BEHAVIOUR OF RUTHENIUM IN NUCLEAR REACTOR ACCIDENTS WITH AIR INGRESS

Ph.D. thesis

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1. Introduction

Earlier severe accident studies considered that mainly gaseous and volatile fission products would be released from the damaged fuel and noble metals like ruthenium present in the irradiated fuel as alloy precipitates would not be released to any significant extent. This assumption is true up to moderate temperature levels (below 2000-2050 °C) and under poorly oxidising conditions.

However, the Chernobyl accident and the later investigations indicated that in highly oxidising atmospheres, especially under air ingress conditions, metallic ruthenium can be oxidised to volatile RuO$_3$ and RuO$_4$ at moderately high temperature and almost completely released from the damaged fuel. Before ruthenium oxidation could begin, zirconium cladding and UO$_2$ fuel matrix, at least locally, had to be oxidised. Thus, ruthenium release kinetics would depend on both fuel oxidation kinetics and ruthenium oxidation kinetics. Of its oxides, RuO$_4$ partially remains gaseous in a metastable state even when cooling down to room temperature, and consequently is able to reach the containment building as a gas during a severe accident scenario.

The volatility of ruthenium oxides, the significant amount of Ru produced in a light water reactor core (15.8 % of the $^{235}$U fission reactions) and the high radiological impact of fission product ruthenium in the short- and middle-term, via the isotopes $^{103}$Ru ($t_{1/2}$=39.3 d) and $^{106}$Ru ($t_{1/2}$=368.2 d), make this element important in the source term evaluations.

In spite of the many investigations devoted to the ruthenium release phenomena, prediction of consequences of severe accidents with air ingress is still a challenge and needs further model development in severe accident codes. A work package of the SARNET (Severe Accident Research Network) project deals with producing and synthesizing information on ruthenium release and transport with the aim of validating or improving the corresponding modelling in the European ASTEC (Accident Source Term Evaluation Code) severe accident analysis code.

Therefore, several experiments were performed recently to study ruthenium chemistry under conditions prevailing in a hypothetical severe accident. The RUSET (RUthenium Separate Effect Test) experimental program was launched with the same purpose in the Atomic Energy Research Institute of the Hungarian Academy of Sciences in 2002.

The object of the RUSET program was to explore the behaviour of ruthenium oxides in the primary circuit during an air ingress accident. Possible transport of ruthenium oxides through the reactor coolant system was aimed to investigate in simplified experiments, i.e. the deposition and re-evaporation of gaseous ruthenium compounds in a temperature gradient zone in air stream. New data from the RUSET measurements provide complementary information to the results of preceding experiments and could help in interpretation of integral tests and model development to base estimations on realistic assumptions about the chemical nature of the radionuclides.
2. Objectives of the work

A small part of RuO₄(g) does not decompose to RuO₂(s) during cooling and can exist in a metastable state with an appreciable partial pressure at room temperature⁠¹⁻². The fundamental goal of my work was the quantification of the fraction of RuO₄(g) remaining in the gas phase in the course of cooling. This gaseous form could potentially reach the reactor containment during an air ingress accident. Another main objective of my work was the identification of those factors which could influence the quantity of metastable RuO₄(g) in the cooled down outlet air under severe accident conditions.

I intended to investigate the effects of high temperature reactions of Ru with other fission products on the amount of gaseous ruthenium compounds in the cooled down escaping air stream.

Possible formation of Cs₂RuO₄ could increase the volatility of Ru during an air ingress accident³. Therefore, I planned to study with exceptional interest the influence of high temperature reactions of ruthenium oxides with caesium compounds on the quantity of gaseous ruthenium species in the ambient temperature outlet air.

Since the volatility of fission product caesium⁴ and molybdenum is much higher than that of ruthenium, Cs and Mo will be deposited on the cold surfaces of the reactor coolant system earlier than ruthenium oxides during a severe accident scenario. For this reason I planned to investigate the effect of Mo- and Cs-oxide deposits on the decomposition/deposition of ruthenium oxides, as well as the possible trapping effect of Cs/Cs-oxide deposits on ruthenium oxides⁵ in a descending temperature zone.

There is rather limited experience with the transport, deposition and re-evaporation of ruthenium oxides in the reactor coolant system in case of an air ingress⁶. In the above case stainless steel surfaces of the primary circuit were assumed to be oxidised. In order to examine the deposition and re-evaporation of ruthenium oxides under representative circumstances, I had the intention of doing investigations with stainless steel and oxidised stainless steel surfaces along the temperature gradient of the experimental facility.

I wanted to compare the effects of stainless steel surfaces with those of quartz, alumina, zirconium alloy or oxidised zirconium alloy surfaces on the decomposition of ruthenium oxides in the descending temperature zone. The influences of other fission products released from the simulated fuel samples were planned to investigate at the different surface materials as well.

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3. Experimental methods

High temperature conditions were established in a vertical furnace. The reaction chamber was a quartz tube with a larger diameter part at the stable temperature section of the furnace containing the simulated fuel sample. The sample consisted of solid state mixture of inactive elements and compounds representing the investigated fission product (FP) components or metallic ruthenium powder (<5 micron) in a ZrO$_2$ matrix.

With the applied air flow rate, the evaporation of given chemical forms of Ru was fast enough to result in equilibrium partial pressures for ruthenium oxides (RuO$_3$ and RuO$_4$) in the high temperature area (1000-1200 °C) of the experimental facility. The ruthenium oxides escaped from the high temperature zone were collected at two locations:

(i) in an inner tube, i.e. on the surface of different materials: quartz/stainless steel (SS)/alumina/zirconium alloy (E110)/in-steam pre-oxidised SS or E110, placed into the outlet tube of the reaction chamber to determine the amount of deposited RuO$_2$ in the descending temperature section (1100-100 °C) of the facility, and

(ii) in an alkaline hypochlorite absorber solution at the final air outlet to remove quantitatively the gaseous ruthenium oxide components from the outlet gas after cooling down.

In order to investigate the effect of Mo-oxide and Cs/Cs-oxide deposits on the decomposition and deposition of ruthenium oxides, the inner tubes were covered by evaporation of either molybdenum powder or caesium compounds in high temperature air stream before their use in some experiments.

The total weight of deposited components in the descending temperature section (1100-100 °C) in a given sampling period was measured by weighing the quartz or alumina inner tubes before and after their use. The difference in mass reflects the amount of precipitated RuO$_2$ if no other FP but Ru is present. In the presence of other FP elements, the amount of deposited RuO$_2$ in the quartz inner tubes was measured by reducing RuO$_2$ quantitatively to Ru by a heat treatment at 1100 °C in 5%H$_2$+N$_2$ gas stream and then by dissolving Ru in alkaline hypochlorite solution. The ruthenium content of alkaline hypochlorite solutions was measured by spectrophotometry. In some cases after the experiments the quantity of Ru and other FP elements remained in the ZrO$_2$ matrix was verified by mass spectrometry.

The axial distribution of the simulated fission products deposited on the quartz and alumina surfaces was determined with acceptable resolution by using the micro-beam X-ray fluorescence (µ-XRF) technique. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) were applied to study the morphology and extent of precipitation of FP species on the SS surface along the temperature gradient.
4. Summary

The RUSET experimental program was launched with the purpose of investigating high temperature ruthenium oxidation and transport through a temperature gradient zone in air stream. This was done with the objective of exploring the possible behaviour of ruthenium oxides in the primary circuit during an air ingress accident.

In separate effect tests at 1000-1200 °C Ru oxidation rate and content of Ru in escaping cooled down air flow have been studied with special emphasis on effects of other fission product elements on the formation and transport of volatile ruthenium compounds.

The influences of different surfaces (quartz, stainless steel, zirconium alloy, alumina, oxidised metal, and surfaces with Mo or Cs deposits) on the decomposition and re-evaporation of ruthenium oxides along a temperature gradient zone of 1100 to 100 °C in air stream have been investigated. This was done in the presence of other fission products as well.

The results showed that Ru evaporates in form of Ru$_3$O$_7$ and RuO$_4$; both reached saturation concentration in the high temperature area at the applied experimental conditions. In the descending temperature section of the experimental device, between about 1100 and 600 °C, the Ru$_3$O$_7$ and most of the RuO$_4$ ($\approx$95%) decomposed on the quartz surface and formed Ru$_2$O$_7$ crystals; while the partial pressure of Ru$_3$O$_7$ in the escaping air was in the range of $10^{-6}$ bar, far above the value that would be expected from equilibrium ($\approx10^{-20}$ bar at 25 °C$^7$). The decomposition of RuO$_4$ and RuO$_4$ to Ru$_2$O$_7$ is a heterogeneous phase chemical reaction catalysed efficiently by the quartz surface, its inhomogeneity and the formed Ru$_2$O$_7$ particles. On the other hand, under the given test conditions, the surface catalysed decomposition process of Ru$_4$O$_4$ to Ru$_2$O$_7$ was not fast enough to follow entirely the equilibrium with the temperature. In the later phases of tests Ru releases originated from the deposited Ru$_2$O$_7$ by re-evaporation, at quartz surfaces resulting in about $10^{-6}$ bar partial pressure of RuO$_4$ in the outlet gas. No aerosol formation was found under the applied test conditions.

The RUSET tests with different tube materials in the descending temperature section (1100-100 °C) demonstrated that the heterogeneous phase decomposition of Ru$_3$O$_7$ to Ru$_2$O$_7$ is catalysed more efficiently by the quartz and alumina surfaces than by the SS surface. On the other hand, the extent of re-evaporation of Ru$_2$O$_7$ deposit from the SS surface (probably because of the finer Ru$_2$O$_7$ particles formed on it) was higher than from the quartz or alumina surfaces. However, the larger crystals of Ru$_2$O$_7$ formed on the quartz surface showed increasing re-evaporation rate in the later phases of the experiments.

The presence of Mo$_3$O$_7$ layers decreased the Ru$_3$O$_7$ precipitation extent on all investigated surfaces. Based on the results of experiments performed with quartz surfaces (inner tubes), molybdenum oxides which are simultaneously present in the vapour phase hinder the surface catalysed decomposition of ruthenium oxides efficiently and result in nearly one order of magnitude greater RuO$_4$ partial pressures in the ambient temperature escaping gas compared to pure Ru oxidation. In a lesser degree, but the steam content of air was also found to reduce the surface catalysed decomposition of RuO$_4$ to Ru$_2$O$_7$ at quartz surfaces and thus enhance the concentration of RuO$_4$ in the outlet air.

The trapping effect of caesium deposits on ruthenium in the temperature gradient zone was proved in the case of SS surface. On the contrary, Cs deposition on alumina and especially on quartz surfaces decreased the decomposition of ruthenium oxides and increased the RuO$_4$ concentration in the outlet air. In the latter case, Cs was found to change the quartz surface by diffusing into the quartz material or forming caesium silicate, diminishing its catalytic effect on decomposition of RuO$_x$ to RuO$_2$, and thus resulted in one order of magnitude higher RuO$_4$ partial pressure in the escaping air than in the case of pure quartz surfaces.

Similarly to the effect observed for Cs precipitates in the descending temperature section, the presence of other fission products in the evaporation area (at 1100 °C) reduced the partial pressure of RuO$_4$ in the outlet air at the SS tube and increased it at the quartz and alumina tubes compared to the pure Ru oxidation. At all types of surfaces, the maximum value of concentration of RuO$_4$ in the escaping gas appeared with a time delay in the presence of other fission products in the sample.

High temperature reaction with caesium changed the form of the released ruthenium and (with quartz surfaces) caused a time delay in appearance of its peak concentration in the ambient temperature escaping gas. If Cs was present in the charge, ruthenium escaped from the high temperature region partly in form of caesium compounds (probably Cs$_3$RuO$_4$) and deposited at relative low temperatures (on quartz surface between about 900 and 400 °C) compared to the pure RuO$_2$ precipitation. The deposition mechanism in this case is simple condensation, and this process lowered the ruthenium concentration in the outlet air.

In presence of barium oxide and rare earth oxides in the sample (at 1000 and 1100 °C), barium ruthenate and rare earth ruthenates are formed resulting in reduced and extended Ru escape from the high temperature area.

When zirconium (E110) cladding material was placed in the temperature gradient zone, no Ru transmittance occurred until the high temperature end of the zirconium tube was completely oxidised. After the intense oxidation of the E110 tube, Ru release occurred only in the presence of other fission product species in the time frame of experiments (360 min).

Pre-oxidation of SS surfaces in steam had no significant effect on the ruthenium passage under the given test conditions. In the case of pure Ru oxidation, pre-oxidation of SS in steam slightly increased the decomposition of RuO$_x$ (RuO$_4$) to RuO$_2$ compared to the effect of pure metal surface. If other fission products were present in the high temperature area, the presence of oxide scale in the descending temperature region slightly enhanced the Ru release. As regards E110, pre-oxidation in steam had an effect on the Ru transmittance only when it was performed outside of the breakaway regime (at 1100 °C). Otherwise the formed oxide scale (at 800 °C) was not protective against the intense air oxidation and the pre-oxidation had no effect on the Ru release.

Measurements demonstrated the importance of surface quality in the descending temperature zone on the heterogeneous phase decomposition of ruthenium oxides to RuO$_2$. This confirms that the presence of stainless steel/oxidised stainless steel surfaces, molybdenum and caesium deposits in the reactor coolant system can play an important role in the ruthenium source term of a hypothetical air ingress accident.

Possible formation of Cs$_2$RuO$_4$ which is more volatile than the ruthenium oxides (above about 500 °C) could decrease the gaseous Ru concentration in the cooled down escaping air compared to the pure ruthenium oxides because of its different deposition mechanism (condensation).
The presence of water or molybdenum oxide vapours in air, and MoO$_3$ deposits on the cold surfaces of the reactor coolant system would decrease the surface catalysed decomposition of RuO$_x$ to RuO$_2$, and increase the partial pressure of metastable gaseous RuO$_4$ in the cooled down air stream. However, during an air ingress accident copious aerosol formation could be expected which may have also significant effect on the transport of ruthenium oxides through the primary circuit.

Probably the most interesting finding of the above presented work is the trapping effect of Cs deposits of the SS surface on ruthenium in the temperature gradient zone which was proved only in one measurement. The possible formation of caesium ruthenate at high temperatures and the ruthenium-caesium-stainless steel interaction in the descending temperature section seem to be important phenomena of the Ru passage through the primary circuit, and need to be investigated in more detail in the future.
5. Theses

1. The decomposition of gaseous ruthenium oxides (RuO$_3$ and RuO$_4$) to solid RuO$_2$ is a surface catalysed heterogeneous phase chemical reaction. In metastable state, RuO$_4$ could remain in the cooled down, ambient temperature escaping air stream at a concentration ($\approx$10$^{-6}$ bar at quartz surfaces) far above the equilibrium value ($\approx$10$^{-20}$ bar) since the decomposition of RuO$_4$ to RuO$_2$ stops at $\approx$800 °C. (The surface catalysed decomposition process of RuO$_4$ to RuO$_2$ is not fast enough to reach equilibrium during the fast temperature change.) The partial pressure of RuO$_4$ in the ambient temperature outlet gas arising from the deposited RuO$_2$ by re-evaporation is also equal to the equilibrium concentration at $\approx$800 °C ($\approx$10$^{-6}$ bar at quartz surfaces) [2,4].

2. The heterogeneous phase decomposition of RuO$_x$ to RuO$_2$ is catalysed more efficiently by the quartz and alumina surfaces than by the stainless steel surface. The extent of re-evaporation of RuO$_2$ deposit from the stainless steel surface (probably because of the finer RuO$_2$ particles forming on it) is higher than from the quartz or alumina surfaces. On the other hand, the larger crystals of RuO$_2$ precipitate forming on the quartz surface show increasing re-evaporation rate in time [1].

3. The presence of molybdenum oxides in the vapour phase or on the surfaces of the temperature gradient zone decreases the surface catalysed decomposition of ruthenium oxides and increases the partial pressure of RuO$_4$ in the ambient temperature air outflow. Molybdenum oxides which are simultaneously present in the vapour phase hinder the deposition of ruthenium oxides more efficiently than the MoO$_3$ layers on the surfaces of the descending temperature section [1,2,3].

4. Compared to the Ru release in form of pure ruthenium oxides, the possible formation of caesium ruthenate or other caesium-ruthenium compounds could lower the concentration of gaseous ruthenium species in the cooled down air outflow because their deposition mechanism (condensation) is different from that of the ruthenium oxides. On the other hand, caesium deposits on stainless steel surfaces of a temperature gradient zone trap slightly the ruthenium oxides from the vapour phase. Ru adsorbs in a greater extent on the stainless steel surface if caesium is present than as pure ruthenium oxides. On the contrary, caesium deposition on the quartz or alumina surfaces reduces the catalytic effect of these surfaces on the decomposition of ruthenium oxides and thus increases the concentration of RuO$_4$ in the cooled down outlet air [1,2].

5. High temperature reactions of ruthenium with barium or rare earth oxides at 1000-1100 °C result in reduced Ru escape from the high temperature area presumably because of the formation of barium ruthenate and rare earth ruthenates [2,3].
6. Publications related to the Ph.D. dissertation

**Journal Publications**


**Posters**

6. N. Vér, L. Matus, A. Pintér, J. Osán, Z. Hózer, Effects of different surfaces on the transport and deposition of ruthenium oxides in high temperature air, 10th Multinational Congress on Microscopy 2011, Urbino, Italy, 4-9 September, 2011.


**Conference presentations**


7. Other publications

Journal Publications


Posters


Conference presentations


25. M. Horváth, Z. Hózer, M. Kunstár, L. Matus, N. Vér, Reaction of Zr1%Nb in Air and Nitrogen, 26th Bundle Interpretation Circle, Alkmaar, the Netherlands, 24 April 2006.