Nordisk kernesikkerhedsforskning
Norrænar kjarnöryggisrannsóknir
Pohjoismainen ydinturvallisuustutkimus
Nordisk kjernesikkerhetsforskning
Nordisk kärnsäkerhetsforskning
Nordic nuclear safety research

NKS-118
ISBN 87-7893-179-7

Experiments on the behaviour of ruthenium in air ingress accidents - Progress report

Teemu Kärkelä, Ulrika Backman, Ari Auvinen, Riitta Zilliacus,
Maija Lipponen, Tommi Kekki, Unto Tapper & Jorma Jokiniemi

VTT Technical Research Centre of Finland

February 2006

Abstract

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In an accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium can 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 it is formed and how it behaves. In our experiments RuO2 is exposed to diverse oxidising atmospheres at a relatively high temperature.

In this report, the experimental system for the ruthenium behaviour study is presented. Also preliminary results from experiments carried out during year 2005 are reported. In the experiments gaseous ruthenium oxides were produced in a furnace. Upon cooling RuO2 aerosol particles were formed in the system. They were removed with plane filters from the gas stream. 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 mass balance and achieve better time resolution three experiment using radioactive tracer were carried out.

Key words

Ruthenium, Air ingress, Fission product transport

NKS-118
ISBN 87-7893-179-7

Electronic report, February 2006

The report can be obtained from
NKS Secretariat
NKS-775
P.O. Box 49
DK - 4000 Roskilde, Denmark

Phone +45 4677 4045
Fax +45 4677 4046
www.nks.org
e-mail nks@nks.org

EXPERIMENTS ON THE BEHAVIOUR OF RUTHENIUM IN AIR INGRESS ACCIDENTS - PROGRESS REPORT YEAR 2005

Authors Teemu Kärkelä

Ulrika Backman

Ari Auvinen

Riitta Zilliacus

Maija Lipponen

Tommi Kekki

Unto Tapper

Jorma Jokiniemi

Publicity: Public

VTT PROCESSES

Research organisation and address
VTT Processes
P.O. Box 1602
FIN-02044 VTT, FINLAND

Project manager
Ari Auvinen

Diary code (VTT)
PRO3/0053T/05

Customer
NKS
Fortum Nuclear Services Ltd
P.O.Box 10
00048 Fortum

Contact person
Nici Bergroth

Order reference
AFT/NKS-R(05)12/5

Project title and reference code
Experiments on the behaviour of ruthenium in air ingress accidents
C5SU00765

Report identification & Pages **Date**
PRO3/P3054/05 23.12.2005
1+11 p.

Report title and author(s)
Experiments on the behaviour of ruthenium in air ingress accidents - progress report year 2005
Kärkelä, T. ; Backman, U.; Auvinen, A.; Zilliacus, R.; Lipponen, M.; Kekki, T.; Tapper U.; Jokiniemi, J.

Summary

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In an accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium can 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 it is formed and how it behaves. In our experiments RuO_2 is exposed to diverse oxidising atmospheres at a relatively high temperature.

In this report, the experimental system for the ruthenium behaviour study is presented. Also preliminary results from experiments carried out during year 2005 are reported. In the experiments gaseous ruthenium oxides were produced in a furnace. Upon cooling RuO_2 aerosol particles were formed in the system. They were removed with plane filters from the gas stream. Gaseous ruthenium species were trapped in 1M NaOH-water solution, which is capable of trapping RuO_4 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 mass balance and achieve better time resolution three experiment using radioactive tracer were carried out.

Distribution

Publicity
Public

Project manager **Reviewed and approved by**

Ari Auvinen
Group Manager

1. INTRODUCTION

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In an accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium can oxidise and form volatile ruthenium species, RuO_3 and RuO_4, which can be transported in the containment. In contrast to 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 consequence calculations associated with severe nuclear reactor accidents, ruthenium accounts for >10% of the effective lung dose. In order to prevent radioactive ruthenium from spreading in gaseous form in case of an accident in a nuclear power plant it is of interest to know how it is formed and how it behaves. In our experiments RuO_2 has been exposed to diverse humid oxidising atmospheres at high temperatures. The formation and decomposition of gaseous ruthenium species has been studied as well as the decomposition products. The most important experimental parameters are the temperature of the furnace, the cooling rate of the gas and the composition of the humid oxidising atmosphere.

2. EXPERIMENTAL FACILITY

2.1 RuO_2 OXIDATION EXPERIMENTS IN HUMID CONDITIONS

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.

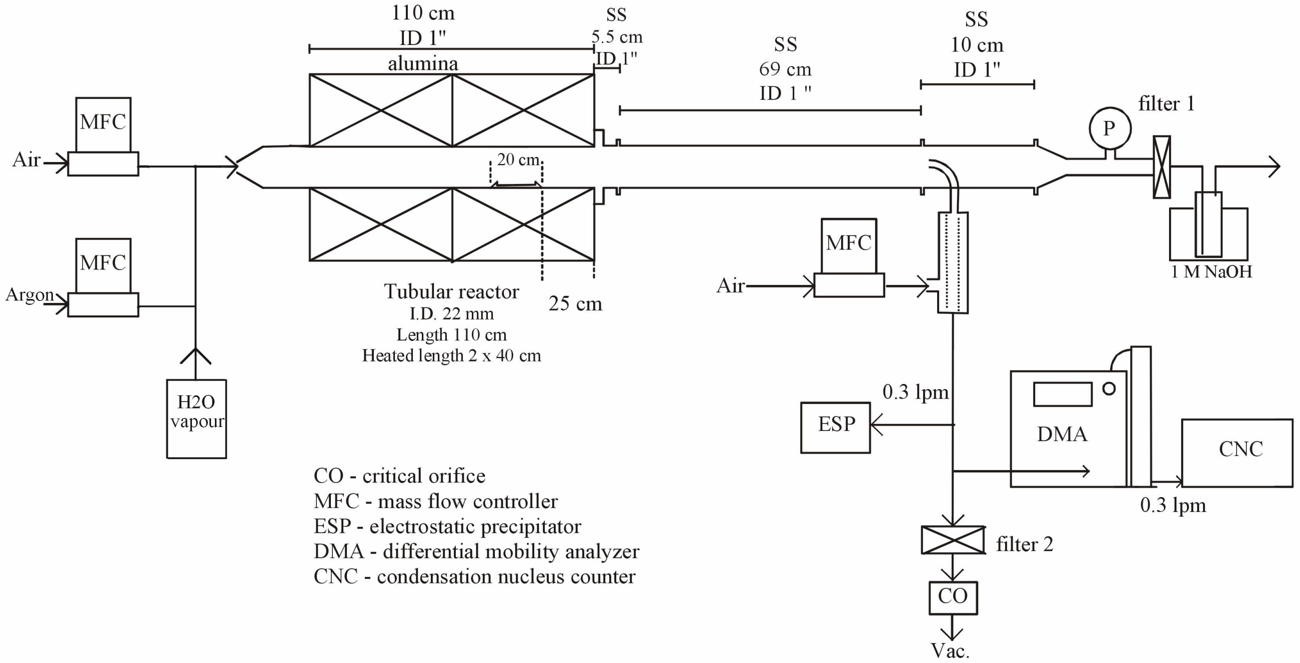

Figure 1: Experimental set-up for ruthenium experiments.

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

As the gas exited the reactor, it cooled in a stainless steel (AISI 316L) tube and the gaseous ruthenium oxides decomposed partly to RuO_2 particles. Aerosol particles were filtered out at point 106 cm downstream of the reactor. The filters used were polycarbonate (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 and so minimising the 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 fumed 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 ANALYSIS OF THE SAMPLES

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.

3. EXPERIMENTAL MATRIX

Eight experiments have been carried out during year 2005. The details of the experiments can be found in table 1. During the experiments the gas flow through the reactor was 5 l/min. In first three experiments and in the sixth experiment the gas flow was saturated with water vapour at 30°C. In the other experiments different amounts of steam was injected into the gas stream, while oxygen partial pressure was kept constant. Radioactive tracer was used in the last three experiments.

In experiments with saturated air flow the reactor set point was either 1300 K, 1500 K or 1700 K. The durations of the experiments 1, 2 and 6 were 45, 40 and 41 minutes respectively. The third test was a revaporisation experiment with a much longer duration. In revaporisation experiment the reactor set point was 1700 K and the furnace tube was the same as used in the second experiment.

However, ceramic crucible with RuO_2 powder was removed from the furnace. All ruthenium released in the revaporisation test was thus deposited on tube surfaces in the second experiment.

Table 1: Details of the experiments.

Exp	Reactor T	Flow rate	Gas	Tube material (from furnace to filter)	Duration	Other
#	K	lpm			min	
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

In steam feed experiments 4, 5, 7 and 8 the temperature ranged from 1100 K to 1500 K. The gas flow was a combination of steam, argon and air. Oxygen partial pressure was kept constant even though steam volume fraction was changed. Experiment 5 was a "revaporisation" experiment with RuO_2 powder sample placed inside the furnace. The duration of the revaporisation experiment was 372 minutes. Duration of other steam feed experiments varied between 23 and 45 minutes.

In the experiments 6, 7 and 8 radioactive tracer was used in order to close the mass balance and to get on-line data about the behaviour of ruthenium during experiment. In these experiments the furnace set point was either 1300 K or 1500 K. In experiment 6 air was saturated with water, while during experiments 7 and 8 the gas flow was a combination of steam, argon and air.

4. RESULTS

The preliminary results are summarised in table 2. 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 are constant throughout the experiment.

4.1 RUTHENIUM RELEASE RATE

Ruthenium release rate results are presented in figure 2. Release rates at dry conditions were measured in an earlier study [Backman et al., 2004]. According to results, the release rate of ruthenium decreases while the oxygen partial pressure is decreased – as expected. Increasing steam partial pressure while keeping the oxygen partial pressure constant seemed to have no effect on release rate. Ruthenium release rate increased from 0,11 to 19,43 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. Higher gas flow rate at 1500 K seemed to also increase ruthenium release rate.

Table 2: Preliminar results of the experiments on the behaviour of ruthenium. Values are presented as ruthenium. Values for transport are corrected for 5 l/min flowrate.

Exp	Reactor T	Ru evaporated	Bubbler	Filter 1	Release rate	Transport: Bubbler	Transport: Filter 1
#	K	mg	mg	mg	mg/min	mg/min	mg/min
1 (SS)	1300	88,5	4,80	0,6	1,97	0,1723	0,0208
2 (SS)	1700	777,0	0,16	> 123,3	19,43	0,0054	> 4,1768
3 (SS)	1700		4,53	4,84		0,0126	0,0134
4 (SS)	1500	223,9	1,01	15,3	9,73	0,0524	0,7944
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	1,2677
7 (SS)	1300	36,8	1,40	2,0	0,82	0,0311	0,0444
8 (SS)	1300	37,5	0,82	0,5	0,83	0,0182	0,0111

4.2 GASEOUS RUTHENIUM TRANSPORT RATE

The rate of RuO_4 gas transport into trapping bubbler can be found in the figure 3 (values as ruthenium). Transport rates at dry conditions were measured in an earlier study [Backman et al., 2004]. RuO_4 transport rate ranged from ~ 0 to 0,17 mg/min. Lowest transport rate of gaseous ruthenium was measured at 1100 K. Transport was highest at 1300 K although release rate continued to increase as the temperature of the furnace was increased. High oxygen partial pressure seemed to favour RuO_4 transport. Also higher flow rate increased transport of gaseous ruthenium. During revaporisation experiment at 1700 K the transport rate was 0,0126 mg/min. As much as 50 % of revaporised ruthenium was transported as RuO_4. It should be noted though that even though the furnace was at 1700 K in that experiment, the oxidation of ruthenium deposits must have taken place at a significantly lower temperature. In all experiments the measured transport rates of gaseous ruthenium were significantly lower than what was previously measured either with alumina tube or with seed particles.

4.3 RUTHENIUM AEROSOL PARTICLES TRANSPORT RATE

As in previous experiments the transport of RuO_2 particles competed with the deposition on the wall 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 lower deposition on the walls. In all experiments most of the released ruthenium still deposited on the surfaces.

The rate of RuO_2 aerosol particles transport into plane filter is in the figure 4 (values as ruthenium). Transport rates at dry conditions were measured in an earlier study [Backman et al., 2004]. RuO_2 transport rate ranged from ~ 0 to 8,8 mg/min at temperatures 1100 K to 1700 K. Transport is increasing while temperature is increasing. This indicates that the aerosol particle formation is increasing while the temperature is increasing. When the oxygen partial pressure is decreasing the RuO_2 transport is also decreasing. In the figure transport is more than 4,18 mg/min at temperature 1700 K in the air saturated with water atmosphere (marked 19/4), because all ruthenium could not be analyzed. During revaporisation experiment 50 % of revaporised ruthenium was transported as RuO_2.

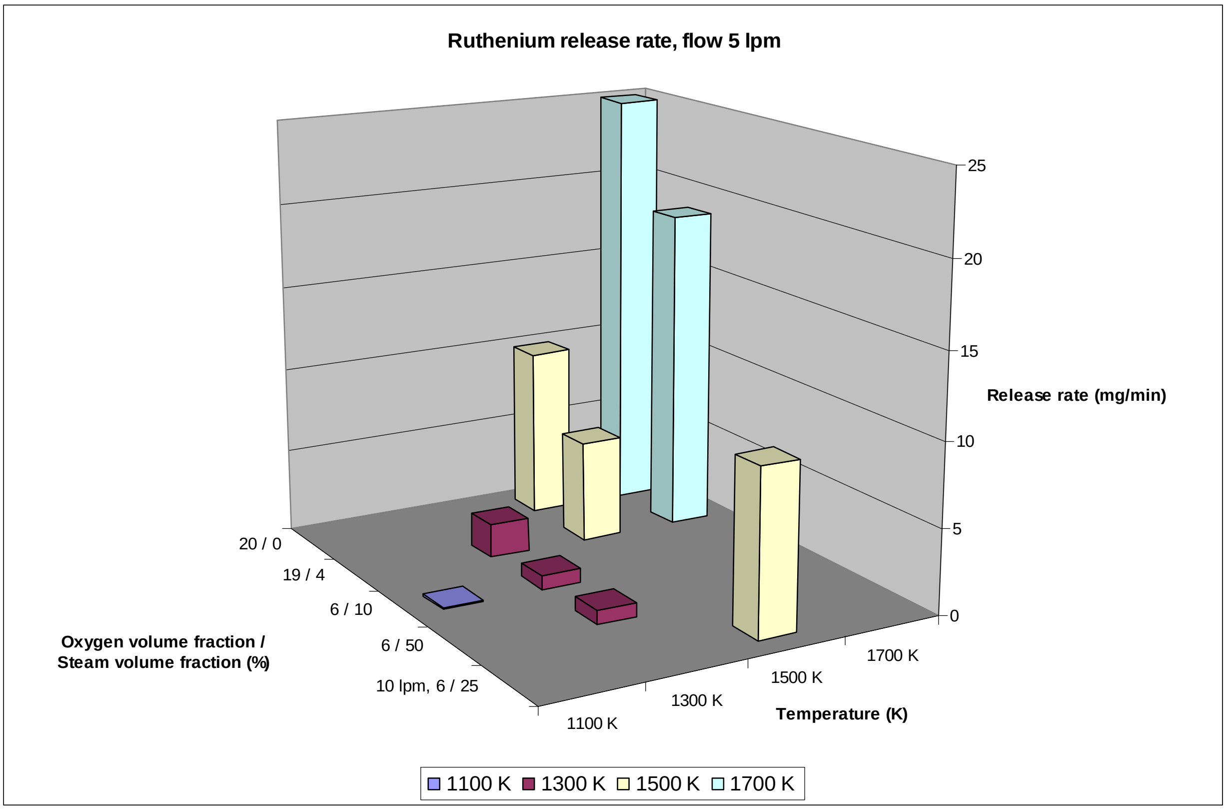

Figure 2: Ruthenium release rate (mg/min). Other units are temperature (K) and oxygen volume fraction / steam volume fraction (%), which presents the partial pressure proportions of oxygen and steam in gas flow. There is one experiment with 10 lpm flow.

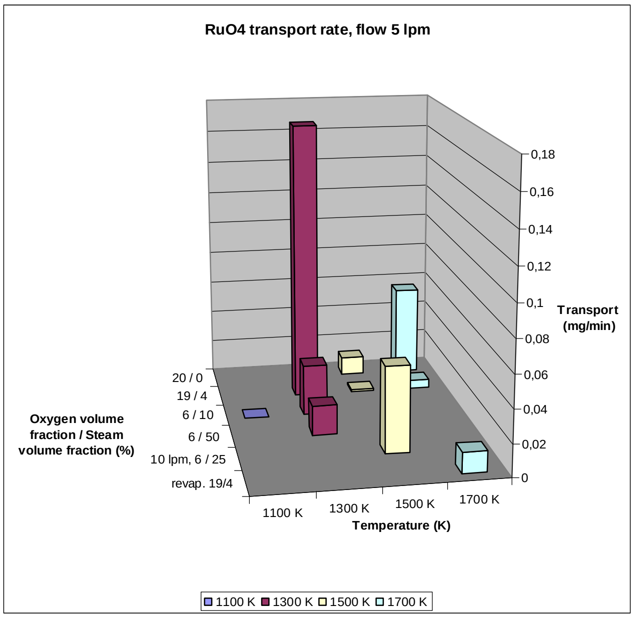

Figure 3: RuO_4 transport rate (mg/min). Other units are temperature (K) and oxygen volume fraction / steam volume fraction (%). There are also 10 lpm flow and revaporisation experiments.

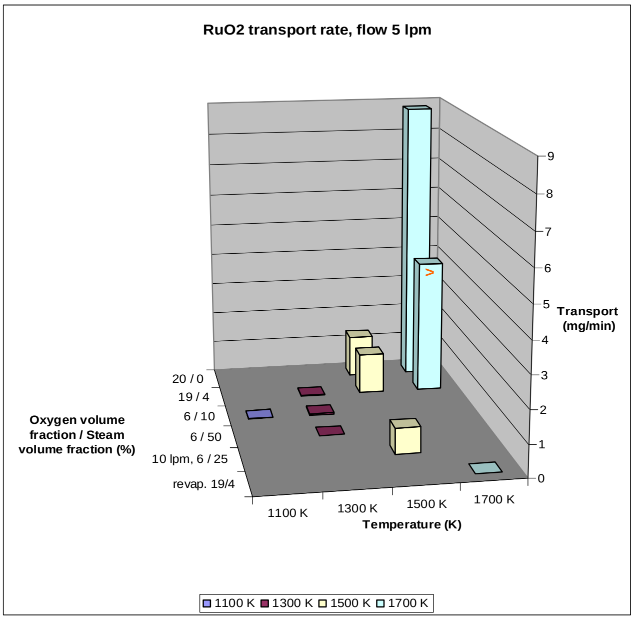

Figure 4: RuO_2 transport rate (mg/min). Other units are temperature (K) and oxygen volume fraction / steam volume fraction (%). There are also 10 lpm flow and revaporisation experiments.

4.4 RADIOACTIVE TRACER MEASUREMENTS

Activated RuO_2 powder was used as γ-tracer in experiments 6, 7 and 8. Five detectors measured the activity of sample in the ceramic crucible, the ceramic tube at the end of furnace, the beginning of stainless steel tube, the aerosol filter and the gas trapping bottle on-line during the experiments (underlining corresponds the curve name). Results from the on-line measurements are presented in figures 5-8. In all experiments most of the released ruthenium deposited on the surfaces.

Data in the figures is raw measurement data. In the figures it can be seen that ruthenium release rate from the crucible is constant. Ruthenium deposition velocity is also constant. However, it seems like the rate of RuO_4 transport (bottle curve) is increasing at the end of measurement. Further experiments are needed to be able to explain the behaviour.

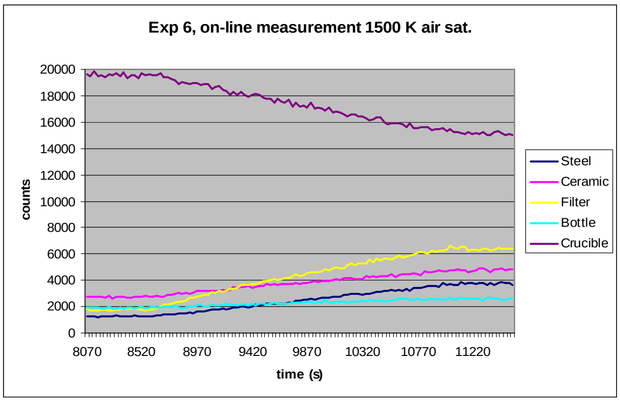

Figure 5: Experiment 6 on-line measurement. Axis units are the measured activity of sample at five location and time.

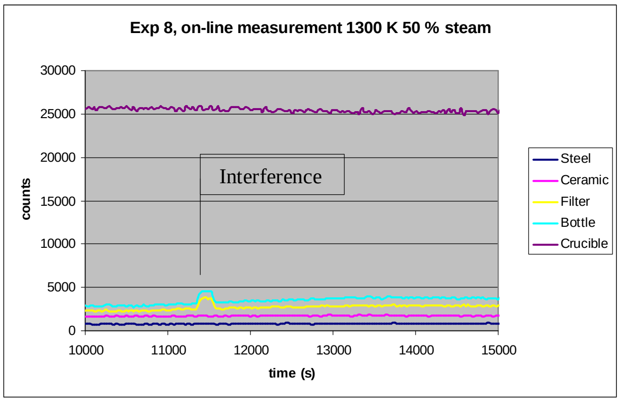

Figure 6: Experiment 8 on-line measurement. Axis units are the measured activity of sample at five location and time.

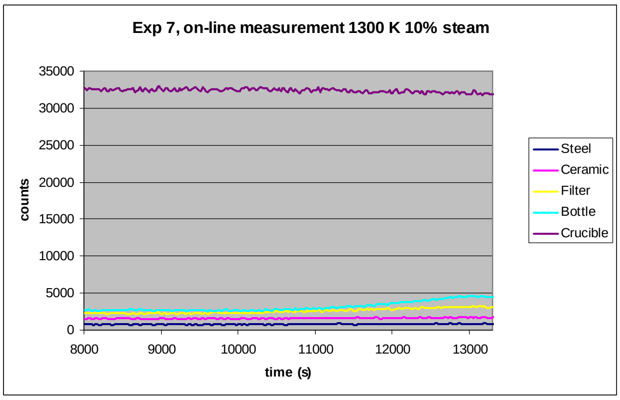

Figure 7: Experiment 7 on-line measurement. Axis units are the measured activity of sample at five location and time.

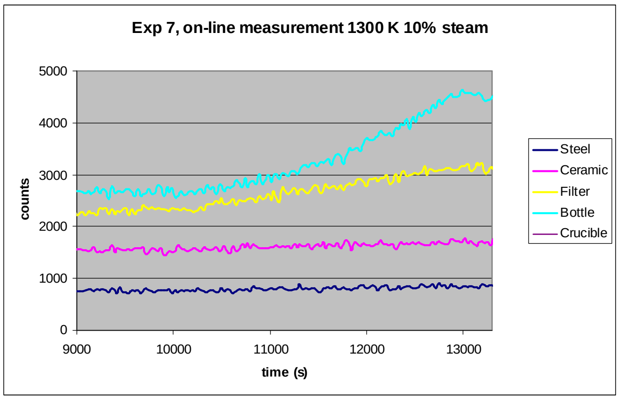

Figure 8: Experiment 7 on-line measurement, without data from the crucible. Axis units are the measured activity of sample at five location and time.

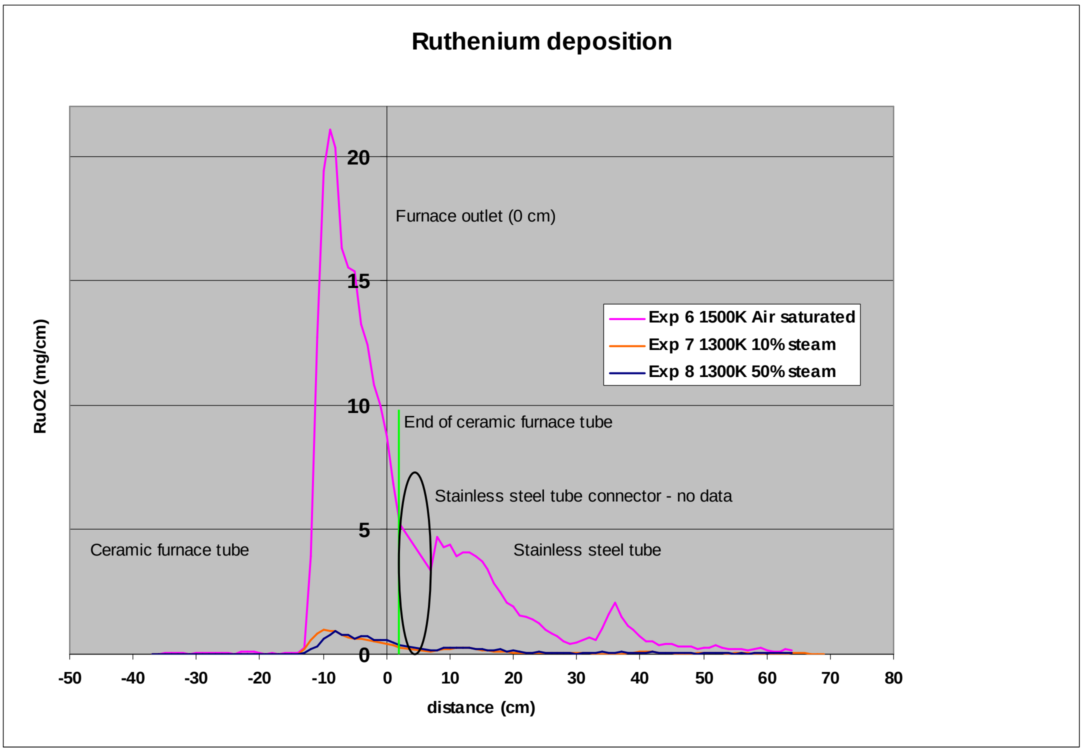

Figure 9: Ruthenium deposition profile in the experiments 6, 7 and 8. Deposition is RuO_2 mass found per centimetre (mg/cm). Furnace outlet is located at 0 cm. There is no deposition data from stainless steel tube connector.

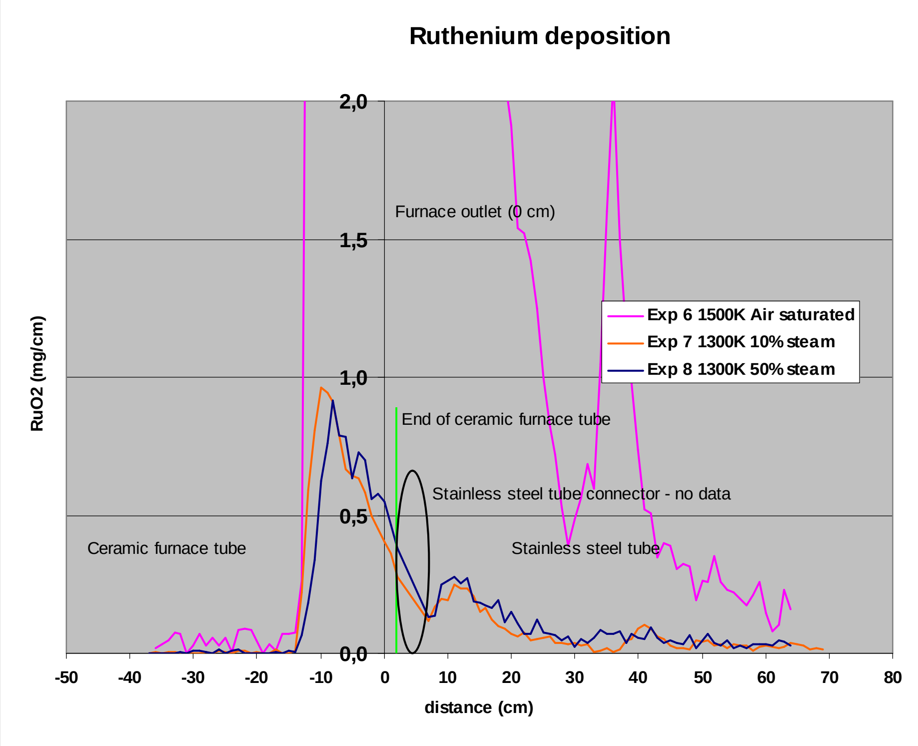

Figure 10: Ruthenium deposition profile in the experiments 6, 7 and 8. Deposition is RuO_2 mass found per centimetre (mg/cm). Furnace outlet is located at 0 cm. There is no deposition data from stainless steel tube connector.

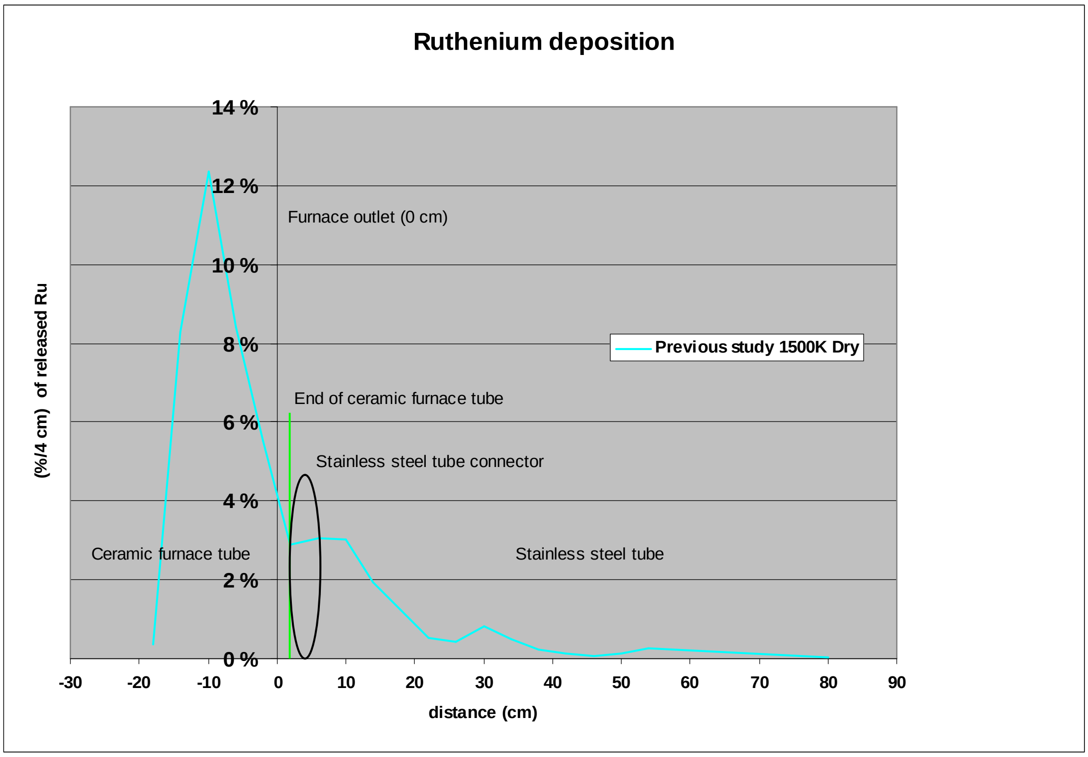

Figure 11: Ruthenium deposition profile in a previous study at 1500 K in dry conditions. Deposition is proportion of RuO_2 mass found of released RuO_2 mass per four centimetres (%/4 cm). Furnace outlet is located at 0 cm.

The measured deposition profiles of ruthenium (RuO_2 mass found per centimetre) inside the ceramic furnace tube and stainless steel tube at the outlet of furnace are presented in figures 9 and 10. In the figure 11 is ruthenium deposition profile in a previous study [Backman et al., 2004]. The deposition profile is proportion of RuO_2 mass found of released RuO_2 mass per four centimetres inside the ceramic furnace tube and stainless steel tube at the outlet of furnace. Furnace outlet is located at 0 cm in the figures. As can be seen the measured profiles correspond very well to each others as well as to the profile measured in a previous study. 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 ceramic furnace tube at the end of furnace (peak is about at -8 cm). At that location there is a large temperature gradient inside the furnace because of insulation. Deposition likely takes place by thermal dissociation of RuO_3 to RuO_2. The second deposition peak is at furnace outlet and it is formed by thermophoresis. The last peak is very clear in experiment 6 (at 36 cm). It is probably deposition by decomposition of RuO_4 at 150-200°C. More gaseous ruthenium was transported both in experiments 7 and 8, in which the third peak is absent, than in experiment 6.

The difference in deposition profiles between temperatures 1500 K and 1300 K in the figures 9 and 10 is mainly due to difference in ruthenium release rate. The speciation of released ruthenium may also have an effect, since there was a difference in oxidation temperature. There is a difference in the first deposition peaks between experiments 7 and 8 also. Probably the increased amount of water vapour in experiment 8 transferred more heat and therefore the dissociation and deposition took place further in the tube.

4.5 AEROSOL PARTICLES PROPERTIES

RuO_2 particles were collected and analysed with the transmission electron microscope (TEM). Representative TEM images are presented in figure 12. The number size distribution of the particles was measured using a DMA/CNC combination. A typical size distribution is presented in the figure 13. The mean particle size was 108 nm and the standard deviation was 1,5. The measured particle size distribution corresponds to the size of agglomerates and is therefore larger than the size of primary particles.

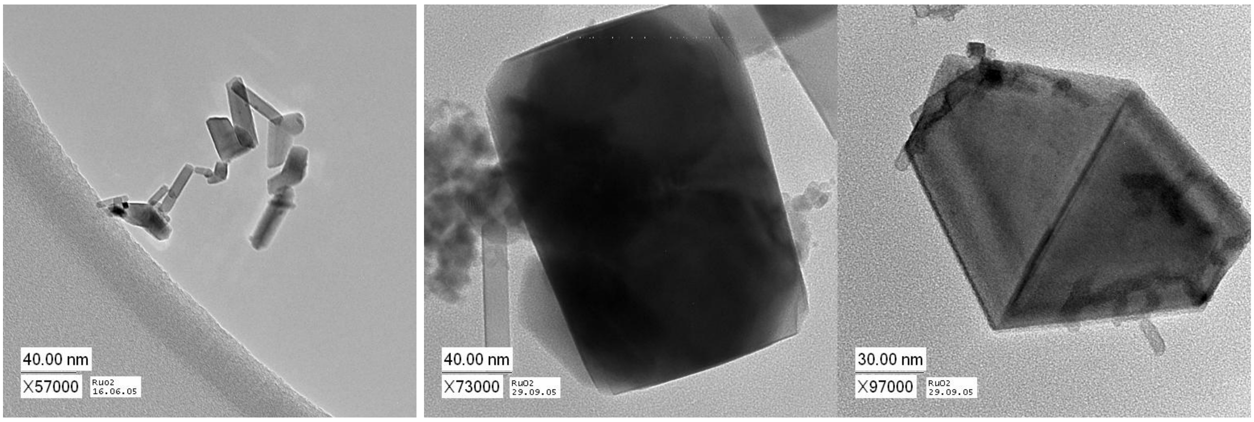

Figure 12: TEM images of RuO_2 particles in the experiments 2 (16.06.05) and 4 (29.09.05).

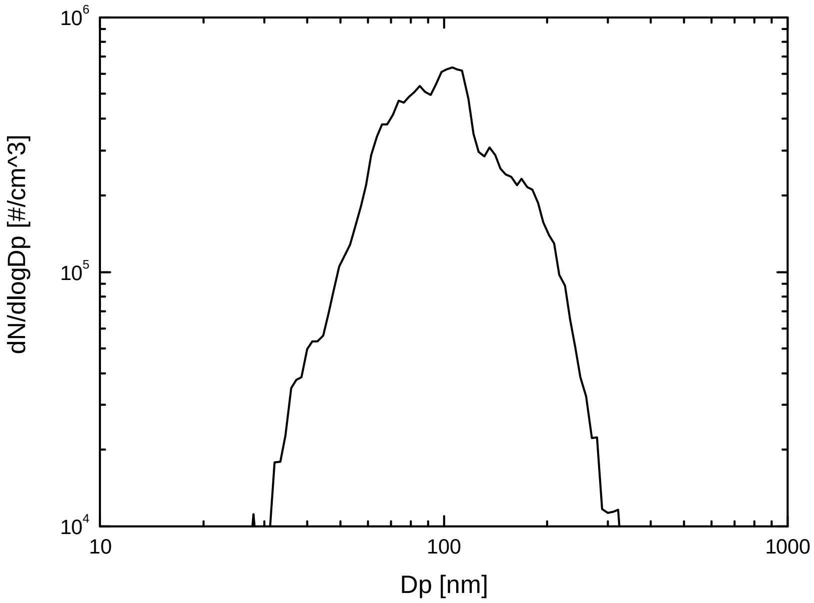

Figure 13: Typical number size distribution of RuO_2 particles (experiment 2).

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.

Eight experiments studying the behaviour of ruthenium in humid oxidising conditions were carried out during year 2005. A significant difference in the decomposition rate of gaseous ruthenium depending on the reactor temperature was found. These experiments did not fully support the previous assumption that water vapour would passivate the steel surface. There seem to be additional important phenomena taking place in the experiments. Three radioactive tracer experiments were conducted, in which ruthenium deposition profiles were measured. These profiles gave new information about ruthenium release and deposition. Further experiments are needed in order to study the release kinetics and the retention of ruthenium at different temperatures and atmospheres. We expect that after experiments planned for year 2006, issues related to ruthenium transport can be solved. Preliminary test matrix for year 2006 experiments in humid oxidising conditions is presented in the table 3.

Table 3: Preliminary test matrix for year 2006 on the behaviour of ruthenium.

Exp	Reactor T	Flow rate	Gas	Tube material (from furnace to filter)	Other
#	K	lpm			
1.	1700	5	Steam/Ar/Air 50/20/30	stainless steel	
2.	1700	5	Steam/Ar/Air 50/20/30	stainless steel	revaporisation
3.	1300	5	Steam/Air 70/30	stainless steel	γ-tracer
4.	1500	5	Steam/Air 70/30	stainless steel	
5.	1700	5	Steam/Air 70/30	stainless steel	γ-tracer
6.	1500	5	Air + RuO_4	stainless steel	γ-tracer water vapour no sample
7.	1500	5	Air + RuO_4	stainless steel	γ-tracer water vapour
8.	1500	5	Air	stainless steel	seed particles low conc. γ-tracer
9.	1500	5	Air	stainless steel	seed particles high conc.

REFERENCES

Jokiniemi J. and Zilliacus R. Esiselvitys ruteniumin käyttäytymisestä hapettavissa olosuhteissa. VTT Kemiantekniikka raportti Dnro 252-01/KET11, 2001.

Backman U., Lipponen M., Auvinen A., Jokiniemi J. and Zilliacus R. Ruthenium behaviour in severe nuclear accident conditions – Final Report. VTT Processes, PRO3/P26/04, 2004.

Bibliographic Data Sheet **NKS-118**

Title	Experiments on the behaviour of ruthenium in air ingress accidents - Progress report
Author(s)	Kärkelä, T., Backman U., Auvinen, A., Zilliacus, R., Lipponen, M., Kekki, T., Tapper, U., Jokiniemi, J.
Affiliation(s)	VTT Technical Research Centre of Finland
ISBN	87-7893-179-7 *(Electronic report)*
Date	February 2006
Project	NKS_R_2002_02
No. of pages	12
No. of tables	3
No. of illustrations	13
No. of references	2

Abstract

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In an accident in a nuclear power plant it is possible that air gets into contact with the reactor core. In this case ruthenium can 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 it is formed and how it behaves. In our experiments RuO2 is exposed to diverse oxidising atmospheres at a relatively high temperature.

In this report, the experimental system for the ruthenium behaviour study is presented. Also preliminary results from experiments carried out during year 2005 are reported. In the experiments gaseous ruthenium oxides were produced in a furnace. Upon cooling RuO2 aerosol particles were formed in the system. They were removed with plane filters from the gas stream. 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 mass balance and achieve better time resolution three experiment using radioactive tracer were carried out.

Key words Ruthenium, Air ingress, Fission product transport

Available on request from the NKS Secretariat, P.O.Box 49, DK-4000 Roskilde, Denmark.
Phone (+45) 4677 4045, fax (+45) 4677 4046, e-mail nks@nks.org, www.nks.org