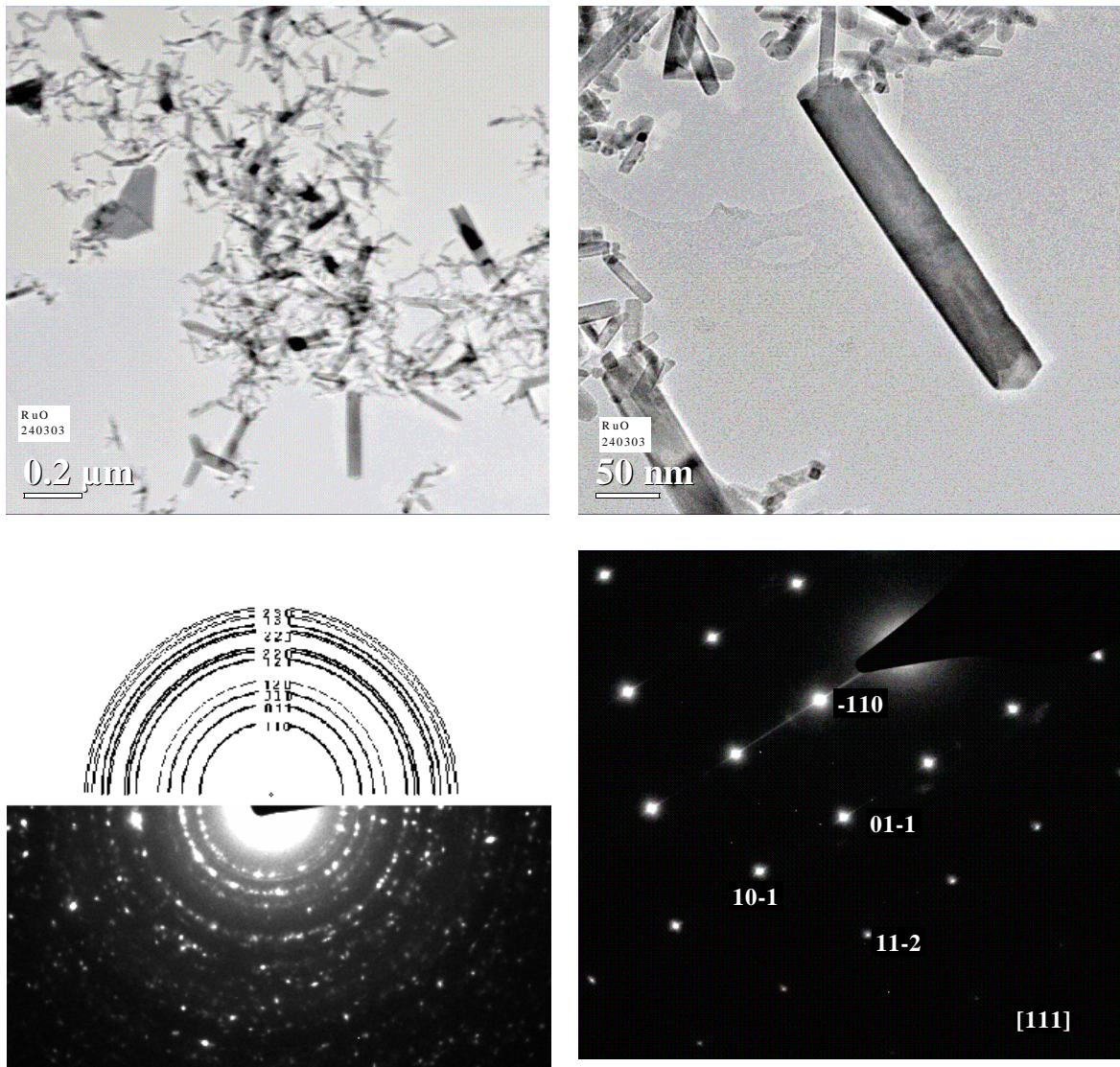
Figure 9: TEM images of RuO$_2$ particles. Diffraction patterns, verifying that the particles are indeed RuO$_2$, are also presented.
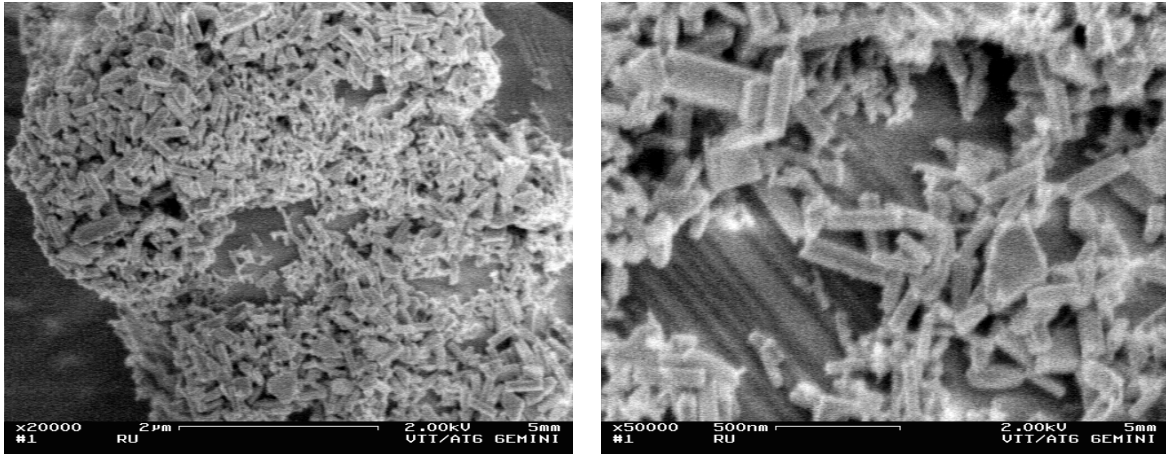
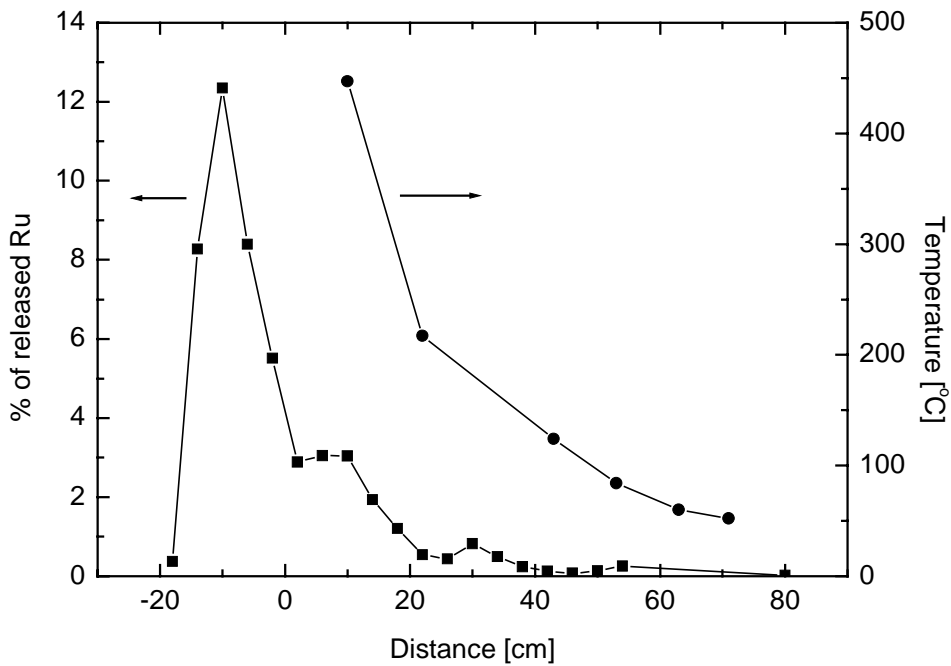Figure 10: SEM images of the wall of the furnace tube. Needle-shaped RuO$_2$ particles can be seen.

Figure 11: Distribution of Ru downstream of the evaporation crucible. The furnace ends at 0 and the release crucible is located at -25 - -45 cm. The gas temperature distribution is also shown.

The number size distribution of the particles was measured using a DMA/CNC combination. The number size distribution in all experiments was quite similar. A typical series of size distributions are presented in figure 12. This measurement was done in experiment #2.
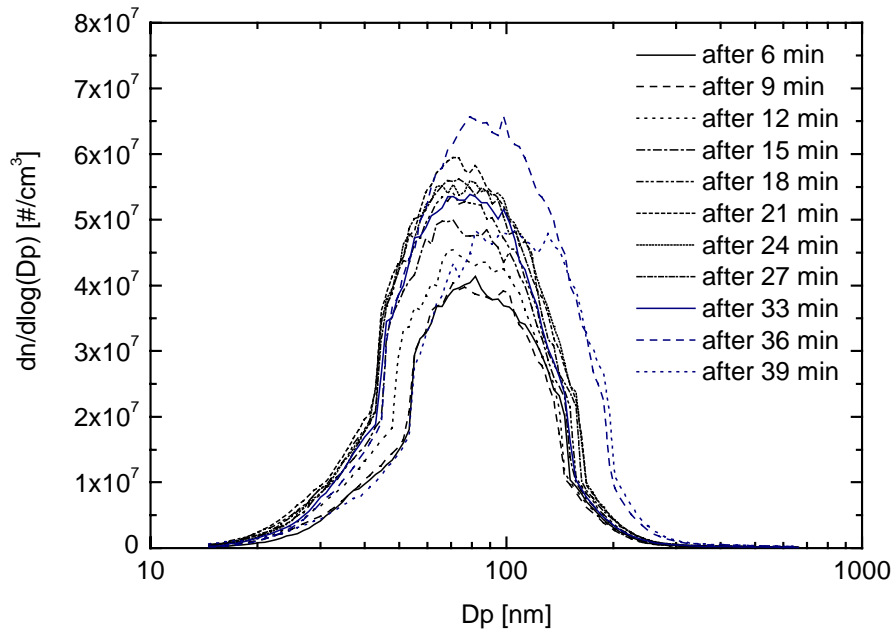

Figure 12: A typical number size distribution series of RuO_2 particles measured by DMA/CNC.

7. CONCLUSIONS

In these experiments the behaviour of ruthenium at high temperature oxidising conditions was studied. The amount of gaseous ruthenium reaching the bubbler was in dry atmosphere with stainless steel tube 0.1 - 0.2 % of the released ruthenium. Using alumina tube or having water vapour in the system increased the gaseous ruthenium reaching the bubbler to 4 % of the released. This is close to the fraction of RuO_4 released if the system is in thermodynamic equilibrium. This leads to the conclusion that RuO_4 does not decompose at all in these two cases. This also indicates that RuO_2 does not catalyse the decomposition of RuO_4.

A major part of the released ruthenium was deposited in the piping, most of it inside the tube furnace, due to RuO_3 decomposition. Deposition by thermophoresis at the outlet of the furnace also took place. Low oxygen concentration and high release temperature decreased the deposited fraction. In the decomposition of gaseous ruthenium needle-shaped RuO_2 particles formed.

About 95 % of the ruthenium was released as RuO_3 in our system, the rest as RuO_4. The release rate was approximately constant 9 - 11 mg/min in air flow at 1500K. The release

rate decreased as the oxygen partial pressure decreased and increased when the oxidation temperature increased.

The results of this study imply that in oxidising conditions in a nuclear reactor core degradation, ruthenium release increases as oxidised gaseous species RuO_3 and RuO_4 are formed. Significant part of the released ruthenium is then deposited on RCS (reactor coolant system) piping. However, in the presence of steam and aerosol particles substantial amount of ruthenium may be released as gaseous RuO_4 into the containment atmosphere.

Further experiments would be needed in order to get more understanding of the behaviour of ruthenium at high temperature oxidising conditions. The time dependence of the release rate could be investigated using on-line monitoring with radioactive tracer. In order to investigate the effect of water vapour experiments where only water vapour is fed should be carried out. In order to investigate if RuO_2 catalyses the RuO_4 decomposition more alumina tubes experiments should be carried out

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APPENDIX A: Measured masses and further details on the experiments.

Experiment	#	1	2	3	4	5	6
Tube material		SS	Alumina	SS	SS	SS	SS
Duration	min	60	45	42	20	60	38
Gas		Air	Air	Air	Air	Air/N_2	Air
Flow rate through furnace	l/min	5	5	5	5	5	5
Furnace temperature	K	1500	1500	1500	1700	1500	1500
RuO_2 in	mg	1117	814	1030	986	935	938
RuO_2 left in crucible after experiment	mg	353	280	412	309	407	425
mass found in							
bubbler	mg	0.64	16.44	0.46	0.79	0.7	15.7
filter, main	mg	16.47 ?	39.2	54.9	126	72.4	70.9
filter, sample	mg	16.19 ?	1.8	-	6.87	2.5	1.5
Tube wash	mg	55.05	5.55	232.4	79.5	34	39.4
flow through bubbler	l/min	3.43	4.18	5	3.57	3.57	3.57
sample flow	l/min	1.57	0.82	-	1.43	1.43	1.43

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Abstract

During routine nuclear reactor operations, ruthenium will accumulate in the fuel in relatively high concentrations. In a steam atmosphere, ruthenium is not volatile, and it is not likely to be released from the fuel. However, in an air ingress accident during reactor power operation or during maintenance, ruthenium may form volatile species, which may be released into the containment. Oxide forms of ruthenium are more volatile than the metallic form. Radiotoxicity of ruthenium is high both in the short and the long term.

The results of this project imply that in oxidising conditions during nuclear reactor core degradation, ruthenium release increases as oxidised gaseous species RuO_3 and RuO_4 are formed. A significant part of the released ruthenium is then deposited on reactor coolant system piping. However, in the presence of steam and aerosol particles, a substantial amount of ruthenium may be released as gaseous RuO_4 into the containment atmosphere.

Key words	Ruthenium, releases, severe accidents, experiments.