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Interactions of $\text{RuO}_4(\text{g})$ with different surfaces in nuclear reactor containments

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Abstract

During a severe nuclear reactor accident with air ingress, ruthenium in the form of RuO₄ can be released from the nuclear fuel. Hence, it is important to investigate how the reactor containment is able to reduce the source term of ruthenium.

This work has investigated the distribution of RuO₄ between an aqueous and gaseous phase in the temperature interval of 20-50°C by on-line measurements with an experimental set-up made of glass. The experiments showed that RuO₄ is almost immediately distributed in the aqueous phase after its introduction in the set-up in the entire temperature interval. However, the deposition of ruthenium on the glass surfaces in the system was significant. The speciation of the ruthenium on the glass surfaces was studied by SEM-EDX and ESCA and was determined to be the expected RuO₂.

Experiments of interactions between gaseous ruthenium tetroxide and the metals aluminium, copper and zinc have been investigated. The metals were treated by RuO₄ (g) at room temperature and analyzed with ESCA, SEM and XRD. The analyses show that the black ruthenium deposits on the metal surfaces were RuO₂, i.e. the RuO₄ (g) has been transformed on the metal surfaces to RuO₂(s). The analyses showed also that there was a significant deposition of ruthenium tetroxide especially on the copper and zinc samples. Aluminium has a lower ability to deposit gaseous ruthenium tetroxide than the other metals.

The conclusion that can be made from the results is that surfaces in nuclear reactor containments will likely reduce the source term in the case of a severe accident in a nuclear power plant.

Key words

Deposition, Ruthenium tetroxide, Ruthenium dioxide, Ruthenium speciation

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<p>Summary</p> <p>During a severe nuclear reactor accident with air ingress, ruthenium in the form of RuO₄ can be released from the nuclear fuel. Hence, it is important to investigate how the reactor containment is able to reduce the source term of ruthenium.</p> <p>This work has investigated the distribution of RuO₄ between an aqueous and gaseous phase in the temperature interval of 20-50°C by on-line measurements with an experimental set-up made of glass. The experiments showed that RuO₄ is almost immediately distributed in the aqueous phase after its introduction in the set-up in the entire temperature interval. However, the deposition of ruthenium on the glass surfaces in the system was significant. The speciation of the ruthenium on the glass surfaces was studied by SEM-EDX and ESCA and was determined to be the expected RuO₂.</p> <p>Experiments of interactions between gaseous ruthenium tetroxide and the metals aluminium, copper and zinc have been investigated. The metals were treated by RuO₄ (g) at room temperature and analyzed with ESCA, SEM and XRD. The analyses show that the black ruthenium deposits on the metal surfaces were RuO₂, i.e. the RuO₄ (g) has been transformed on the metal surfaces to RuO₂(s). The analyses showed also that there was a significant deposition of ruthenium tetroxide especially on the copper and zinc samples. Aluminium has a lower ability to deposit gaseous ruthenium tetroxide than the other metals.</p> <p>The conclusion that can be made from the results is that surfaces in nuclear reactor containments will likely reduce the source term in the case of a severe accident in a nuclear power plant.</p>	
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Preface

Interactions of RuO₄ with different surfaces that can be found in a Swedish boiling water reactor (BWR) containment have been investigated at Chalmers during years 2006-2008. As a result an increased understanding about the behaviour of RuO₄ in environments that can be compared to conditions in BWR containments has been reached.

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Christian Ekberg

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1. Introduction

During normal operation in a nuclear power plant, relatively high concentrations of ruthenium will be formed by fission of uranium. Calculations made by Wright [Wright 94] show that about 330 kg of ruthenium are formed in the nuclear fuel in a boiling water reactor (BWR) at the end-of-cycle equilibrium core. This can be compared to the amounts of iodine and caesium, 30 kg and 430 kg respectively. The amount of ruthenium increases with burn-up and ²³⁵U enrichment of the fuel. The radiotoxicity from ruthenium originates essentially from the two nuclides ¹⁰³Ru ($t_{1/2} \approx 40$ d) and ¹⁰⁶Ru ($t_{1/2} \approx 1$ y), thus ruthenium is important both in a short and long perspective.

Ruthenium oxides may be formed in the reactor vessel during a severe accident with air ingress [Powers 94]. Events leading to air ingress occur during the late phase of a severe accident. Ruthenium oxides such as RuO₃ and RuO₄ are considerably volatile and can consequently be released from the reactor vessel to the reactor coolant system (RCS) and the containment. There are two main categories of air ingress to the reactor fuel:

1. a melt-through scenario
2. a shutdown sequence with an open vessel lid

The most probable scenario of an air ingress accident in a BWR is during the shutdown cycle with an open reactor lid. Since the atmosphere in the containment contains only a few percent

oxygen during normal operation, it is not probable that significant amounts of oxygen can enter via openings in the reactor vessel created by melt-through. However, during a shutdown cycle with an open reactor lid and higher amounts of oxygen in the containment, a severe accident with air ingress can occur, leading to ruthenium oxidation.

The temperature range in the containment under severe accident conditions will be relatively low, below 150°C. The gaseous oxides RuO(g), RuO₂(g) and RuO₃ (g) are not thermodynamically stable under temperatures below 1000°C and will probably not reach the containment [Mun 06a]. Hence we have concentrated on the behaviour of RuO₄ in a BWR containment environment.

This work was divided into two parts, 1. investigation of the distribution of RuO₄ between an aqueous and a gaseous phase and 2. investigation of the deposition of RuO₄(g) on different metal surfaces. These metals were aluminium, copper and zinc and which are all present in rather large quantities in Swedish BWR containments.

2. Experimental

2.1 Experimental description for the RuO₄ distribution experiments

2.1.1 Experimental set-up

The experimental set-up that has been used for the distribution experiments is shown in figure 2.1. It consists of a reactor vessel connected to two loops, one loop for the water phase and one loop for the gas phase. The volumes of the water and gas phase are chosen to be almost proportional to those phases in a Swedish BWR containment of recent design; the fractions can be seen in table 2.1.

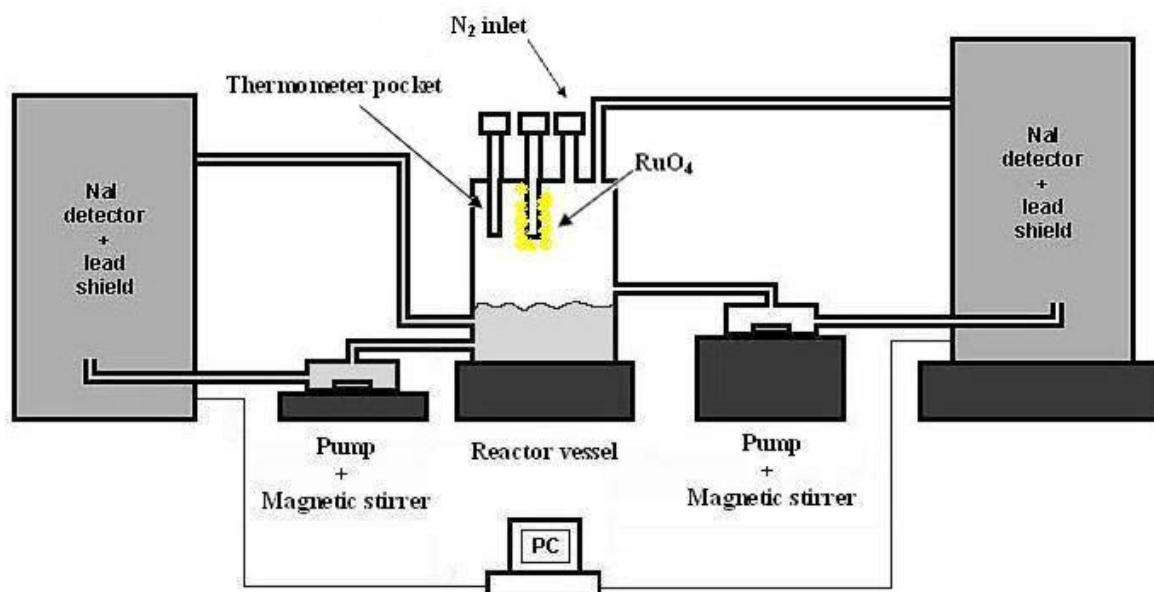
The circulation and transportation in the system was ensured by two specially designed glass pumps of impeller type with a magnet inside, driven by two magnetic stirrers. The magnets in the pumps were glass-enclosed. The flow rate of the aqueous phase was determined by filling up an external vessel 8 times with water from the loop and measuring the filling time. The average flow rate was calculated to $6.3 \pm 0.5 \text{ cm}^3 \cdot \text{s}^{-1}$. The flow rate in the gaseous phase was determined by introduction of bromine gas in the system and measurement of the consumed time for the gas front travelling a pre-defined distance. The procedure was repeated 8 times and the average flow rate was calculated to $4.8 \pm 0.6 \text{ cm}^3 \cdot \text{s}^{-1}$.

The two glass loops passed two 2in. × 2in. NaI(Tl) detectors that were connected, via a scintiSPEC™ analyzer and an USB-port, to a computer. The NaI(Tl) detectors were used to detect the 496 keV γ -rays emitted in the decay of ¹⁰³Ru.

Heating bands, regulated by a transformer, winded around the pipes and the reactor vessel, generated heating of the system. The vessel and pipes were insulated with both insulation tape and aluminium foil. The temperature in the reactor vessel was monitored visually by reading a glass-enclosed thermometer located in the gas phase. Additional thermal sensors were used to monitor the temperature in the both loops.

Table 2.1: Volumes and relative proportion of the experimental set-up and a BWR containment

	<i>BWR</i>	<i>Experiment</i>
Total volume (m ³)	11870	1.01*10 ⁻³
Gas volume (m ³)	8524	7.23*10 ⁻⁴
Fraction	0.72	0.71
Water volume (m ³)	3346	2.90*10 ⁻⁴
Fraction	0.28	0.29


Figure 2.1: The experimental set-up for the RuO₄ distribution experiments.

2.1.2 Experimental procedure

Every experiment was started by filling the aqueous loop and half of the reactor vessel with distilled water. Circulation was then started in the two phases and air bubbles stuck in the loop of the aqueous phase were removed by pulsing the water flow using the pumps. The system was then flushed with nitrogen gas to ensure that only a few percent of oxygen was present. After nitrogen flushing the system had reached an atmosphere almost similar to that in a BWR containment. Gas-MS analyses were performed to analyze the atmosphere in the set-up. The analyses showed that one hour of nitrogen flushing of the system was sufficient to ensure that less than 5 percent of oxygen was present in the atmosphere. Further nitrogen flushing did not result in lower oxygen concentration, explaining a somewhat higher oxygen concentration than during normal operation in a BWR. Gaseous ruthenium tetroxide spiked with an arbitrary amount of ¹⁰³Ru was introduced into the system by letting ¹⁰³RuO₄(cr) vaporize in the gas phase of the reactor vessel. The RuO₄(cr) production procedure is described below, see section 2.3. The distribution of ¹⁰³RuO₄ between the two phases was measured by the two NaI(Tl) detectors.

2.2 Experimental description for the RuO₄ and metal interaction experiments

2.2.1 Experimental set-up and procedure

A sketch of the experimental set-up used for the experiments in this section can be seen in figure 2.2. The set-up is a simple glass bottle, with one or three sample holders in glass. Nitrogen (humid or dry) and $\text{RuO}_4(\text{cr})$ were introduced through openings in the lid of the glass bottle. The temperature in the set-up was room temperature, $\sim 20^\circ\text{C}$.

The aim of the experiments was to study the interactions between $\text{RuO}_4(\text{g})$ and the metals aluminium, copper and zinc, in order to observe differences of the speciation of ruthenium on the different metal surfaces. Furthermore, the impact of the atmosphere in the reaction bottle was investigated. The experiment plan can be seen in table 2.2.

The experiments started with one or three metals placed in the glass bottle. For the experiments with nitrogen atmosphere in the system, the glass bottle was flushed with nitrogen for one hour. Then ruthenium tetroxide crystals, attached on the outer surface of a dry ice cold sample vial inserted into the bottle, were introduced in the system. The crystals began to sublime immediately after removal of the dry ice from the sample vial, and interaction between the metals and $\text{RuO}_4(\text{g})$ started. The reaction time was more than 15 hours, in order to ensure that all $\text{RuO}_4(\text{g})$ had reacted with the surfaces in the system [Mun 07b].

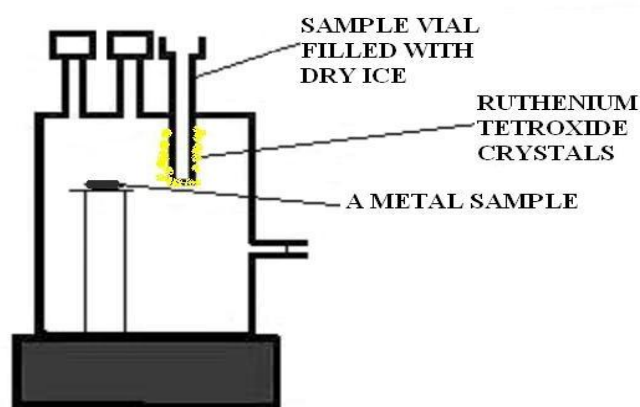


Figure 2.2: The sorption experimental set-up.

2.2.2 Metal sample preparation

The metals used in these experiments were discs of aluminium, copper and zinc. The dimensions of the aluminium and copper samples were 10 mm x 10 mm x 3 mm (thickness) and dimensions of the zinc samples were 17 mm (diameter) x 3 mm (thickness). In order to minimize the presence of an oxide layer on the metal samples and to ensure reliable results from the ESCA analyses, the samples were prepared before the experiments using a polishing machine with a rotational disc. The grinding paper on the rotational disc was gradually changed to paper of less roughness during the polishing procedure, and the paper was finally changed to a polishing cloth and diamond spray. After the polishing procedure the samples were washed in acetone and ethanol in an ultrasound bath. The appearance of the metal sample surfaces was mirror-like after the polishing procedure.

**Table 2.2:** Experiment plan of the RuO₄ and metal

Experiment	Metal	Atmosphere	Humidity
1	Zn	Nitrogen	No
2	Zn	Air	No
3	Zn	Nitrogen	Yes
5	Al	Nitrogen	No
6	Al	Air	No
7	Al	Nitrogen	Yes
9	Cu	Nitrogen	No
10	Cu	Air	No
11	Cu	Nitrogen	Yes
T1	Al Zn Cu	Nitrogen	No
T2	Al Zn Cu	Air	No
T3	Al Zn Cu	Nitrogen	Yes

2.2.3 Analysis techniques

Several analysis techniques were used in this work, for analysing the metal surfaces. The samples were stored under inert nitrogen atmosphere in the time between experiments and analyses, to prevent changes in the chemical state of the adsorbed ruthenium on the metal samples.

1. ESCA

Electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS) was done using an X-ray spectrophotometer (Perkin Elmer PHI5500 Multi Technique System). This technique is useful to characterize the speciation of different elements attached to a surface. An ESCA instrument is using an X-Ray source to ionize electrons from the surface layer of a solid sample. The energies of these electrons are corresponding to the bonding energy of the surface electrons attached the solid sample. The bonding energies of the electrons are characteristic for every element and give information on the chemical bonding, i.e. the chemical state.

2. SEM

Scanning Electron Microscopy (SEM) pictures were taken of some the metal samples, after the ESCA measurements. The pictures give information about the nature of adsorbed ruthenium species and the degree of surface coverage on the metal samples. The SEM equipment was a LEO 1550 with a GEMINI field emission column.

3. XRD

X-Ray Diffraction (XRD) analyses were done to further define the speciation of the ruthenium deposits. The XRD instrument was a Siemens D5000 diffractometer with Cu characteristic radiation, Göbel mirror on primary side and long Soler slits with SOL'X Bruker solid state detector on the secondary side. The instrument has a grazing incidence geometry with 5 degrees fixed incidence angle.

2.3 RuO₄ production

RuO₄ can be produced by several methods, using different solvents and oxidizing agents. In the beginning of the work RuO₄ was distilled by heating a round flask with 5 mg RuCl₃, which was dissolved in minimal amounts of water before adding 5 ml concentrated H₂SO₄ and 0.25 ml 0.1 M KMnO₄. This method has two major disadvantages: first, it is slow at temperatures about 75°C, which is the optimal temperature for volatilizing RuO₄ [Mun 05]. To reach complete ruthenium distillation, at least two hours of reaction time was required. Second, the vapour consists of different by-products, such as manganese, which could be seen as deep-purple crystals deposited on the distillation column.

In this work, a modification of the method developed by Krtil et al. [Krtil 71] was used. 5 mg RuCl₃ dissolved in 3 ml H₂O, 2 ml 2 M Na₂CO₃ and 0.5 g K₂S₂O₈ were used to distill ruthenium tetroxide. The distillation equipment consisted of a round bottle flask where the reaction took place, and mixing was achieved by a glass-enclosed magnet. An exhaust through a 1 M NaOH trap was connected to the column to prevent ¹⁰³RuO₄ from escaping. An arbitrary gas flow of oxygen through the system was ensured by connection to a gas tube. Complete ruthenium distillation was reached within 40 minutes at 75°C. The melting point of solid ruthenium tetroxide is 27°C, but it already sublimates at temperatures below 7°C [Runkle 79]. To keep the crystals in a solid form, the RuO₄ vapour was allowed to condense to yellow RuO₄ crystals on the outer surface of a sample vial filled with dry ice.

3. Results and discussion

3.1. Results from the RuO₄ distribution experiments

The intention of this work was to determine the partition coefficient of RuO₄, defined as in equation (1), in the temperature interval 20-50°C.

$$K_d = [\text{RuO}_4]_{\text{aq}}/[\text{RuO}_4]_{\text{g}} \quad (1)$$

However, at 20°C, the activity of ¹⁰³Ru in the gas phase decreased to the detection limit within five minutes after the introduction of RuO₄(cr) to the gas phase. The ¹⁰³Ru activity also decreased in the aqueous phase by about 25 % within 2 h. Since no obvious leakage had been noticed, the conclusion was made that ruthenium in some form had been accumulated in the system and sorbed on the glass surfaces. Deposits of a black powder on the glass surfaces could be seen with the naked eye, supporting this conclusion. Similar phenomena continued at elevated temperatures. In the experiments at 50°C, less ¹⁰³Ru activity was transferred to the aqueous phase immediately after the introduction of ¹⁰³RuO₄(cr) in the gaseous phase, compared to the experiments at 20°C. Nevertheless, the concentration of RuO₄ in the gaseous phase decreased close to the background level in about 15 min and decreased in the aqueous phase by about 15 % within 2h.

The nitrogen atmosphere was exchanged for purified air in some experiments, but no differences could be discerned between these experiments and the experiments with only nitrogen in the system.

Experiments were also performed at 50°C in which the aqueous phase was excluded, i.e. there was only nitrogen in the experimental set-up. This system cannot be compared with the

containment in a BWR under severe accident conditions, but it was of interest for later experiments to observe the behaviour of gaseous ruthenium tetroxide in the dry glass equipment. The concentration of RuO₄ decreased by 65 % over a period of 2 h, which confirmed the extensive adsorption of ruthenium on the glass surfaces. The concentration versus time plots of the experiments in this section of the work can be seen in appendix A.

Because of the accumulation of ruthenium in the system, the glass equipment was measured by an external HPGe detector. The measurements showed that the conclusion was correct: ruthenium in some form had been adsorbed on the glass surfaces. Due to the unusual geometric form of the measurement objects no calibrated detectors were available and it was therefore difficult to ascertain the exact quantity of ¹⁰³Ru on the different glass surfaces. Most of the sorbed ruthenium on the glass surfaces was found in the reactor vessel, where RuO₄ was introduced. There were also visible marks of sorbed ruthenium in the form of gray-black spots on the glass, particularly in joints, at glass corks and in the circulation pumps. Large deposits of ruthenium were also observed in the reactor vessel, which can be seen in figure 3.1.

3.2 Deposition rate of RuO₄ on the glass surfaces of the experimental set-up

Because of the significant deposition of RuO₄ on the glass surfaces in the system, investigations of the deposition on such surfaces were also performed. These investigations were outside the initial scope of the project. However, this part is included in this report to show the great ability of RuO₄ to deposit on almost inert surfaces, like glass.

The deposition rate of ruthenium tetroxide can be expressed as a first-order equation:

$$\frac{dm_d}{dt} = k_D A [Ru]_m \quad (2)$$

where m_d is the mass of deposited ruthenium, k_D is the deposition rate ($m \cdot s^{-1}$), A is the deposition area (m^2) and $[Ru]_m$ ($mg \cdot m^{-3}$) is the concentration of ruthenium in the aqueous or the gaseous phase. Equation (2) can be arranged with the help of mass balances to

$$[Ru]_t = [Ru]_0 \cdot e^{-k_D \frac{A}{V} t} \quad (3)$$

where $[Ru]_t$ is the ruthenium concentration ($mol \cdot dm^{-3}$) at time t , $[Ru]_0$ is the initial ruthenium concentration ($mol \cdot dm^{-3}$) and V is the volume (m^3). The equations can be used to calculate the deposition rate of RuO₄ on the glass surfaces for each phase.

The deposition rate, k_D , was broadly estimated to be $0.001 m \cdot s^{-1}$ for ruthenium deposition on the glass surfaces in the aqueous phase, at 20°C. The disappearance of ruthenium from the gaseous phase was too fast to make even a crude estimation of the k_D value. The results can be seen in table 1. The k_D values from the experiments in which the aqueous phase was present in the set-up are very uncertain, because the absorption of RuO₄ in the aqueous phase is included in these values.



Figure 3.1: The reaction vessel after the completed experiments. Observe the black spots of ruthenium deposits.

In an attempt to achieve a more reliable flow of the two phases in the experimental set-up, the glass pumps were in some experiments at 20°C exchanged to two electric pumps with a pump house made of anodized aluminium. These pumps were soon rejected, however, owing to even more extensive accumulation of ruthenium in the experimental set-up. The deposition rate was similar to that in the experiments with the usual glass pumps, but the flow rates, however, were considerably higher, 28 cm·s⁻¹ and 20 cm·s⁻¹ in the aqueous phase and the gaseous phase, respectively. Observe that the deposition rate in table 3.1, of the experiments with aluminium pumps, is calculated for the whole system (glass surfaces + aluminium surfaces). Significant amounts of black spots of deposited ruthenium were seen in with the naked eye on the surfaces in the aluminium pump house.

Table 3.1: The estimated deposition rates on the glass surfaces in the experimental set-up.

Temperature (°C)	Present phases	Pump type	Estimated k_D (m·s ⁻¹) gaseous phase	Estimated k_D (m·s ⁻¹) aqueous phase
20	aqueous, gaseous	glass	-	0.001
50	aqueous, gaseous	glass	0.1	0.0005
50	gaseous	glass	0.01	-
20	aqueous, gaseous	anodized aluminium	0.11	0.001

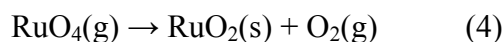
Because of the sorption of ruthenium tetroxide, all glass components in the experimental set-up were washed with dichromate sulphuric acid in order to ensure that very low concentrations of organic material existed on the surfaces. Reactions with organic material on the glass surfaces could be a reason for the extensive sorption of ruthenium. However, no noticeable difference between the experiments done before and after the washing was observed.

3.2.1 Speciation of the deposited ruthenium on the glass

Owing to substantial ruthenium deposits on the glass surfaces in the RuO₄ distillation column and the experimental set-up, it was necessary to examine the nature of adsorbed ruthenium. To do that, glass slides were stained by RuO₄ vapour in the distillation set-up. The glass slides were cleaned with ethanol and acetone, but also with dichromatic sulphuric acid to

ensure no organic contamination. The slides were placed approximately 15 cm from the aqueous surface in the distillation column and the substrate temperature was about room temperature. After staining the glass slides with gaseous ruthenium tetroxide the surfaces were covered with gray-black spots or a thin layer, depending on the amount of RuO_4 produced in the column. The adhesion of ruthenium tetroxide on the slides was extensive. Since the same distillation column was used for the production of ruthenium crystals and the staining of the glass slides, the walls in the column were covered with a thick black layer.

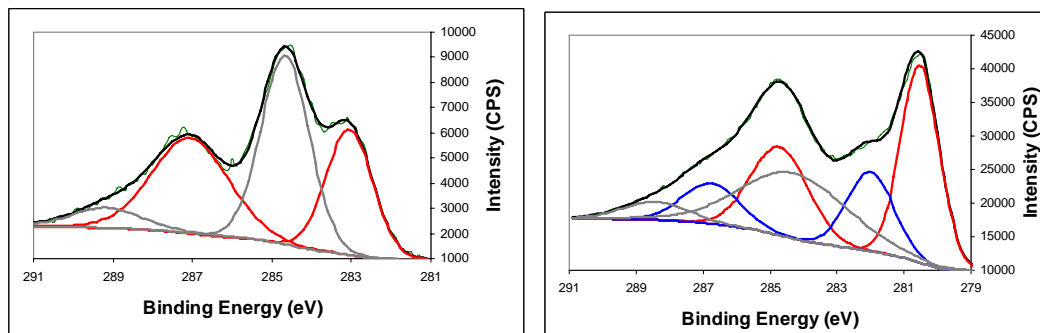
Reaction of RuO_4 with glass is rather controversial, and some authors [Klein 83], [Wood 85], [Yuan 93], have reported reactions of RuO_4 with glass surfaces at elevated temperatures, 150-300°C. They propose reaction (4) as a conceivable process for the sorption mechanism of ruthenium on glass surfaces.



Others, such as Igarashi et al [Igarashi 92], have found that no sorption of ruthenium occurs even in cooled glass tubes.

The stained glass slides in this work were first investigated by ESCA to identify the speciation of ruthenium on the surfaces. The ESCA measurements were done on two glass slides stained by $\text{RuO}_4(\text{g})$, but with different after-treatment. The first slide was stored at room temperature and in air; the second glass slide was heated to 300°C during 14 h in air. Both slides were analyzed with ESCA one day after the ruthenium tetroxide treatment. The aim of the heating was to remove water from the hydrous ruthenium deposit. Water in the crystal structure can complicate the ESCA spectra because of non-desirable changes of the binding energy of the emitted electrons, even if the oxidation state of the deposited ruthenium is not changed.

The two ESCA spectra, with a magnification of the major ruthenium peaks Ru 3d5/2 and Ru 3d3/2, of the two glass slides can be seen in figure 3.3. The spectra are complex mostly due to the inevitable carbon peak (C1s) at ~284.5 eV. Even with very careful cleaning of the glass slides with dichromatic sulphuric acid, carbon contamination was difficult to prevent. The spectra contain several components to get a fit of high quality. The main ruthenium peak Ru 3d5/2 in the two spectra is located at apparent differing energies levels, as expected due to the differing water content. In the ESCA spectrum of the heated sample, the Ru 3d5/2 peak is located at 280.5 eV, which corresponds to RuO_2 in the literature [Briggs 90]. The main ruthenium peak in the ESCA spectrum of the non-heated glass sample is located at 283.0 eV, which is a binding energy that is slightly too high even for hydrous ruthenium dioxide ($\text{RuO}_2 \cdot \text{H}_2\text{O}$). However, the only reasonable explanation for the location of the ruthenium peak is a very high water content in $\text{RuO}_2 \cdot \text{H}_2\text{O}$. The high water content is confirmed by ESCA spectra in appendix B, where a magnification of the oxygen peak O1s can be seen. The water peak in the oxygen at 532.6 eV is broad, large and dominating in the “total” oxygen peak. A magnification of the oxygen peak of the heated glass slide can be seen in appendix B. In that spectrum, an oxygen peak can be seen at 528.9 eV, which originates from the oxygen in the RuO_2 [Kim 74a]. So the conclusion from the ESCA measurements of the $\text{RuO}_4(\text{g})$ -treated glass, is that the black ruthenium deposits are ruthenium dioxide.



a) The unheated glass slide b) The heated glass slide

Figure 3.3: The peaks in red are the main ruthenium peaks Ru 3d5/2 (283 eV respectively 280.5) and Ru 3d3/2 (287 eV respectively 284.5). The grey peaks are carbon peaks, due to inevitable carbon contamination. The blue peaks are due to spin orbit splitting of the main ruthenium peaks.

The two glass slides were also analyzed with SEM to get a picture of the deposits. An image from the SEM measurements is shown in figure 3.4. It seems that ruthenium is sorbed randomly on the glass surfaces in large dots, with a cracked surface. SEM-EDX (Scanning Electron Microscopy – Energy Dispersive X-Ray) measurements showed that most of the ruthenium was located in the white areas in figure 3.4.

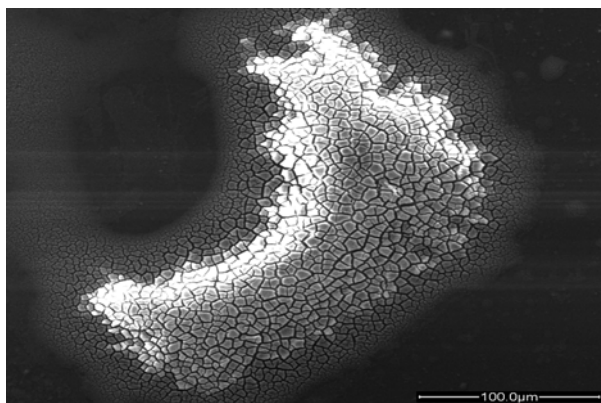


Figure 3.4: A SEM image of a RuO₄(g)-stained glass slide.

An important observation was a change in colour of the ruthenium on the dry ice cold sample vial. The yellow RuO₄ crystals began to sublime immediately after the dry ice pieces were removed from the sample vial. But, there was also at the same time a transformation of yellow crystals into a black ruthenium deposit, directly on the sample vial surface, indicating decomposition and transformation of ruthenium tetroxide to ruthenium dioxide by reaction 4.

3.3 Results from the experiments of the deposition of RuO₄(g) on metal surfaces

3.3.1 The results from the ESCA measurements

All the samples from the experiments, see table 2.2, were investigated with the ESCA method. The objectives were to determine the speciation of the deposited ruthenium on the metal surfaces. Other researchers have reported about RuO₄ transformation to RuO₂ on different metal surfaces like stainless steel [Cains 91], [Mun 07b], see equation 4. Ruthenium dioxide was also found on all the metals used in this work. A typical spectrum from the ESCA measurements of each metal can be seen in appendix B, figures B1a-c. The spectra show a magnification of the two main peaks of ruthenium, Ru 3d5/2 and Ru 3d3/2 peaks.

However, the spectra are very complex hence six components are necessary to obtain a fit of sufficient good quality. The four additional components originate from two Ru peaks due to spin orbit splitting (S-O splitting) and from two carbon peaks due to carbon contamination; compare with results from Mun et al [Mun 07a]. The Ru 3d5/2 peak in the ESCA measurements is around 281.8 ± 0.2 eV, for all samples, which is a higher value than the expected binding energy at 280.9 for RuO₂ [Briggs 90]. The higher value probably depends on the formation of hydrated ruthenium dioxide, RuO₂·H₂O, on the surfaces [Kim 74b]. The humidity in the reaction bottle, see figure 2.2, was relatively high also with dry nitrogen as the atmosphere. This is due to the humidity from ambient air and water from the sample vial with frozen RuO₄ (cr). Table 3.2 shows the differences in the Ru 3d5/2 binding energy for the three different metals. The results show that the speciation of ruthenium on the three metals is similar, i.e. RuO₂·H₂O. There was neither any difference in binding energy for Ru 3d5/2 between the three different atmospheres in the reaction bottle. Hence, the atmosphere does not induce changes in speciation of adsorbed ruthenium on the metal surfaces.

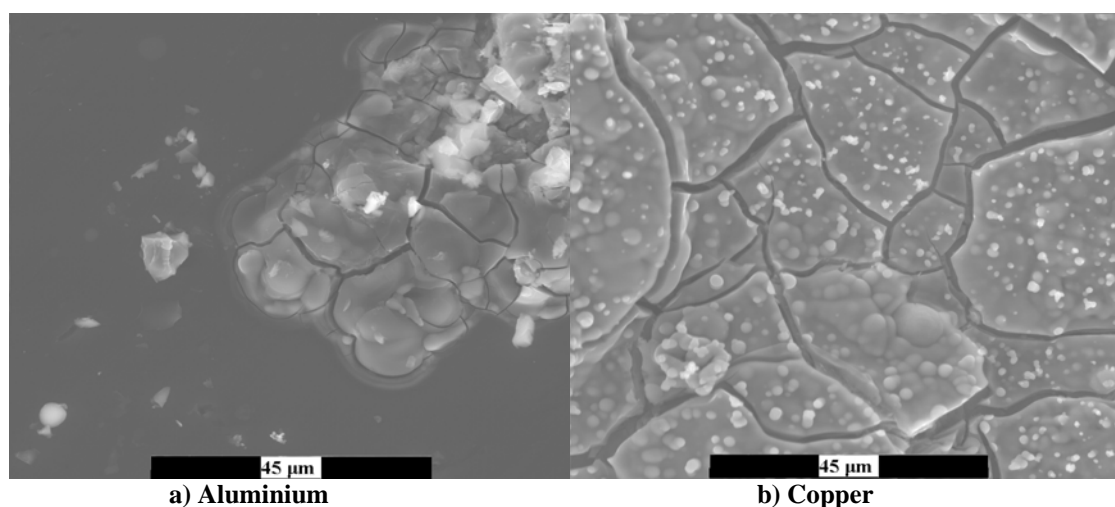
Table 3.2: The average binding energy of the Ru 3d5/2 line for the three metals.

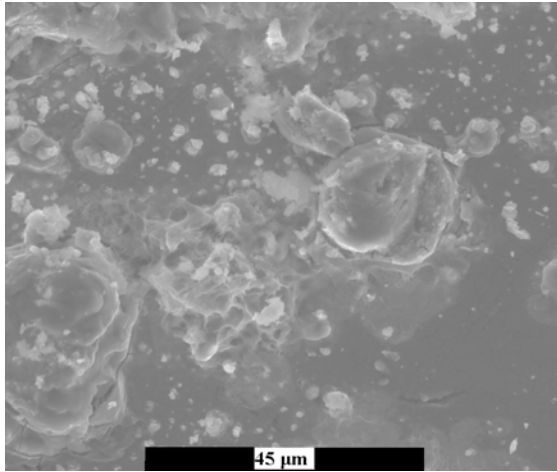
	Al	Cu	Zn
Ru 3d5/2 Energy (eV)	281.7	281.8	281.9
(+-)	0.1	0.1	0.2

3.3.2 The results from the SEM analyses

The metal samples from experiment series T1, T2, and T3 were investigated with SEM, in order to observe differences in the coverage of RuO₂ on the three metals. Examples of SEM pictures can be seen in figure 3.6. The pictures indicate less RuO₂ coverage on the aluminium surfaces than on the copper and zinc surfaces. This was further confirmed with naked eye observations of the amount of black deposits on the surfaces. The copper and zinc pieces had substantial amounts of black deposits on their surfaces while the aluminium pieces only showed black spots of black deposits on the surface, see figure 3.7.

The RuO₂ layer appeared to be more uniform on the zinc surfaces than the other two metals.





c) Zinc

Figure 3.6: Representative SEM pictures of the three different metal samples. White area indicates higher concentration of ruthenium than the greyish area.



a) Aluminium, before and after RuO₄ treatment



b) Copper, before and after RuO₄ treatment



c) Zinc, before and after RuO₄ treatment

Figure 3.7: Photographs of three different metals treated with RuO₄.

3.3.3 The results from the XRD measurements

An XRD spectrum of an arbitrary copper sample can be found in figure 3.8 and XRD spectra of a zinc and aluminium sample can be found in appendix B. These spectra didn't show any traces on the metal surfaces of the expected ruthenium dioxide. A probable explanation to the lack of ruthenium dioxide peaks is the very thin layer of ruthenium dioxide on the samples. This has been reported earlier by Mun [Mun 06b]. Another explanation could be the water content in the ruthenium dioxide ($\text{RuO}_2 \cdot \text{H}_2\text{O}$) disturbing the XRD analyses. Sugimoto et al. noticed a decrease in the peak intensity and peak width widening in their XRD analyses of hydrous ruthenium hydroxide with increasing water content [Sugimoto 05].

The XRD analyses of the copper samples revealed new information on adsorbed ruthenium though. On both copper samples a copper-ruthenium compound was found, copper ruthenium oxide hydroxide ($\text{Cu}(\text{RuO}_2(\text{OH})_4)$), which is an orthorhombic compound first discovered by Nowgorocki [Nowgorocki 67] and later characterized by Hansen [Hansen 96]. This kind of compound was not found on the aluminium and zinc samples. The presence of this copper ruthenium compound on the copper surface provides evidence that a reaction between the copper metal and ruthenium tetroxide/dioxide takes place. The ratio between the amount of ruthenium dioxide and copper ruthenium oxide hydroxide on the copper surfaces was, however, not determined in this work due to difficulties in analysing RuO_2 using X-Ray diffraction measurements.

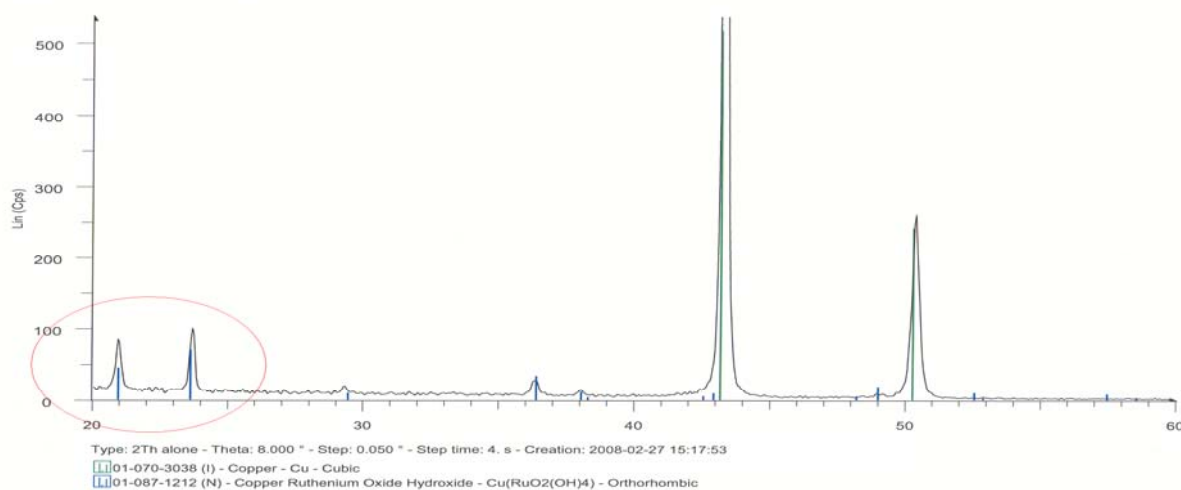


Figure 3.8: An XRD spectrum of a copper sample. Observe the peaks inside the red ring, which indicate the $\text{Cu}(\text{RuO}_2(\text{OH})_4)$ compound on the copper surface.

4. Conclusions

This work was the first project at Chalmers on the behaviour of ruthenium tetroxide during severe accident conditions in a nuclear power plant. The performed experiments of the interactions between gaseous ruthenium tetroxide and different surfaces, which can be found in Swedish BWR containment, show that RuO_4 can be deposited on several different surfaces. The nature of the ruthenium deposits on all surfaces investigated was the non-volatile ruthenium dioxide species, hydrous or anhydrous. Due to extensive interactions between

RuO₄ and the glass walls of the experimental set-up, investigation of the deposition rate of gaseous RuO₄ on the metals could not be done. The distribution of RuO₄(g) between an aqueous and a gaseous was also difficult to investigate, due to the extensive adsorption of RuO₄(g) on the glass surfaces.

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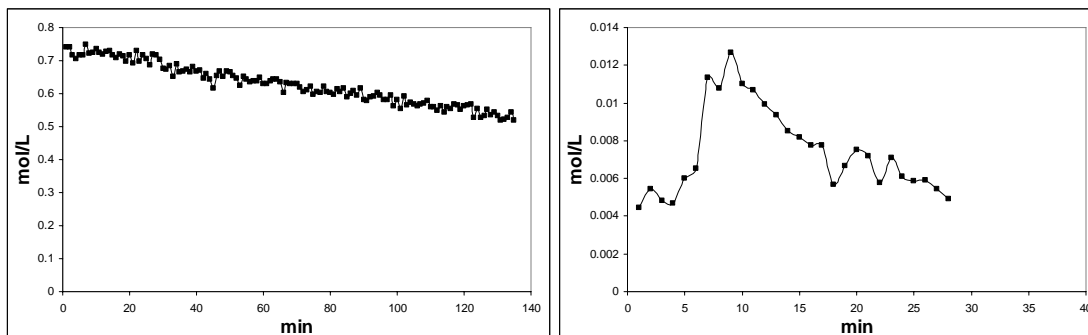
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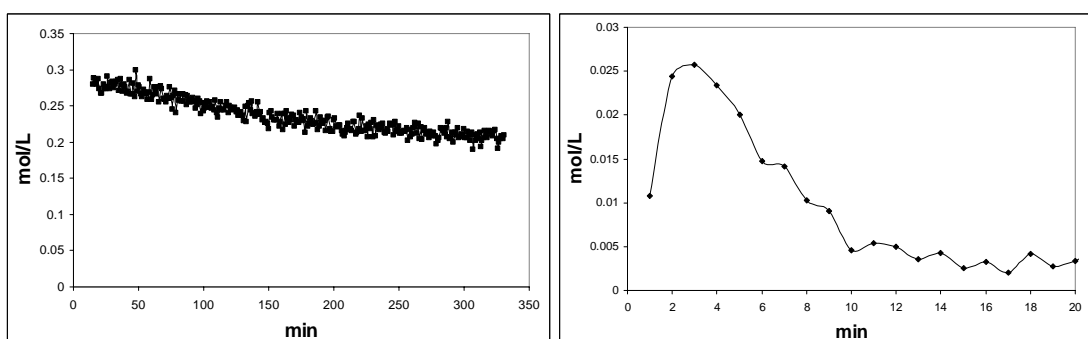
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Appendix A


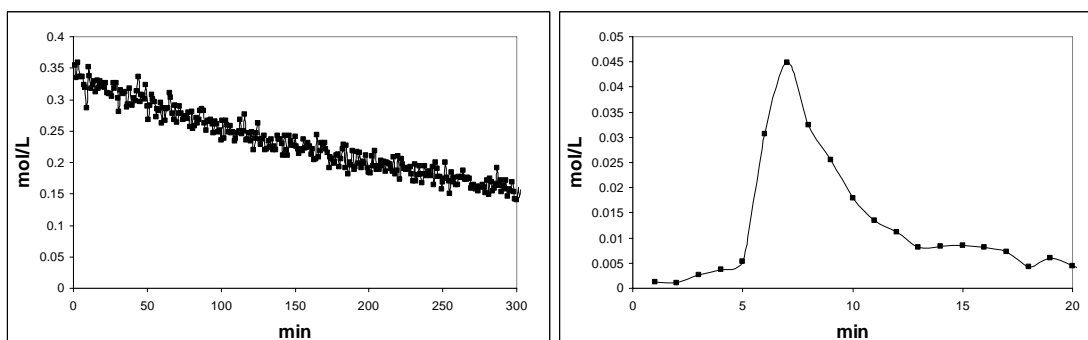
a) The aqueous phase

b) The gaseous phase

Figure A.1: Concentration vs. time of the experiments at 20°C, with both phases presented.


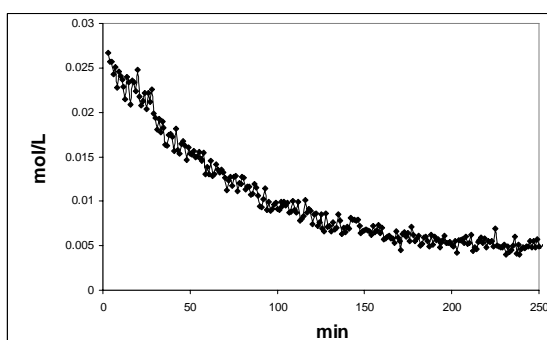
a) The aqueous phase

b) The gas phase

Figure A.2: Concentration vs. time of the experiments at 50°C, with both phases presented.


a) The aqueous phase

b) The gaseous phase

Figure A.3: Concentration vs. time of the experiments at 20°C, with anodized aluminium pumps.

Figure A.4: Concentration vs. time for the experiments with the water phase excluded.

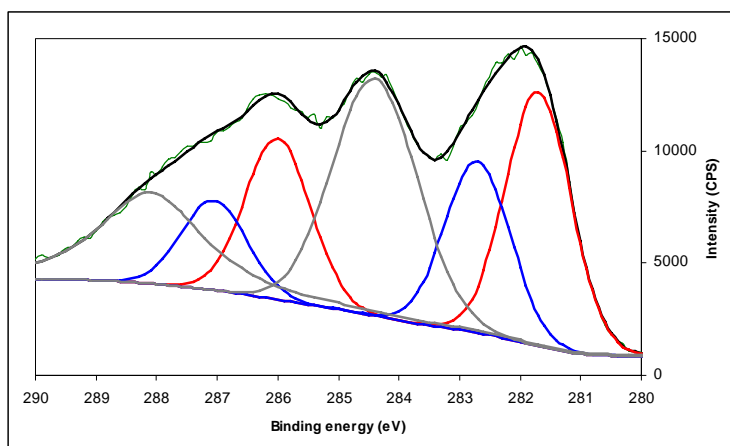
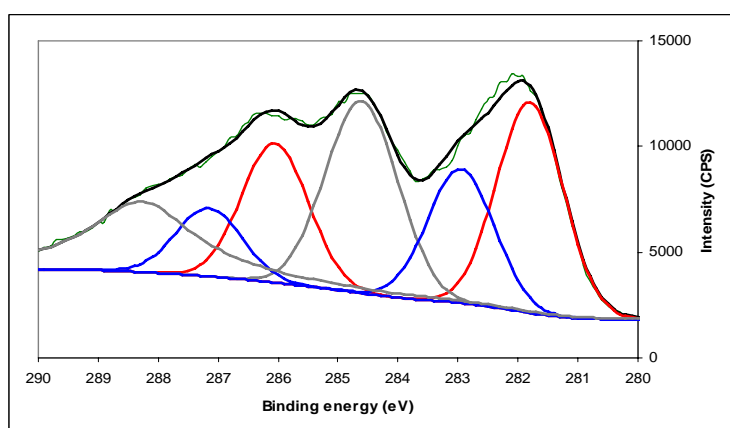
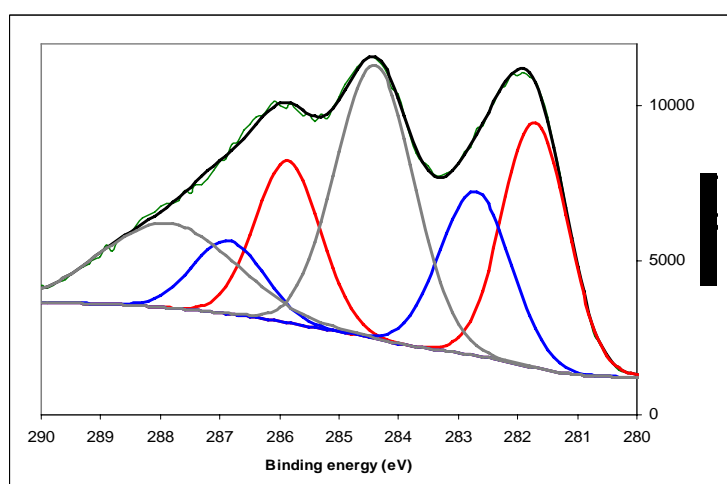
Appendix B

a) Aluminium

b) Copper

c) Zinc

Figure B1a-c: Representative ESCA spectra of the three different metal samples. The two red peaks around 281.8 eV and 285.9 eV are the Ru 3d_{5/2} respectively Ru 3d 3/2 binding energies. The two blue peaks around 282.8 eV and 287.0 eV are the S-O splitting of the Ru 3d_{5/2} respectively Ru 3d 3/2 binding energies. The two brown peaks at 284.5 eV and 288.0 eV are the binding energy of C1s. The carbon peaks were visible due to carbon contamination.

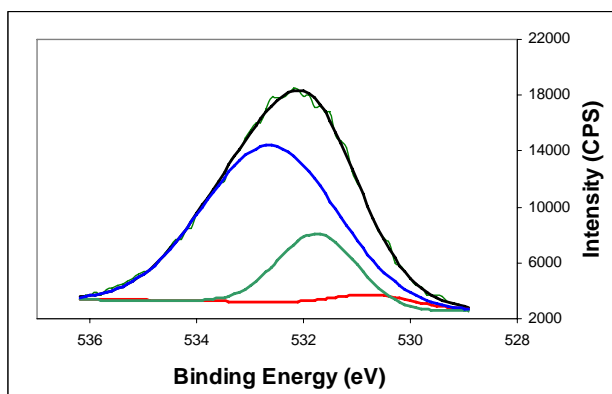


Figure B1: A magnification of O1s peak of the unheated glass slide.

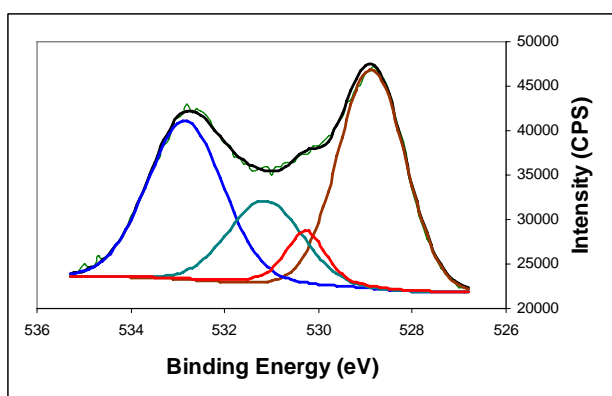


Figure B2: A magnification of O1s peak of the heated glass slide.



Appendix C

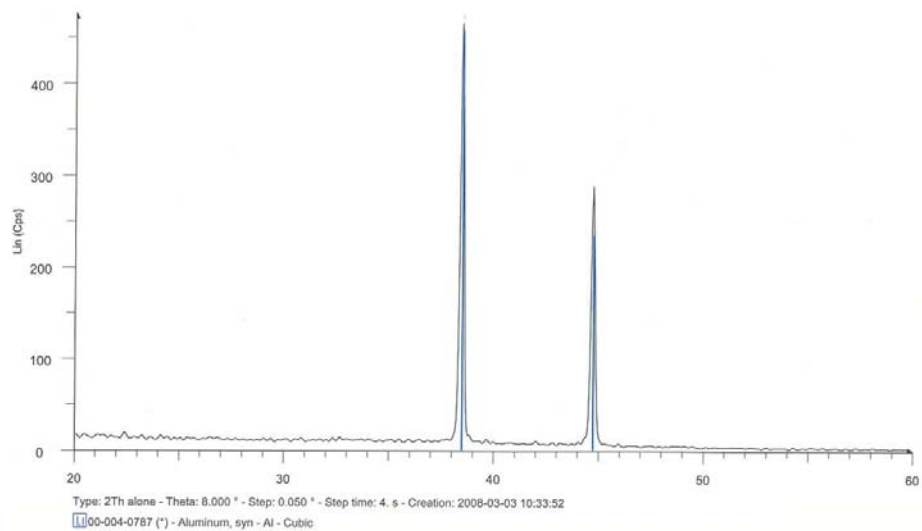


Figure C1: An XRD spectrum of a aluminium sample treated with RuO₄(g)

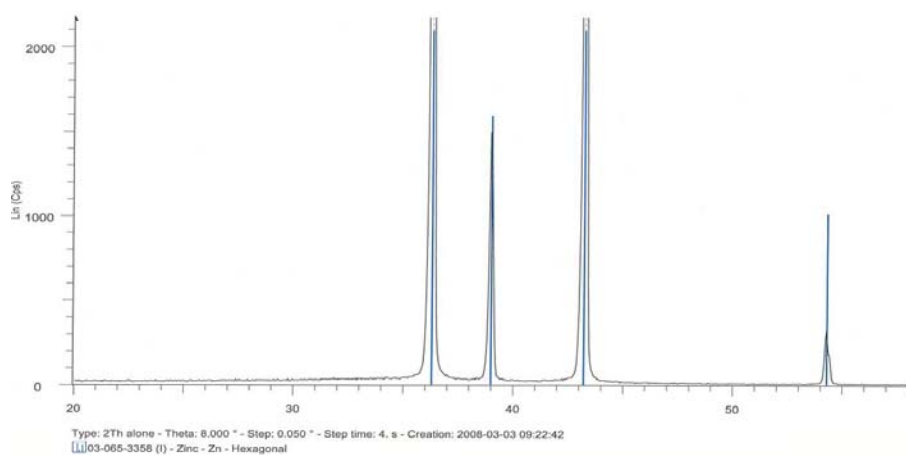


Figure C2: An XRD spectrum of a zinc sample treated with RuO₄(g)

Title	Interactions of RuO ₄ (g) with different surfaces in nuclear reactor containments
Author(s)	Joachim Holm, Henrik Glänneskog and Christian Ekberg
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Date	July 2008
Project	NKS-R / Ruthenium Releases
No. of pages	21
No. of tables	4
No. of illustrations	8+7
No. of references	19
Abstract	<p>During a severe nuclear reactor accident with air ingress, ruthenium in the form of RuO₄ can be released from the nuclear fuel. Hence, it is important to investigate how the reactor containment is able to reduce the source term of ruthenium.</p> <p>This work has investigated the distribution of RuO₄ between an aqueous and gaseous phase in the temperature interval of 20-50°C by on-line measurements with an experimental set-up made of glass. The experiments showed that RuO₄ is almost immediately distributed in the aqueous phase after its introduction in the set-up in the entire temperature interval. However, the deposition of ruthenium on the glass surfaces in the system was significant. The speciation of the ruthenium on the glass surfaces was studied by SEM-EDX and ESCA and was determined to be the expected RuO₂.</p> <p>Experiments of interactions between gaseous ruthenium tetroxide and the metals aluminium, copper and zinc have been investigated. The metals were treated by RuO₄ (g) at room temperature and analyzed with ESCA, SEM and XRD. The analyses show that the black ruthenium deposits on the metal surfaces were RuO₂, i.e. the RuO₄ (g) has been transformed on the metal surfaces to RuO₂(s). The analyses showed also that there was a significant deposition of ruthenium tetroxide especially on the copper and zinc samples. Aluminium has a lower ability to deposit gaseous ruthenium tetroxide than the other metals.</p> <p>The conclusion that can be made from the results is that surfaces in nuclear reactor containments will likely reduce the source term in the case of a severe accident in a nuclear power plant.</p>
Key words	Deposition, Ruthenium tetroxide, Ruthenium dioxide, Ruthenium speciation