



**KFKI Atomenergia Kutatóintézet**  
**KFKI Atomic Energy Research Institute**



**Joint Research Centre**

# **OXIDATION AND RELEASE OF RUTHENIUM FROM SHORT FUEL RODS ABOVE 1500 °C**

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N. Vér<sup>1)</sup>, M. Kunstár<sup>1)</sup>, B. Alföldy<sup>1)</sup>, K. Mueller<sup>2)</sup>**

- 1) KFKI Atomic Energy Research Institute**  
**2) European Commission, Joint Research Centre,  
Institute for Energy, The Netherlands**

**April 2005**



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## 1. INTRODUCTION

The release of fission products from high temperature NPP bundles in air atmosphere has got enhanced attention because recent studies proved relatively high probability of such events. The oxidative atmosphere changes substantially the release rate of fission products.

Exceptionally important from this point of view is the ruthenium, which is produced in substantial amount during the fission of uranium. The metal has a negligible vapour pressure even at very high temperatures. In oxygen containing gas atmosphere (air) volatile ruthenium-tetroxide is formed with boiling point is 130°C. The fall-outs after the Chernobyl accident proved the importance of this effect.

In the AEKI oxidation experiments have been made in frame of many projects. The main works belonging to these studies were the CODEX-AIT-1 and CODEX-AIT-2 (**CO**re **D**egradation **EX**periment-**A**ir **I**ngress **T**est), where important information has been gained about the degradation process suitable for code development [1,2,3]. In these cases the fuel rods contained only fresh fuel pellets and the release results were limited to uranium only. We made numerous separate effect tests for supporting the evaluation of results.

A series of ruthenium air oxidation experiments was performed in the recent years [4] with non-active fission product representatives in ZrO<sub>2</sub> or UO<sub>2</sub> powder. In the first tests only Ru was used, later the other elements were added as well. Isothermal tests were conducted between 1000-1200 °C (most of them at 1100°C) with air providing information on the behaviour of ruthenium-tetroxide formed by this way. Fission products were collected in special collectors, their amount was determined in the post-test examination. The results of the tests showed, that under high temperature conditions in air atmosphere the total amount of ruthenium was released from the furnace. Max. 10% of ruthenium reached the room temperature samplers during the total experimental time (several hours). In the later phase of the tests ruthenium-tetroxide was formed and released from the deposited ruthenium-dioxide. The presence of other fission products delayed the release of ruthenium, but did not decrease the released mass. The experiments with powder indicated that in the air ingress phase of a severe accident most of the ruthenium would be oxidised and released in form of volatile oxides from the reactor core. Most of the released ruthenium would deposit on the cold surfaces (600-700 °C) of the primary circuit and the containment. The ruthenium release would be continued if high temperature air flows along these surfaces, the release to the room temperature environment rate can be estimated as 10<sup>-6</sup> bar partial ruthenium-oxide pressure.

Another experimental series has been carried out at higher temperatures (1400-1500°C) with short fuel rod samples. Two types of fuel rods were used:

- fuel rods with original UO<sub>2</sub> pellets and Zr cladding. Fission product simulants were added into the gap between pellets and cladding.
- fuel rods with fabricated pellets. The pellets were prepared of UO<sub>2</sub> powder mixed with fission product simulants using cold pressing method.

The results showed the retention effect of the pellet and the cladding in comparison with earlier tests performed with powder. However the release of fission product from the short fuel rods was significant in some tests. The release of ruthenium to the room temperature collectors varied between 0 and 17%. Large amount of ruthenium (20-30%) was found on the surfaces of alumina rods used for sampling in the high temperature region of the furnace outlet. The results showed large scatter concerning the release rate of ruthenium. The most

important factor in the retention of ruthenium release was the integrity of fuel rod cladding. If the cladding remained intact during the test (even if the Zr was completely oxidised), no ruthenium was released, the high temperature air had no access to the pellets and volatile oxides were not produced. No ruthenium release was observed in experiments with steam atmosphere, the Ru release was related to oxygen ingress phase of the tests. The competition between Zr oxidation and Ru release was also observed: the Ru release was delayed by the oxidation of Zr cladding. The short fuel rod tests confirmed the conclusions of the powder test series on the correlation between ruthenium release rate and partial pressure of ruthenium oxides. It indicates that in the environmental release of ruthenium its tetroxide plays important role, while the amount of trioxide is not present in the released gas. The tests indicated that  $\text{RuO}_4$  can get into reaction with constructional materials in the outgoing path from the furnace and this reaction can influence the amount of absorbed Ru in the solutions (i.e. the release in gaseous phase).

The main objective of the present work was the investigation of release of ruthenium during air oxidation of model fuel rod segments with original zirconium-alloy tubes containing uranium-dioxide and fission product components representing a middle range burn-up level. It was expected that a new series of short fuel rod tests at higher temperatures will provide information on the

- partial pressure of ruthenium-oxides at 1600 and 1700°C in 1 bar air and Ru equilibrium, ( $\text{RuO}_2$  is decomposed at these temperatures),
- the release of other fission elements and their precipitation on the walls of alumina outlet tubes in function of temperature,
- the influence of water vapour on the release of different species,
- the partial pressure of  $\text{RuO}_4$  in the outlet gas,
- the relevant equilibrium temperature where the decomposition process is stopped.

In the service contract No. 32.0227 four experiments were specified together with the necessary post-test examinations regarding the solid precipitates and the solutions used for absorbing the volatile Ru compounds. The temperature of the oxidation was planned to be near to the melting point of zirconium alloy, at 1600°C and 1700°C, the gas atmosphere at two cases should be pure air and at another two contain water vapour as well simulating a gas atmosphere which is most likely during a severe accident.



## 2. EXPERIMENTAL SETUP

The experimental setup used in the present tests was similar to the setup used in the previous short fuel rod experiments [5].

The high temperature area was an inductively heated furnace. It was connected to a gas inlet system and at the outlet side at first to decreasing temperature tubes and then to gas absorbers. The maximum temperature of the furnace is above 1700 °C, it can hold this high temperature through hours as the planned experimental conditions made it necessary. The schematic view of the furnace can be seen in Figure 1. The power supply of the furnace was a 40 kW, 440 kHz generator. The samples used for the experiments did not contain enough metal parts for taking up energy enough for achieving the high temperature, therefore a tungsten ring was placed around the high temperature stage of the alumina tube. It was the energy absorber as indirect heater for the furnace area. The inner part of the furnace was an aluminium-oxide ceramic tube with diameters 18/14 mm. A ZrO<sub>2</sub> sample holder was at the bottom of heated area supported from the lower end of alumina tube, the sample was placed on this. The inlet gas was introduced into the lower end of Al<sub>2</sub>O<sub>3</sub> tube. Around the Al<sub>2</sub>O<sub>3</sub> tube and the tungsten energy absorber a thermal isolation was applied from ZrO<sub>2</sub> just and another alumina tube holding them together. This isolation layer has a 10 mm diameter hole at the height of the sample. A pyrometer working at two wavelengths measured the temperature of tungsten absorber ring through this hole. Another temperature control device was a W5%Re/W26%Re thermocouple with tantalum envelope placed between the inner aluminium-oxide tube and the molybdenum ring. The high temperature stage described above was closed into an outer quartz tube containing streaming high purity argon for protecting the tungsten against oxidation.

The inlet gas was mixed from high purity argon and air, in some cases also steam was added. The streaming of argon and air components was measured with pressure difference on capillaries. The pressure differences were measured with liquids in U tubes connected to the two ends of capillaries. They were calibrated before the start of experiments.

The released ruthenium oxides were collected at two places. Just above the furnace the outlet gas was streaming through an alumina tube, where it was cooled down from the furnace temperature to the ambient one. Large part of the volatile ruthenium-tetroxide was converted to non-volatile dioxide. A small fraction of RuO<sub>4</sub> was transported with the gas flow and it was absorbed in diluted sodium hydroxide solution containing 0.05M NaOCl. To get time resolved data both the outlet alumina tube and the absorber solution were changed at every 1/2 - 1 hour. 5 pieces of alumina tubes and 5 absorption device were prepared for every test (see Figures 2 and 3). The arrangement of outlet tubes can be seen in Figure 1. The inner alumina tube is fitted tight in the upper part of reaction chamber Al<sub>2</sub>O<sub>3</sub> tube with PTFE (Polytetra-fluoroethylene) strips.

The weight change of the inner outlet tubes was measured to see the amount of deposit. At earlier experiments, when only ruthenium powder was in the furnace, it has given a good information regarding to RuO<sub>2</sub> deposit. At the present experiments other volatile fission products were also charged into the matrix. They resulted in higher weight increase than the total amount of Ru charged. It made necessary to determine the Ru in the deposit. It was performed in the frame of post-test investigations.

To avoid the pollution of the laboratory and the environment by uranium the experimental device was closed into a plexiglas-chamber (Fig. 3) connected to effective ventilation through a molecular sieve filter. The outlet gas after the absorbers was filtered as well by an alkaline solution. The effectiveness of the absorption was indicated by the fact, that no yellow colour appeared in the second alkaline solution even after many experimental series. (The alkaline-ruthenates have intensive orange/yellow colour, which indicate the presence of Ru in the solution with acceptable sensitivity above 0.1 µg/ml. – see chapter 5)

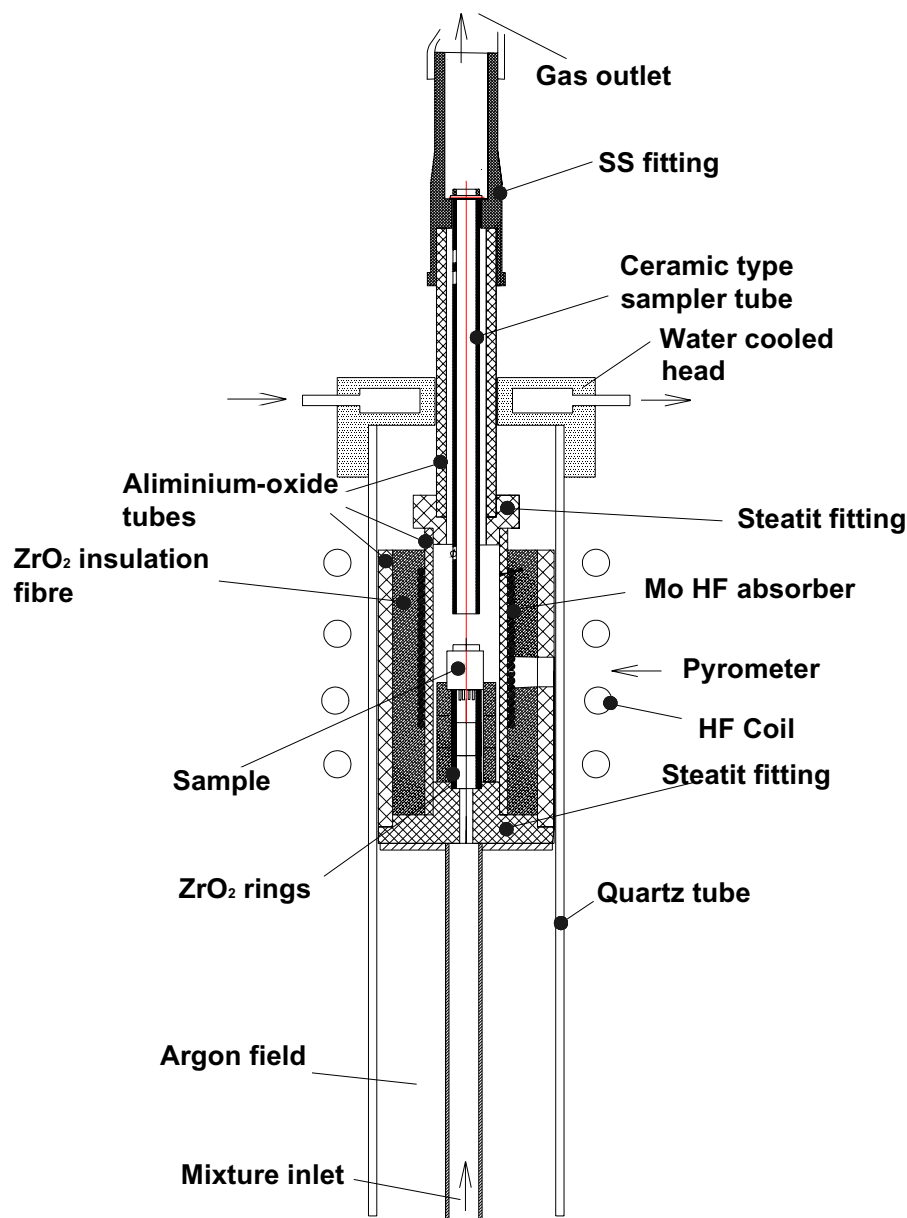


Fig. 1. Schematic view of high temperature furnace

The high temperature experiments were performed with computer controlled data acquisition to record continuously all of the main data. During the tests various data (temperature, gas flowrate and composition) were recorded. After the tests the samples from the outlet tube and the solution were analysed. Elemental distribution of the released materials on the alumina tube was examined and the concentration of Ru in the solutions was measured. These data gave basic information on the integrated release, the transfer mechanism and the deposition on cold surfaces.

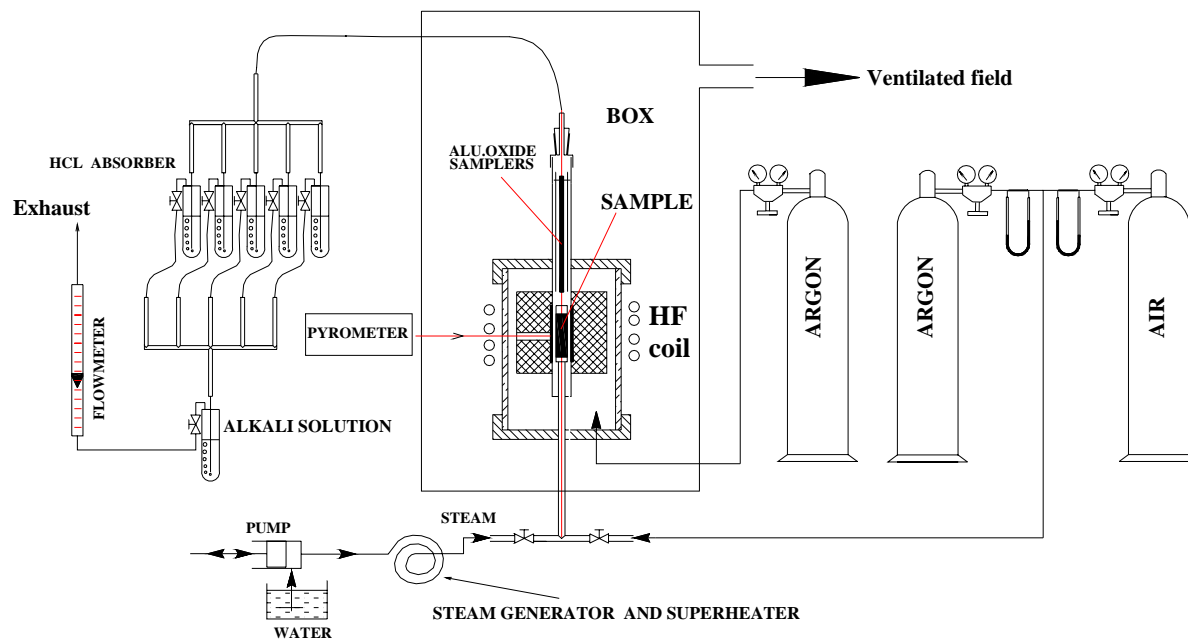


Fig. 2. Scheme of the experimental set-up

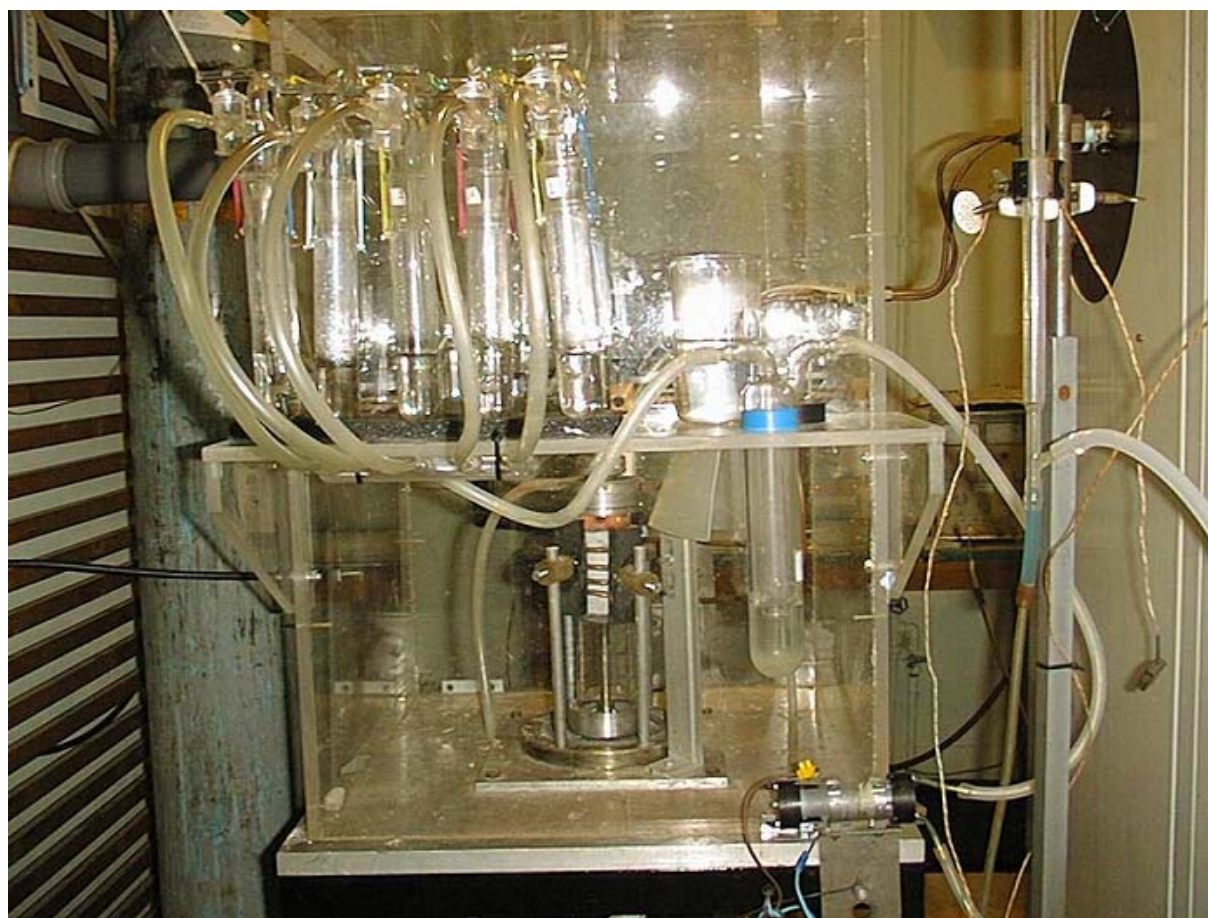


Fig. 3. Photograph of the experimental set-up

Fig. 4 shows the furnace of the facility during a test. Sampling solution together with the connecting quartz tube is shown in Fig. 5.

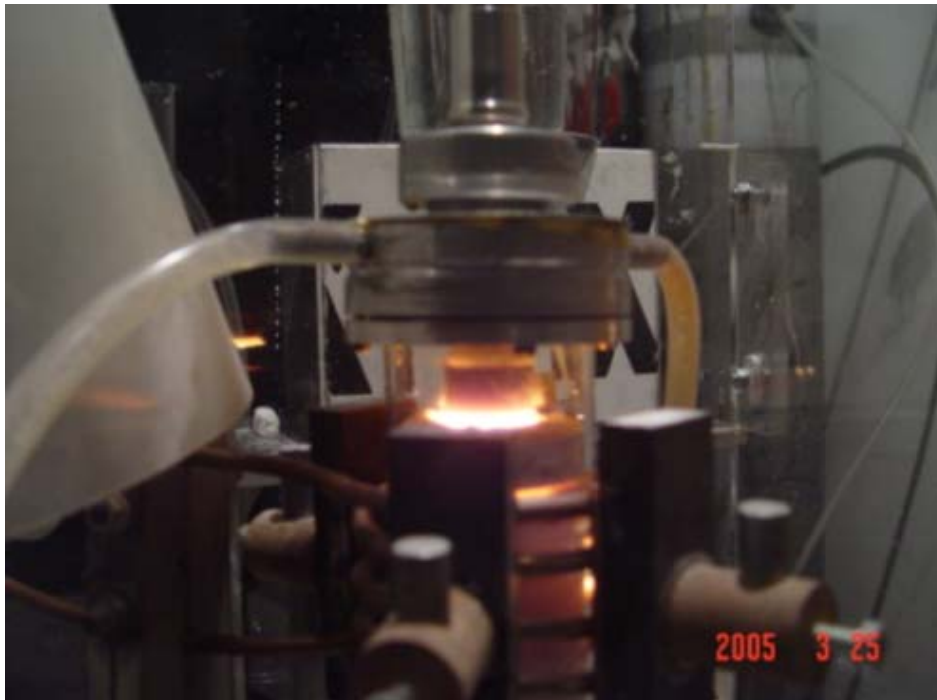


Fig. 4. Photograph of the furnace

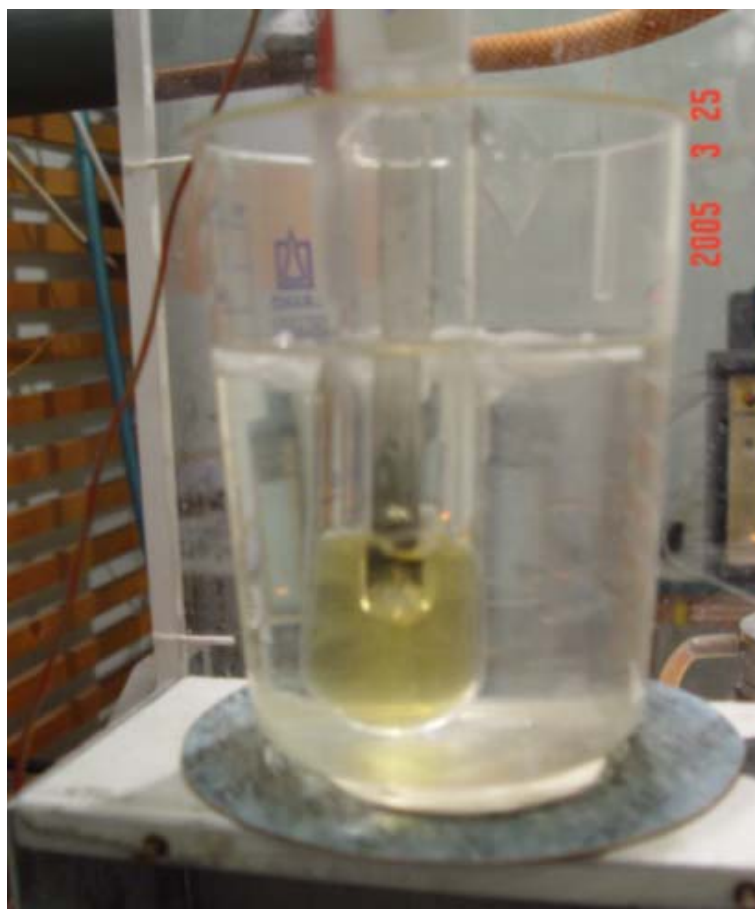


Fig. 5. Connection of the sampling solution to the outlet tube of the facility

### 3. PREPARATION OF FUEL ROD SAMPLES

The separate effect tests planned in this series were performed with pellets surrounded by Zircaloy cladding. The cladding was for ~3 mm shorter than the pellet and there was relatively large gap between the cladding and pellet in order to make possible the access of air to the surface of pellets.

The pellets contained the characteristic fission products, including both volatile and non-volatile components (Ru, Mo, Cs, I, Ba, Se, Sn, Ag, Sb, Cd, Te, Nd, Ce and Zr). They were produced from mixture of powdered components with high pressure. The UO<sub>2</sub> pellets containing Ru and other fission products have been prepared for the tests of powder at high pressure. The mixture represented 44 MWd/kgU burn-up level. The same type of pellets was used in the previous series of tests [5].

The total mass of powder used for pellet preparation contained 185.2 g UO<sub>2</sub> and 7.4 g compounds of fission product simulants (Table 1).

No	Compound	Mass (mg)	Mass (%)
1	Cs <sub>2</sub> CO <sub>3</sub>	747.70	0.39
2	CsI	141.80	0.07
3	BaCO <sub>3</sub>	807.70	0.42
4	Ru	933.70	0.48
5	CeO <sub>2</sub>	756.60	0.39
6	Mo	677.40	0.35
7	Se	10.93	0.006
8	Sn	18.34	0.01
9	Ag	18.22	0.009
10	ZrO <sub>2</sub>	1076.90	0.56
11	Sb	5.68	0.003
12	Cd	29.31	0.02
13	Te	133.40	0.07
14	Nd <sub>2</sub> O <sub>3</sub>	2060.20	1.07
Total		7417.88	3.85

Table 1. Composition of fuel pellets

From the mixture an amount for one pellet has been separated and weighted at every case. A few drops diluted alkali-silicate solution (water-glass) was added and thoroughly mixed. This mixture was filled into the press tool (Figure 6). After one minute of high pressure treatment the pellet was pushed out from the tool and dried.



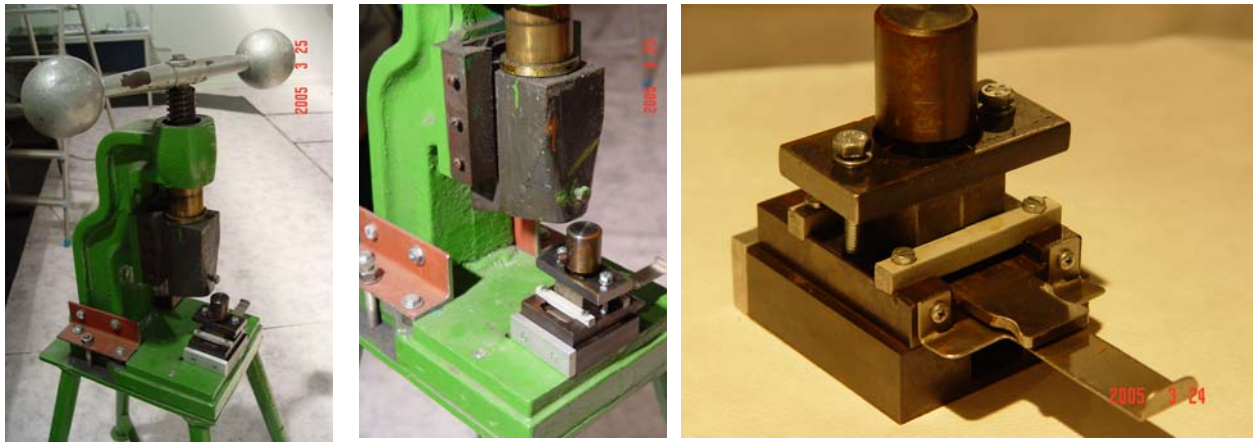


Fig. 6. Press tools for pellet preparations

High temperature heat treatment (sintering) was not applied because some of the FP components were volatile at high temperature and they would escape from the pellet. The diameter of prepared pellets was 7.6 mm, the density of original pellets milled for the present work was  $10.5 \text{ g/cm}^3$ , the density of pellets prepared as described above was  $5.5 \text{ g/cm}^3$ .

## 4. DESCRIPTION OF EXPERIMENTS

In the present experimental series seven short fuel rod tests have been performed. The numbering of the tests is related to the continuation of the previous series [5]. The details of the tests are described in the following paragraphs.

### No. 5.

The first experiment of the current series was performed at 1700 °C in air atmosphere. The carrier gas was argon. The sample was not pre-oxidised in this test. Air injection started at 1500 °C. Temperature measurement in this test was performed with the help of a pyrometer (Fig. 7). The fuel sample had no cladding, only one single pellet was tested (Fig. 8). The solutions indicated high release of gaseous Ru species at the beginning of the test.

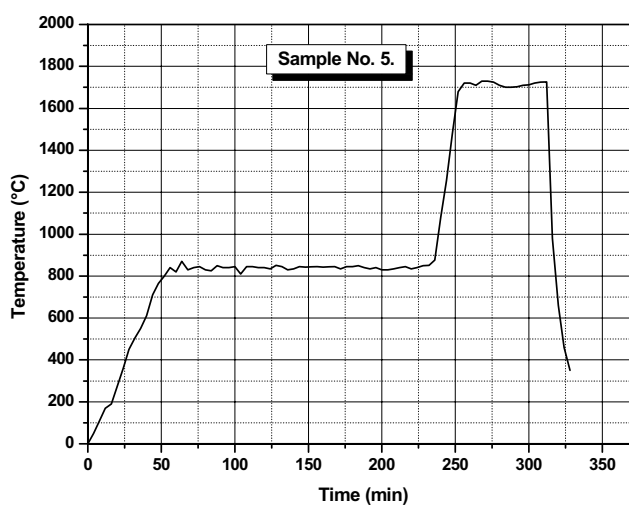


Fig. 7. Temperature history curve of experiment No. 5



Fig. 8. View of the pellet after experiment No. 5.

**No. 18.**

For test No. 18 the experimental setup was modified: some silicon rubber tubes were used in the outlet part of the facility instead of quartz tubes and the fuel sample had a short Zircaloy cladding. Pre-oxidation was carried out at 1000 °C in air for 18 minutes. The experiment was performed at 1600 °C in air atmosphere. The temperature rise between 1000 and 1600 °C was done in inert gas atmosphere (Ar).

The temperature was measured with a combined pyrometer-thermocouple system. The pyrometer was applied during the whole duration of the test, while thermocouple measurements were taken only at the beginning and at the end of the isothermal high temperature phase of the test. This approach made possible a more accurate measurement of the temperature, than in the previous tests. The thermocouple was located very close to the investigated sample. The pyrometer was focusing on the external surface of the Mo susceptor. The thermocouple could survive the measurement, for it was not kept for long time in oxidising atmosphere. The pyrometer data were less reliable due to emissivity changes, however the pyrometer provided important information on the stability of thermal conditions at the established power level. In Fig. 9 both thermocouple and pyrometer data are presented. Up to 1400-1500 °C the two signals go together, but above this temperature the pyrometer data are lower for ~150 °C, than the thermocouple readings. Pyrometer data showed some changes during the test, but the thermocouple data confirmed, that the temperature was kept with acceptable accuracy. The pyrometer readings probably were influenced by the change of the surfaces of the Mo susceptor and the quartz window, for this reason the thermocouple data are considered as characteristic test temperature. The same approach was applied in the subsequent tests.

The liquid solutions indicated no Ru release at all in this test. However dark depositions were seen on the surface of tubes coming from the hot part of the furnace. It was concluded later, that probably the silicon rubber tube had chemical reactions with Ru oxides and prevented the release of gaseous Ru oxides into the absorber.

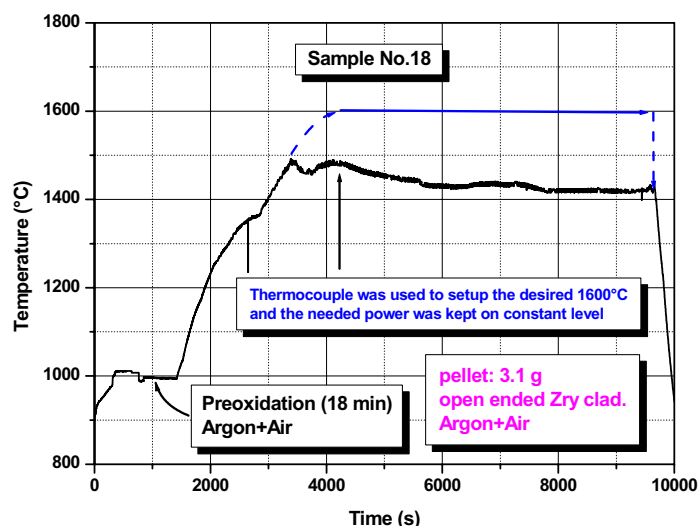


Fig. 9. Temperature history curve of experiment No. 18



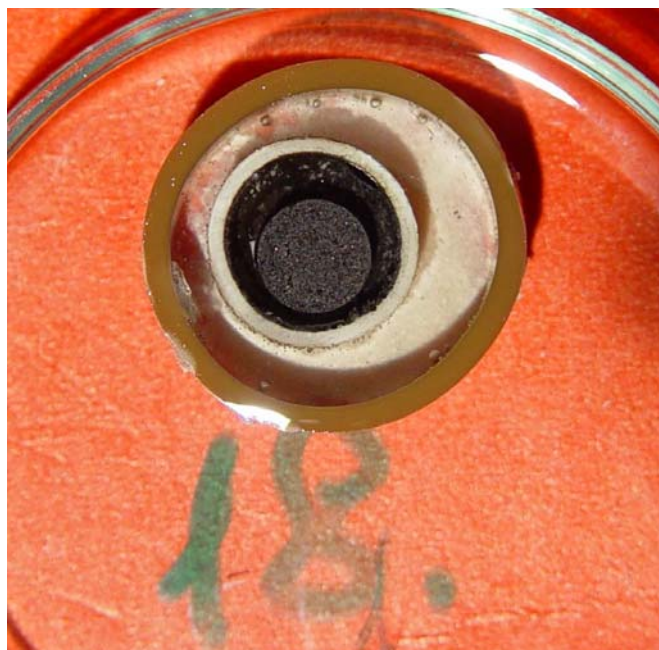


Fig. 10. Cross section of the short fuel from test No. 18.

**No. 19.**

Experiment No. 19 was carried out at 1700 °C in air atmosphere. Pre-oxidation took place in air at 1000 °C for 18 minutes. After the pre-oxidation phase the test had to be stopped due to technical reasons, so the furnace was cooled down (Fig. 11). The high temperature treatment was performed later, starting from cold state (Fig. 12). The temperature was measured with the pyrometer-thermocouple system.

The fuel sample had a short Zr cladding. Silicon rubber tubes were not used in this test. Fast release of Ru was detected in the absorber solutions.

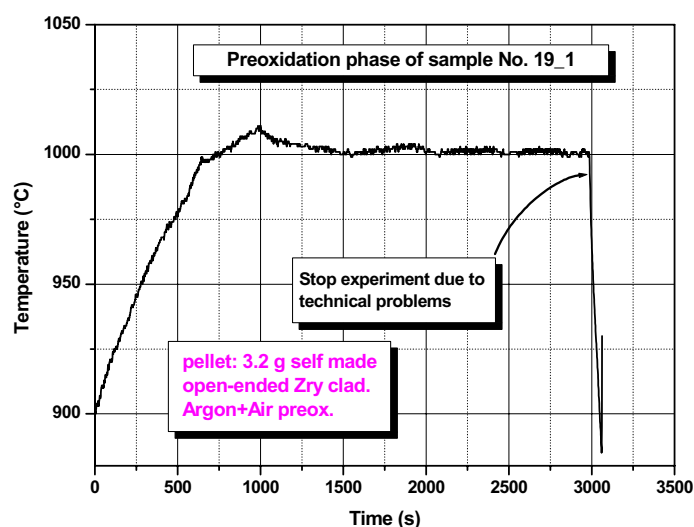


Fig. 11. Temperature history curve during pre-oxidation in experiment No. 19

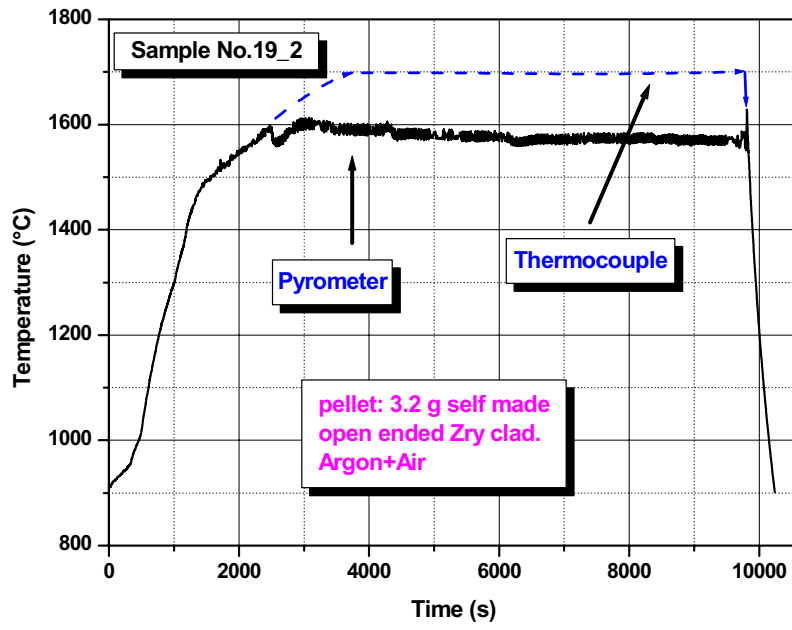


Fig. 12. Temperature history curve of experiment No. 19

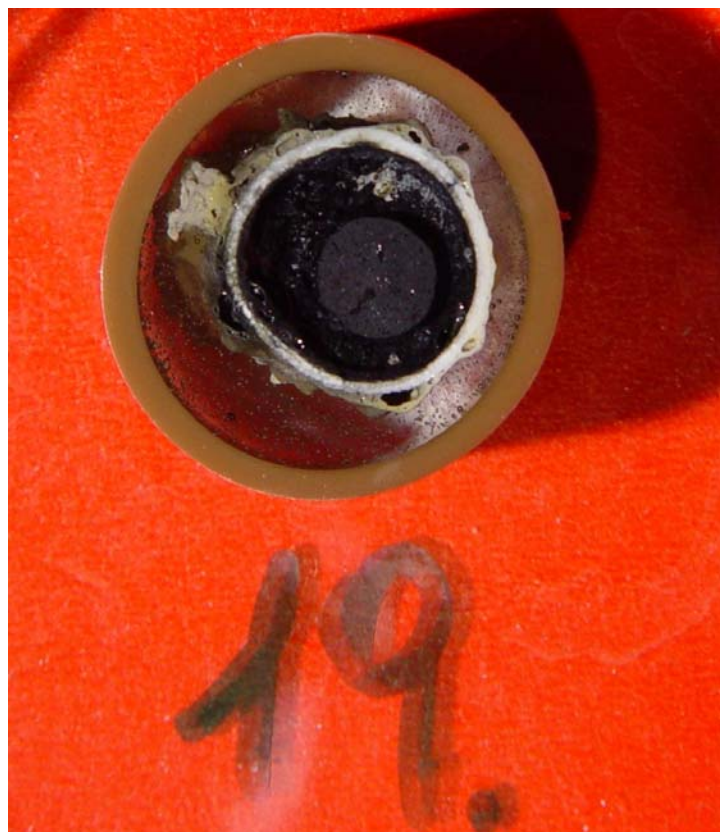


Fig. 13. Cross section of the short fuel rod from test No. 19

**No. 20a.**

Test No. 20a was carried out in steam atmosphere, the carrier gas was argon again. The fuel sample included one pellet and one short piece of cladding. Pre-oxidation was carried out at 1000 °C in air for 18 minutes. The temperature of 1600 °C was kept for several hours, but no signs of Ru were seen in the solutions. The temperature was measured with the pyrometer-thermocouple system. Depositions were seen on the outlet part of the furnace.

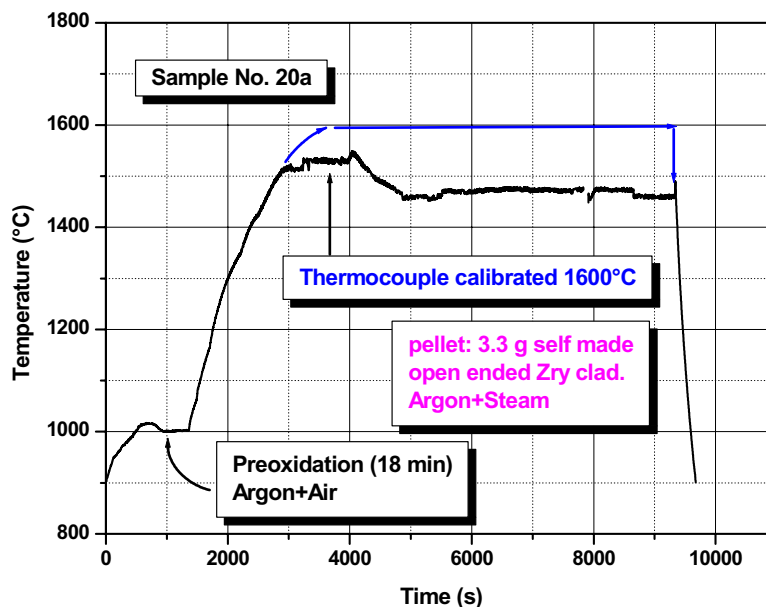


Fig. 14. Temperature history curve of experiment No. 20a.

The fuel sample was not removed from the furnace, but another test was carried out with the same sample.

**No. 20b.**

Test No. 20b was carried out with the same fuel sample and with the same configuration of the facility as in test No. 20a. The test was performed in steam atmosphere at 1700 °C. The temperature was measured with the pyrometer-thermocouple system. Even at this temperature no Ru was released to the room temperature part of the facility.

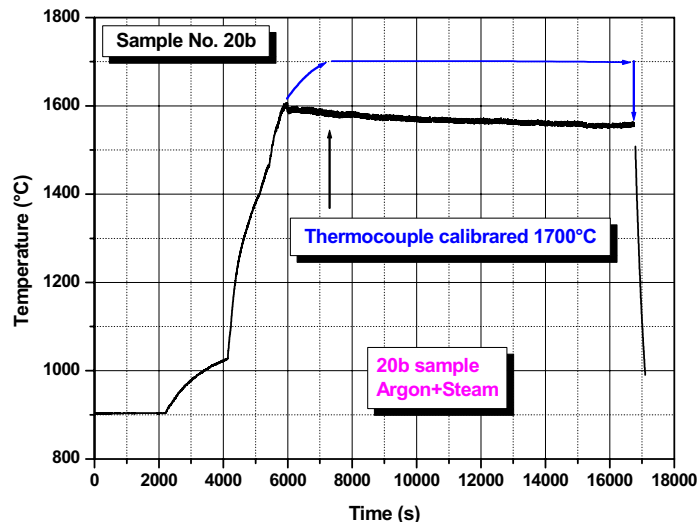


Fig. 15. Temperature history curve of experiment No. 20b

The view of the fuel sample is shown in Fig. 16. The cladding was heavily oxidised and the pellet diameter reduced due to densification at high temperature. The left side picture shows the position of pellet during the test. In the right side picture the pellet was removed from the cladding.



Fig. 16. Short fuel rod sample after test No. 20b

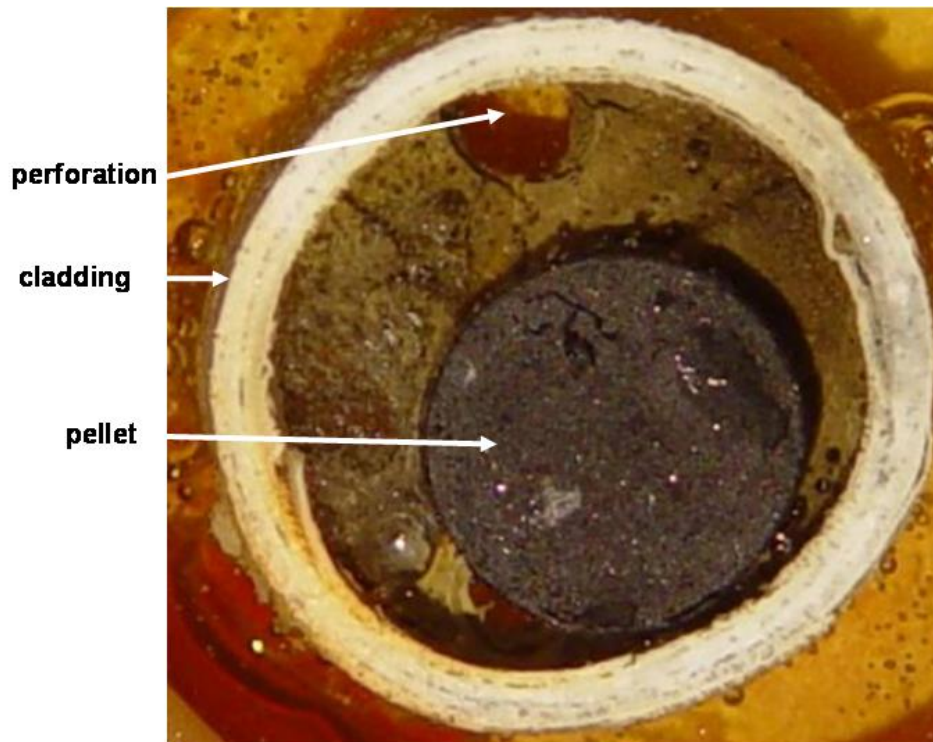


Fig. 17. Cross section of the short fuel rod from test No. 20



**No. 21.**

In test No. 21 we tried to repeat test conditions of experiment No. 18, but the silicon rubber tubes were replaced by quartz ones. Pre-oxidation was carried out at 1000 °C in air for 18 minutes, the experiment was performed at 1600 °C. The temperature was measured with the pyrometer-thermocouple system. In this test continuous release of gaseous Ru oxide was detected in the liquid samplers.

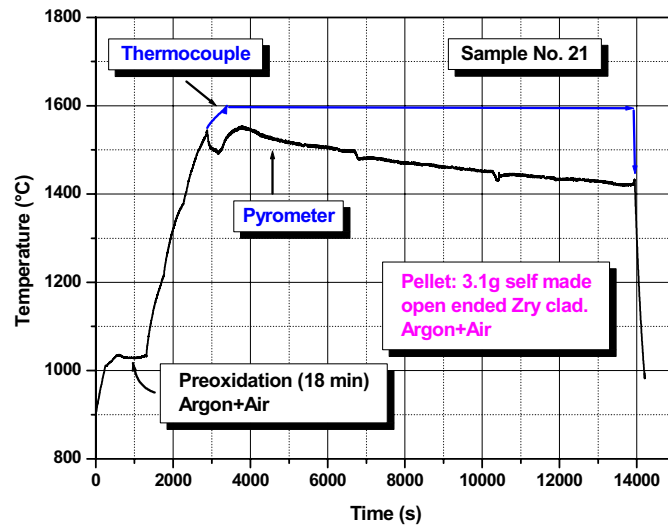


Fig. 18. Temperature history curve of experiment No. 21

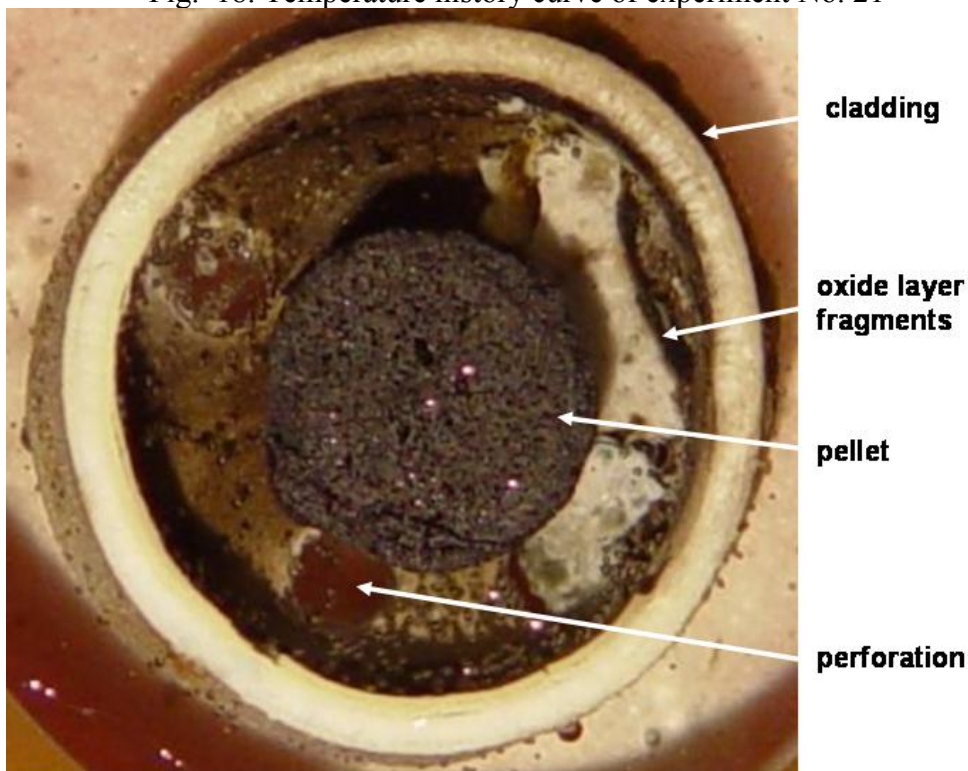


Fig. 19. Cross section of the short fuel rod from test No. 21

**No. 22.**

The last test of this series was performed at 1800 °C in air. Pre-oxidation was carried out at 1000 °C in air for 18 minutes. The temperature was measured with the pyrometer-thermocouple system. The conditions resulted in fast and significant gaseous Ru release.

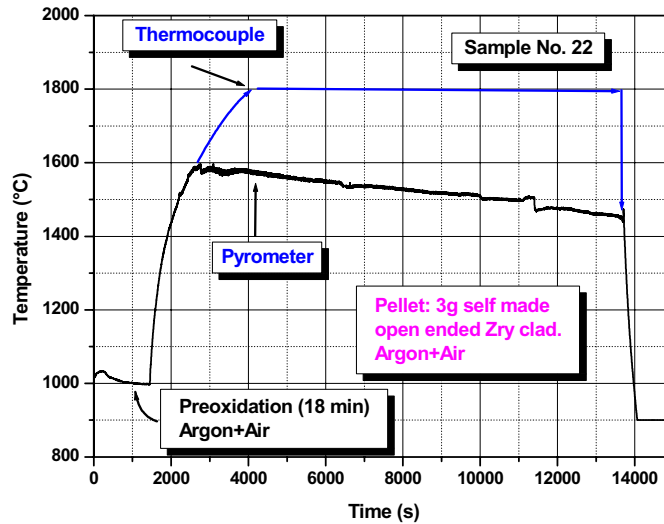


Fig. 20. Temperature history curve of experiment No. 22

Densification of the fuel pellet resulted in significant change of size and density. Fig. 21 shows the state of cladding after the test, state of the pellet after the test and for illustration the state of the pellet before the test. ~50% reduction of the original size of the pellet can be observed. Due to high temperature treatment the sintering lead to pellet density close to the theoretical value.

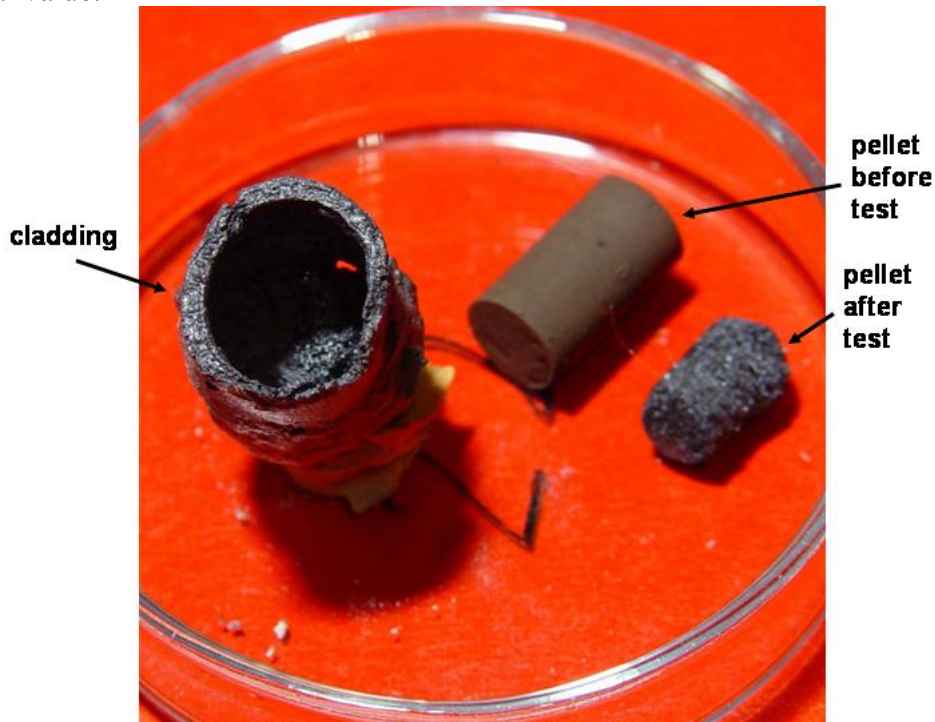


Fig. 21. A short fuel rod sample, test No. 22



Fig. 22. Cross section of the short fuel rod from test No. 22

**Summary of test parameters**

The main parameters of the experiments are summarized in Table 2.

No.	Cladding	Fuel sample	Atmosphere	Temperature
5	No	1 pellet 3,3 g	0,36 l/min Ar + 0,1 l/min air	1700 °C
18	Zircaloy	1 pellet 3,1 g	0,35 l/min Ar + 0,2 l/min air	1600 °C
19	Zircaloy	1 pellet 3,2 g	0,35 l/min Ar + 0,2 l/min air	1700 °C
20a	Zircaloy	1 pellet 3,3 g	0,35 l/min Ar + ~0,1 g/min steam	1600 °C
20b			0,35 l/min Ar + ~0,2 g/min steam	1700 °C
21	Zircaloy	1 pellet 3,1 g	0,35 l/min Ar + 0,2 l/min air	1600 °C
22	Zircaloy	1 pellet	0,65 l/min Ar + 0,2 l/min air	1800 °C

Table 2. Summary of test parameters



## 5. CHEMICAL ANALYSIS

During the present work two types of chemical analytical tasks had to be solved as post test investigations;

a./ to measure the ruthenium content of absorber solution for determining the  $\text{RuO}_4$  partial pressure in the outlet gas after cooling down,

b./ to determine the amount of  $\text{RuO}_2$  precipitated in the outlet alumina tubes.

The basic method employed in our laboratory was the spectrophotometric determination. However to find the best chemical form of Ru for the measurements some efforts had to be made. The  $\text{RuO}_4$  at test No.5 was absorbed in acidic solution, the later in basical medium. After numerous experimental efforts finally the method developed by Larsen and Ross at Argonne N.L. [10] has been found to be the most convenient. At this method perruthenate is the species to be measured in alkaline solution containing hypochlorite with low concentration. If the alkaline concentration is about 1 M and the hypochlorite is 0.05 M the ruthenium is in septivalent form (perruthenate) and stable for many days. Our results confirmed their published reproducibility. The sensitivity of this method slightly lower than at others, but the long time stability is far more advantageous. The concentrations of alkaline and hypochlorite are allowed to be in a fairly broad range. The hypochlorite should be between 0.1-0.01 M. Without hypochlorite a slow reaction toward ruthenate formation makes the colour of solution unstable, in case of too much hypochlorite a slow escape of  $\text{RuO}_4$  takes place. According to our experiences the change of colour does not exceed 0.3 %/day relating to the concentration values.

The acidic solutions showed a long time continuous changing of their absorbance, for this reason modification of method was necessary. The ruthenium species in acidic solutions are in complex formations when various components built into the inner complex layers with a very slow process, the time scale extends for many days. Moreover the absorbancies are depending on the species in the complex, which are influenced by the components of the solution. Similar troubles were seen if some colour developing compounds suggested in the literature have been used. These methods demanded a meticulous time sequence, exact pH values, moreover all ionic concentrations and even undetected minor components influence the colour development. According to our experience not only the complex formation rises troubles, but catalytic effect of ruthenium species initiates the decomposition of some suggested colour development agent.

### ***Ruthenium content in absorber solutions***

At test No.5 the 1 M HCl solutions were used as absorber solutions like at earlier tests. Their ruthenium concentrations were measured by spectrophotometer also without any further treatment [4]. According to our experiences these hydrochloric acid ruthenium solutions are not stable in many days time range, even if the sensitivity of measurement is enough for the task. The colour of earlier used organic development materials investigated at us for ruthenium analysis was changing with time, presumable a very slow complex formation and the oxidation character of Ru compounds made this effect. Due to this time-dependence only

the application of an accurate time-table lead to reproducible results. For the calibration RuCl<sub>3</sub> solutions with known Ru content were measured on the same way as the samples. At the calibration the wavelength dependence of absorption was determined and the measurements were made at the maximal absorbance value. The wavelength dependence of absorption can be seen in Fig. 23, moreover the calibration plot is given in Fig. 24.

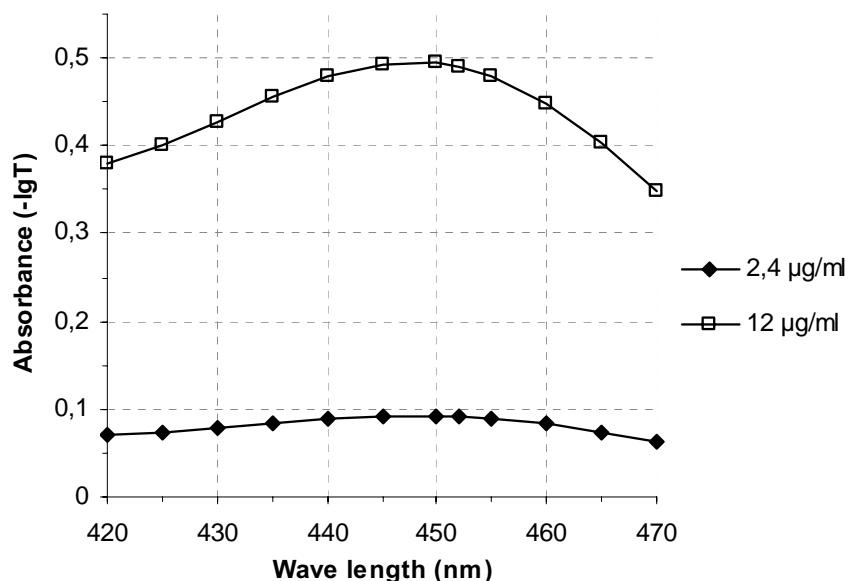


Fig. 23. Wavelength dependence of the absorption of RuCl<sub>3</sub>

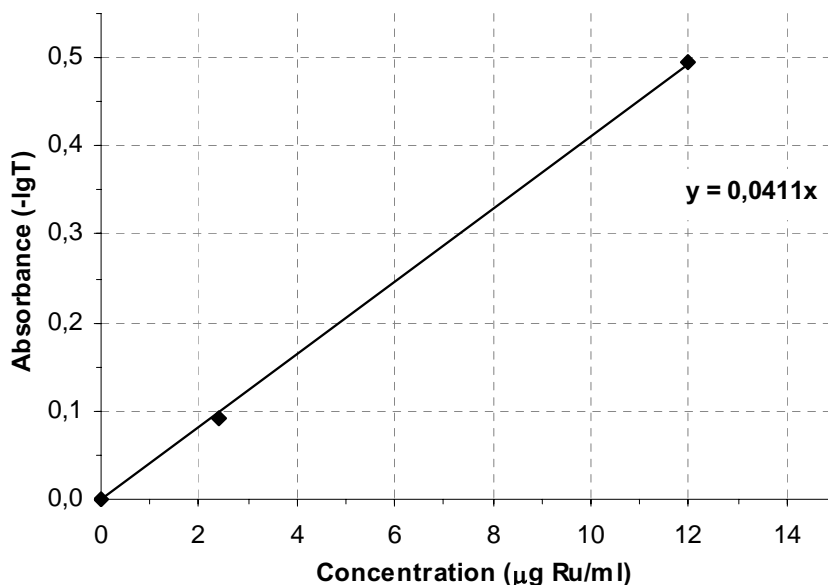


Fig. 24. Concentration dependence of light absorption of RuCl<sub>3</sub> solution at 450 nm

The alkaline hypochlorite solution is also convenient as absorption medium for RuO<sub>4</sub>, but in this case Larsen and Ross suggested to cool the absorber solution in ice bath. Because in the perruthenate the Ru does not form complexes it is not necessary to keep very strict concentration values and time sequence, therefore the preparation of samples for spectrophotometric tests is definitely easier.

The wavelength dependence of perruthenate absorption is shown in Fig. 25, the absorbance in function of concentration calibration plot in Fig. 26. The molar absorbance we found was in good agreement with that published in [10].

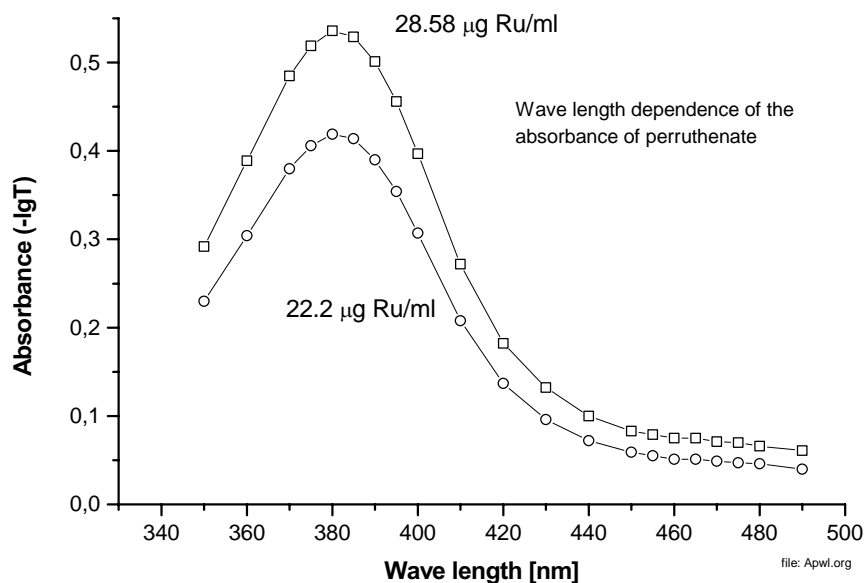


Fig. 25. Absorption of perruthenate in function of wavelength.

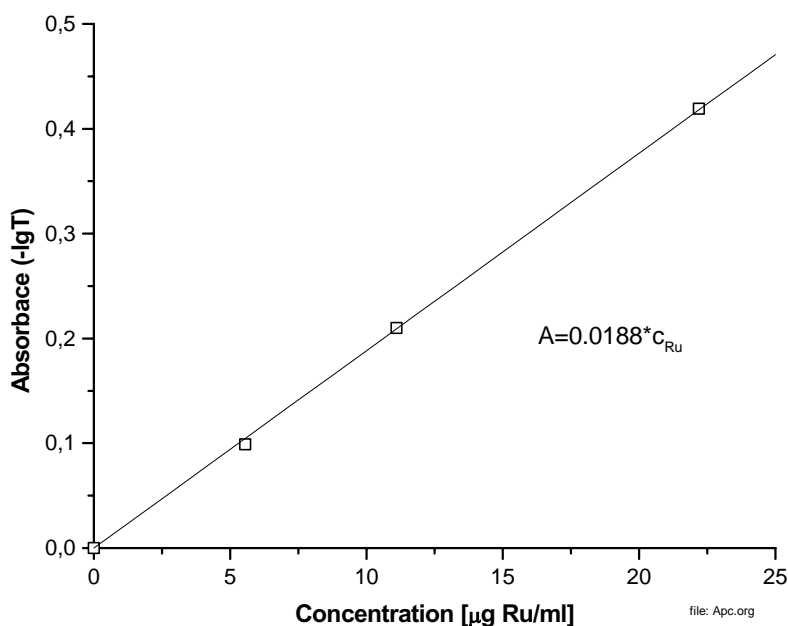


Fig. 26. Calibration plot of perruthenate at 380 nm.

The partial pressure of RuO<sub>4</sub> in the escaping gas was calculated from the amount of Ru in the absorber solution and the volume of gas flowed through at the given sampling. Using the equilibrium equation published in [6] the temperature was calculated, where the

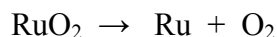


chemical process has been stopped. It seems so, that the partial pressure of RuO<sub>4</sub> in the cooled down escaping gas is depending on the partial pressure of RuO<sub>4</sub> in the high temperature gas formed in the furnace. Roughly we found so, that the partial pressure in gas after the cooling down was about ten times lower than the concentration in the high temperature furnace area, if the partial pressure of oxides is high. Certainly the time necessary to attain the equilibrium is in the range of the residence time of outlet gas in the decreasing temperature area. In Table 3. the temperature values are given, which would result in these partial pressures in equilibrium. These values are not high, but it may be explained by the low RuO<sub>x</sub> partial pressures in presence of UO<sub>2</sub>, more accurate to express by the UO<sub>x</sub> formed in the air atmosphere.

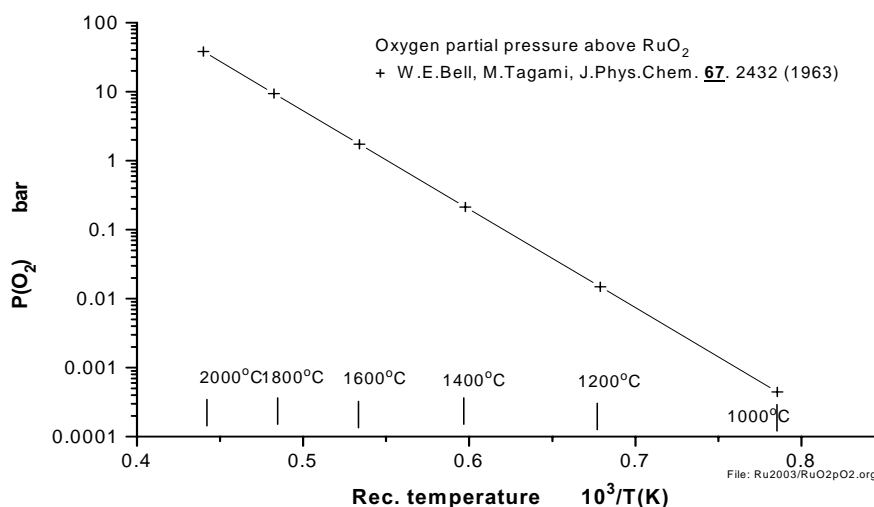
As it was mentioned above the absorber solutions were changed during the tests. It gave the possibility to assess the RuO<sub>x</sub> escape from the furnace area with time. The Ru powder was distributed in the whole volume of pellets prepared in our laboratory, it resulted in a more slower escape compared to earlier short fuel rod tests, where the fission product simulant were not mixed into the pellet, but were place in the gap between pellet and cladding [5].

### ***Ruthenium precipitations on outlet alumina tubes***

The determination of the amount of ruthenium deposited on the outlet alumina tubes was a more sophisticated problem. The RuO<sub>2</sub> is an exceptionally stable species. A direct dissolution would be troublesome (HF, melting with alkalis, etc.). We used a possibility, that the Ru-dioxide has a substantial decomposition with reasonable large oxygen pressure above 1000°C according to the process as



The partial pressure of O<sub>2</sub> above RuO<sub>2</sub> in function of the temperature can be seen in Fig. 27 [7]. The reduction process can be accelerated by adding hydrogen to the gas flow to take away the oxygen formed.



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Fig. 27. Partial pressure of oxygen above RuO<sub>2</sub> in function of temperature

At earlier experiments 5 mg Ru was evaporated during 5 hours heating. At 1100°C the ruthenium oxide precipitated at the inner surface of the outlet tube became quantitatively soluble in the argon flow. This process had not resulted in acceptable solubility, when 25 mg Ru was used at the test. After numerous experiments for checking the ruthenium balance 5 hours heat treatment at 1100°C in 5%H<sub>2</sub>+ N<sub>2</sub> gas flow proved to give adequate results. Certainly the larger RuO<sub>2</sub> crystals needed longer time for escape of oxygen by diffusion from middle part of solid particles. After the heat treatment mentioned the Ru metal formed became soluble in hypochlorite-NaOH solution used as medium for spectrophotometric measurements. The results regarding the deposits on outlet alumina tubes, their ruthenium content are summarised in Table 3.

During the numerous pre-test experiments some interesting results were found. To connect the decreasing temperature outlet tube above the furnace, absorbers tubes with different materials (PTFE, silicon rubber, glas) have been used. A gray precipitation appeared on the inner surface of these tubes containing some tenth of mg Ru. This precipitation can be solved by alkaline hypochlorite solution. After literature studies we got to the conclusion, that it was certainly RuO<sub>2</sub>.xH<sub>2</sub>O formed through low temperature hydrolysis of RuO<sub>4</sub> by the surface humidity. The Ru deposit in these tubes was depending even on the cleaning process of tubes. After a hypochlorite cleaning the Ru precipitation was lower, about 3-4 %. Earlier tests, when the cleaning was performed by alkaline H<sub>2</sub>O<sub>2</sub> solution, resulted up to 10 % of 5 mg starting Ru mass.

In the inlet tube of the absorber device similarly a black ring formed just at the start of the absorber solution wetted stage, where the hypochlorite solution was a thin layer. At the change of the absorber, when larger amount of liquid reached that ring, it was dissolved. Probably it was also RuO<sub>2</sub>.xH<sub>2</sub>O formed through low temperature hydrolysis.

### Chemical analytical results

The chemical analytical results regarding the ruthenium analysis in frame of this activity are summarised in Table 3.

No.	Sam- ple	Ru cont. [mg]	Temp. [°C]	Ru in abs. [mg]	Ru on Al <sub>2</sub> O <sub>3</sub> [mg]	Gas int. [dm <sup>3</sup> / min]	Time [min]	Gas vol. [dm <sup>3</sup> ]	Ru pp furnace [bar]	Ru pp absorber [bar]	Eq. Temp. [°C]
5	5-1	16,48	1700	0,02		0,46	165	75,9		4,95E-08	
	5-2			1,47	0,36	0,46	24	11	3,93E-05	3,15E-05	946
	5-3			0,00		0,46	50	23		0	
18	18-1	15,03	1600		0,18	0,55	18	9,9			
	18-2				0,10	0,55	30	16,5			
	18-3				0,34	0,55	30	16,5			
	18-4				0,42	0,55	30	16,5			
19	19-1	15,51	1700	0,00	0,06	0,35	34	11,9	1,20E-06	0	
	19-2			0,08	0,00	0,55	30	16,5	1,15E-06	1,15E-06	690
	19-3			0,22	0,56	0,55	30	16,5	1,13E-05	3,21E-06	770
	19-4			0,47	0,59	0,55	62	34,1	7,37E-06	3,26E-06	771
21	21-1	15,03	1600	0,23	0,54	0,55	60	33	5,55E-06	1,66E-06	719
	21-2			0,22	0,20	0,55	60	33	3,05E-06	1,61E-06	716
	21-3			0,18	0,22	0,55	60	33	2,89E-06	1,30E-06	700
22	22-1	14,54	1800	1,34	3,19	0,71	60	42,6	2,50E-05	7,41E-06	834
	22-2			0,80	1,07	0,71	60	42,6	1,03E-05	4,39E-06	794
	22-3			0,46	1,05	0,71	60	42,6	8,36E-06	2,55E-06	752

Table 3. Summarised results of Ru chemical analyses.

The results have been compared with a diagram showing the partial pressure of ruthenium oxides (Fig. 28) in function of temperature, if the oxygen pressure is 0.076 bar like at our experiments. In the figure both the partial pressures of RuO<sub>3</sub> and RuO<sub>4</sub> are plotted and their sum as well according to the formula published by Alcock and his co-workers [6]. Their functions are only valid up to 1580°C at 1 bar, because they used RuO<sub>2</sub> as solid phase. (At lower oxygen pressures to even lower values as can be judged from Fig. 27.) Above this temperature the solid phase is Ru metal, when the formula published by Schäfer, Tebben and Gerhardt [11] is valid.

$$\log K_p = 3100,6/T - 5,9915 + 1,0768 \cdot \log T - 0,2011 \cdot 10^{-3} T - 0,297 \cdot 10^{-5} \cdot T^{-2}$$

It is plotted as dotted line (RuO<sub>3</sub> – Ru) in Fig. 28. This is an exotherm process, the partial pressure of RuO<sub>3</sub> is decreasing with increasing temperature.

The presence of uranium-oxides and fission product components resulted in two effects.

- First, the partial pressures of ruthenium oxides, deposited and escaped sum, are about two orders of magnitude lower than those values obtained with inert solid dilution materials (ZrO<sub>2</sub>). Interesting to see, that this two order of magnitude partial pressure decreasing can be seen on earlier results from tests performed at 1100°C [4]. At that case the relative amount of UO<sub>2</sub> and FP components were substantially less, however even in that case with excess stoichiometric ratio. The present results show increasing escape with temperature, not following the pure Ru-metal tendency. It reflect that the mentioned components have larger influence than the direct ruthenium – oxygen interaction.

- The second effect is the delay of ruthenium escape. In Fig. 29 the average partial pressures of ruthenium oxides are plotted for sample collection intervals.

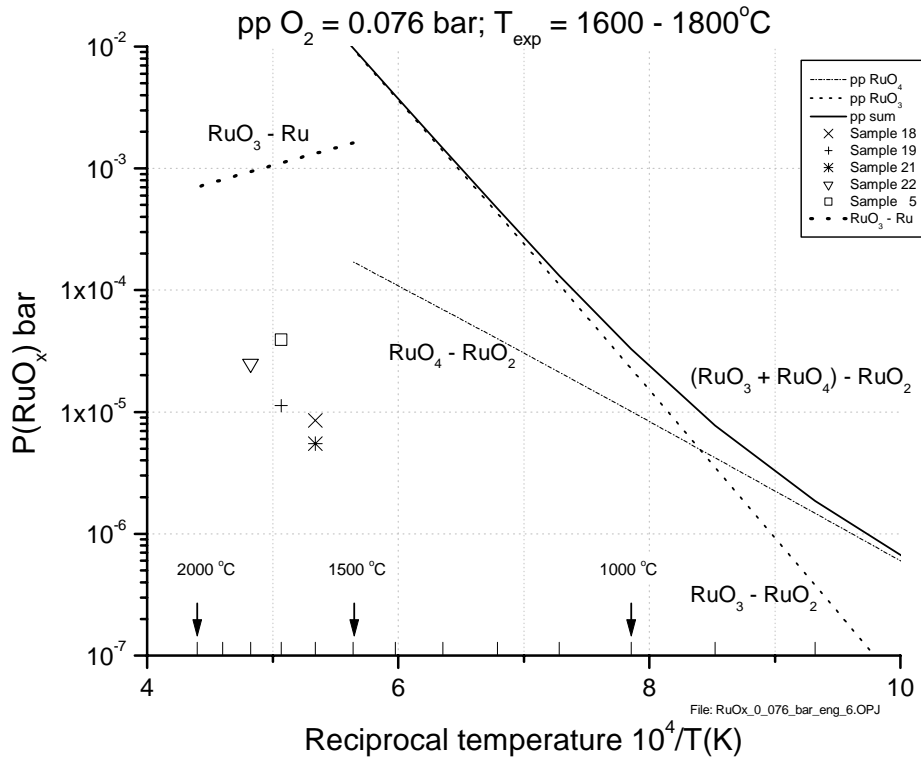


Fig. 28. Calculated partial pressures of Ru-oxides from [6], [11] and the present results

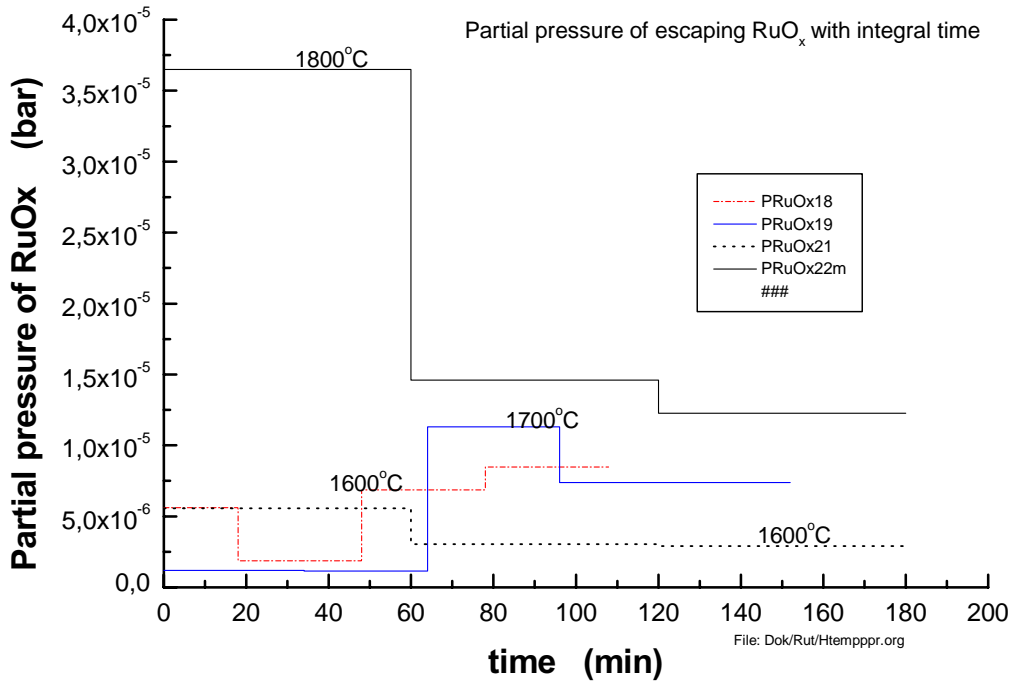


Fig. 29. Average partial pressures on sampling intervals.

As can be judged at 1600 and 1700°C the delay of escaping are at about 60 minutes. Even in this case the delay at the earlier experiments made at 1100°C showed also similar delay times [4]. At the 1800°C experiment (No. 22) the starting delay was shorter, it was in the first 60 minutes period. Interesting to see, that the delays except the case of 1800°C are independent from temperature in the row time scale of sampling.

The first Ru experimental series [4] showed that the fission product simulant components are responsible for the escaping delay and the strong decreasing of partial pressure of ruthenium oxides.

A tests using only argon and steam (No. 20a and 20b) showed no ruthenium escape, proving the known fact, that the ruthenium became volatile only in the presence of oxygen.



## 6. ELECTRON BEAM STUDIES

Alumina rod No. 5-2 and three other samples were selected for these studies. The three samples had the following marks:

27 – the sample was removed from the first alumina rod of test No. 21,

27K – the sample was removed from the first alumina rod of test No. 21,

BCS – the sample was removed from the depositions of the quartz tube in the sampling solution of test No.22.

- We performed direct electron beam studies on alumina rod No. 5-2 having deposits on its surface. We sputtered a thin carbon layer on some parts of the rod in order to decrease the electric charging.
- Samples 27, 27K and BCS were in form of particles filtered out by filtering paper. SEM sample holders were covered by pieces of double-sided carbon conductive tape and touched to the material on the filter. First the samples were studied directly – without any sputtered carbon layer – by SEM and EDX, but before further studies with an EDX with thin window, a thin carbon layer was sputtered on the surface of them.

The following instruments were applied:

- Philips SEM 505 scanning electron microscope (SEM) working at 20 kV and using a few nanoamper beam current. Mostly we made backscattered electron images (BEI).
- LINK AN 10/55 S type electron beam microanalyser (EDX).
- Oxford EDX using thin window suitable for detecting light elements such as oxygen, carbon and boron.

The aim of our SEM studies was twofold:

1. To know the *morphology of deposits* present on the alumina rod No. 5-2.
2. To reveal the nature of deposit and study the elemental composition of it.

### **Analysis of rod 5-2**

We cut seven pieces from the rod No. Ru 5-2, when we finished XRF measurements. We mounted the rod pieces on SEM sample holders covered by adhesive carbon tape. We labelled the samples in a way, that the sample nearest to the outside space got No. 1, then the numbers increased by proceeding to the direction of the oven. We mounted the samples in such a way, that their upper ends were closer to the outside space, while their lower ends to the oven. At the ends and at the middle parts of the samples we always made EDX analysis at magnification of 300-times, which corresponded to about 1 mm<sup>2</sup> area. We also examined sample details with interesting shapes or which have brighter contrast (i.e. higher atomic number of elements), than their neighbourhood, and made images with higher magnification.

Figure 30 shows a typical BEI image taken at the end of the rod Ru 5-2, which was the nearest to the outside space. The EDX spectrum taken from this area can be seen in Figure 31. The BEI image shows relatively low abundance of deposited material. It is in correspondence with the EDX spectrum showing only very small amount of Ru. By moving to the direction of the oven, Mo, Te and Cs appeared, too. Figure 32 shows some deposited particles and an EDX spectrum corresponding to a slightly elongated particle of the BEI image. This image illustrates such a part which was not so far from the outside space. The shape of the particles

is various: globular, elongated and irregular, too. The size of these deposited grains/particles is between 1 and 5  $\mu\text{m}$ .

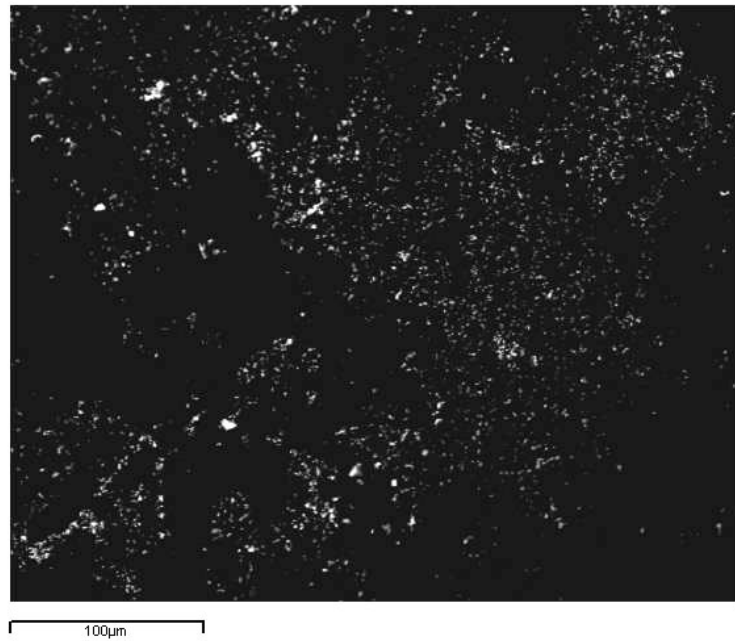


Fig. 30. BEI image of rod piece nearest to the outside space (taken at 300 times of magnification)

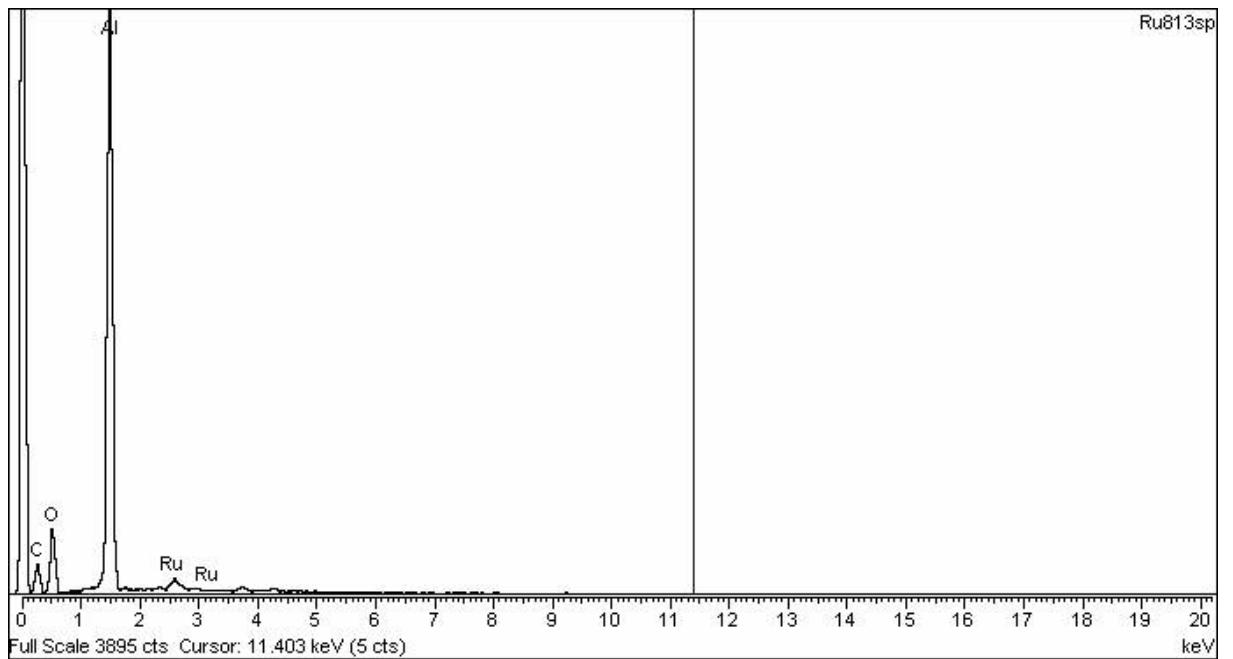


Fig. 31. EDX spectrum of the area corresponding to that of the Figure 30

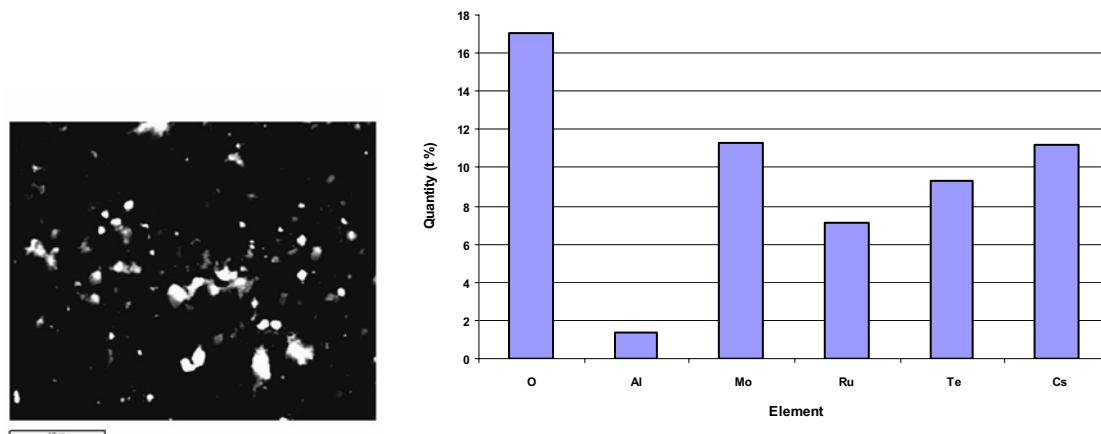


Fig. 32. BEI image and EXCEL diagram (showing the elemental composition of a deposited particle with slightly elongated shape at 3000 times of magnification)

The other end of the rod shows also relatively low abundance of deposited particles, however the EDX analysis shows the presence of relatively high amount of Cs. Small amount of Ru, Mo, W can also be seen. Figure 33 shows the BEI image taken at the other end of the rod, while Figure 34 illustrates the EDX spectrum corresponding to the area of the image.

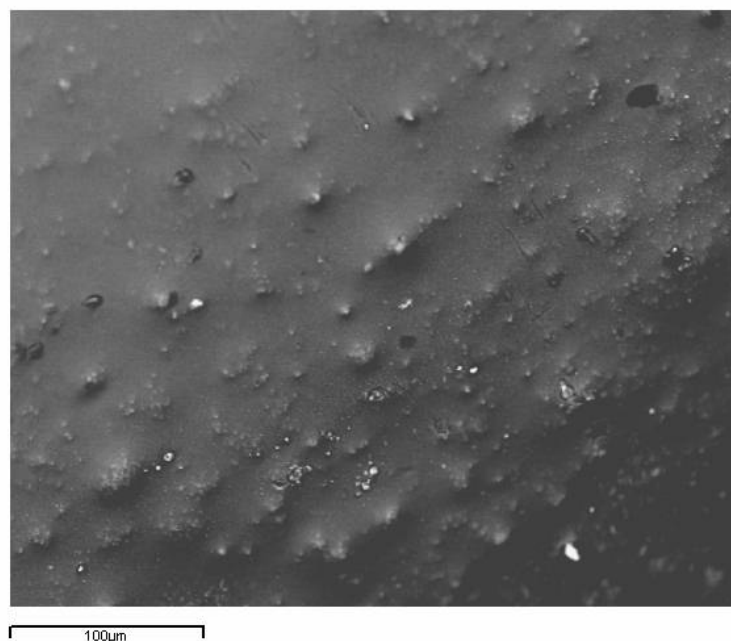


Fig. 33. BEI image taken near to the other end of rod 5-2

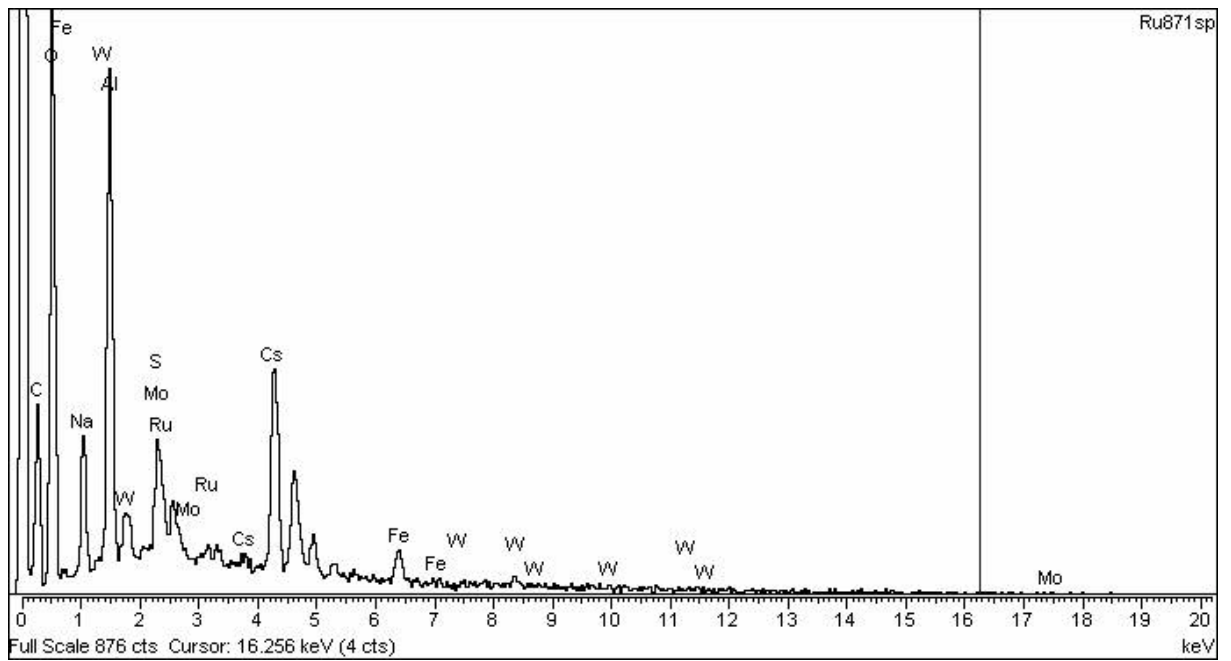


Fig. 34. EDX spectrum corresponding to the area of Figure 33

By analysing the rod pieces by moving from the outside space to the direction of the oven, incrementation of the amount of deposited material can be found. The highest amount of deposited material can be detected for rod piece No. 5 of rod 5-2. Figure 35 shows the BEI image taken at 300 times of magnification from the middle part of this piece. Figure 36 illustrates the EDX result corresponding to the area of Figure 35.

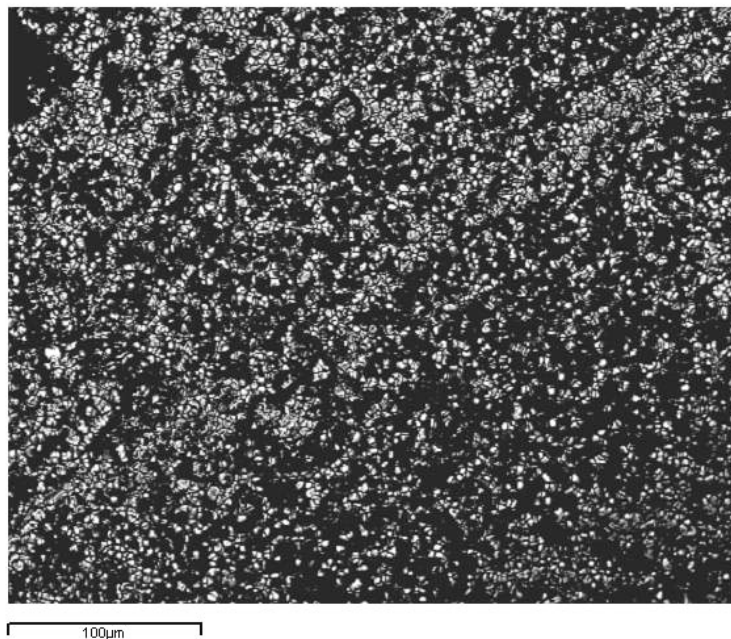


Fig. 35. BEI image taken at about 45 mm far from the outside space

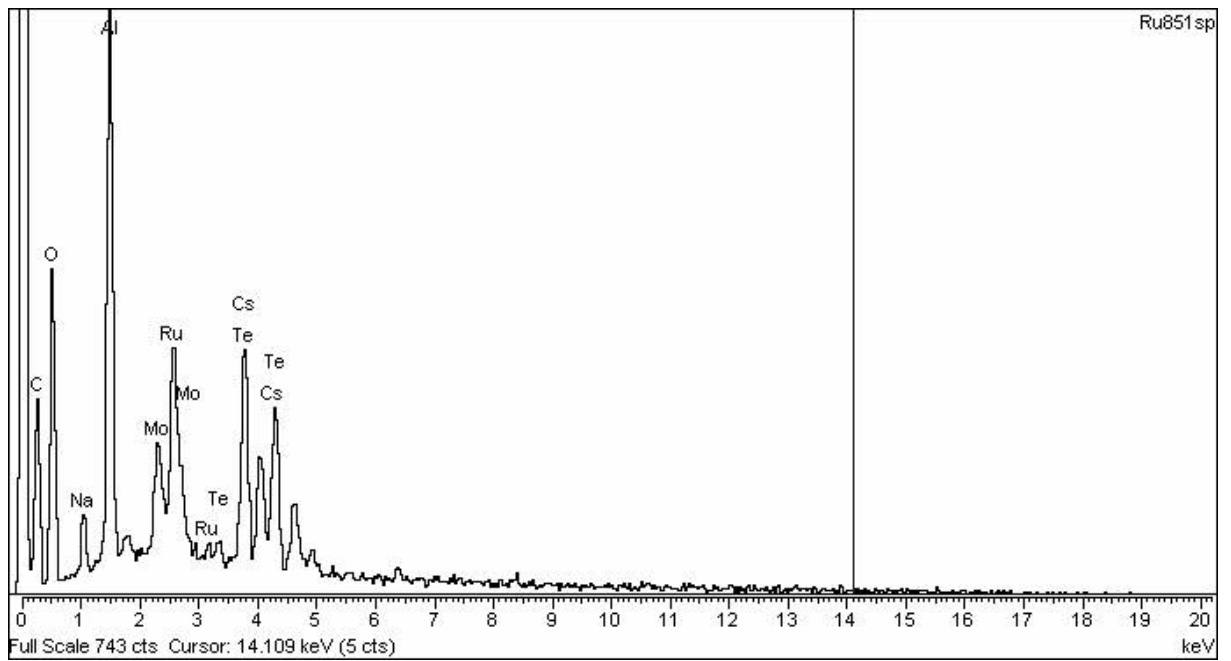


Fig. 36. EDX spectrum corresponding to the area of the Figure 35

Figure 37 contains the quantitative EDX results gained for all measuring places on rod Ru 5-2. The left hand side part of the diagram corresponds to the highest temperature region, while the right hand side to the outside one.

Some quantitative EDX results on sample Ru 5-2

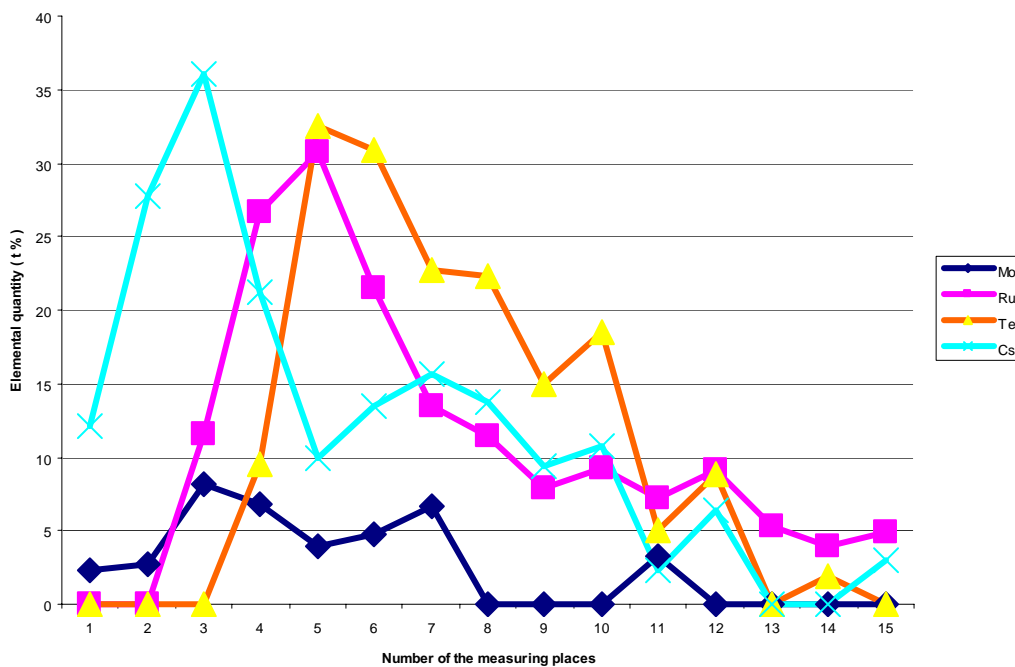


Fig. 37. Quantitative EDX results for rod Ru 5-2 (Point No. 1 was close to the furnace, the distance between points was 8 mm)

This figure shows that Te starts to deposit at relatively low temperature, i.e. near to the outside space. Ru, Mo and Cs form deposits, too, and it is typical to that rod, that Ru, Te, Mo and sometimes Cs can be detected altogether along a relatively wide region of the rod. The maximum value of Cs seems to correspond to the highest temperature region of the rod. These findings are in correspondence with the XRF results. Figure 38 shows a BEI image, where individual grain with rectangular shape, enriched mostly in Ru, can be seen together with the appropriate EDX spectrum.

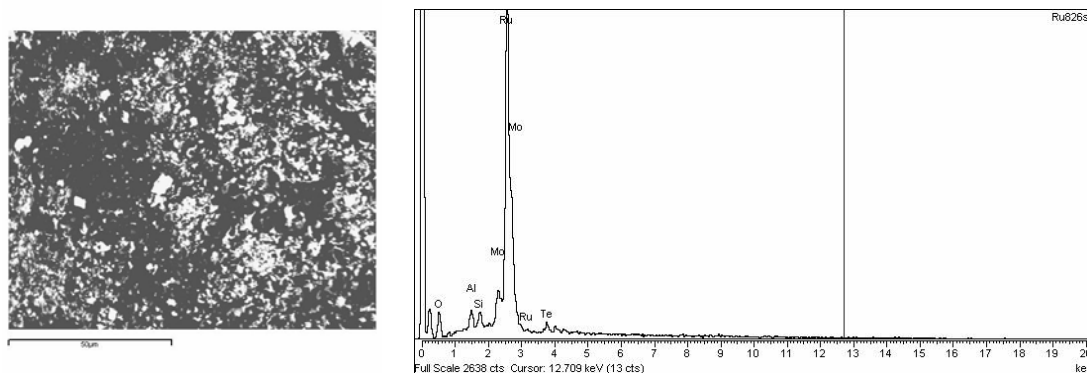


Fig. 38. BEI image showing grains enriched mostly in Ru (3000 times of magnification)

While the amount of Ru is the highest in these grains, they have also some amounts of Mo and Te. Regions having the highest amount of Ru also contain Mo and Te. The quantitative data of some regions having the highest amount from one element are shown in Table 4. By analysing various individual grains and aggregates, small amount of U and W were detected, too.

Element	Max. amount of Te (mass %)	Max. amount of Ru (mass %)	Max. amount of Cs (mass %)
O	10,15	18,91	40,05
Al	8,27	1,56	18,70
Mo	6,50	5,51	2,78
Ru	20,57	68,42	0
Te	38,51	4,54	0
Cs	7,76	0	27,78
U	6,04	0	0
W	0	0	3,67

Table 4. Quantitative EDX results of some interesting grains on rod 5-2

By summarising the results of the electron beam studies, it can be stated, that the EDX analysis of both of larger regions (about 1 mm<sup>2</sup>) and of smaller grains shows deposition of the following elements: Te, Ru, Mo, Cs and sometimes small amount of U, Cd and W. Most of the elements came together, i.e. phases containing them were formed.

### **Analysis of sample 27K**

This sample contained relatively large sized grains - aggregates which were enriched in uranium (and probably in oxygen). Due to the high uranium content, this sample was studied only by the Philips SEM equipped with the LINK AN 10 instrument. (We could not bring it to the other EDX working in another institute.) Figure 40 shows two digital backscattered electron images (BEI) illustrating the sizes and shapes of the U-containing grains.

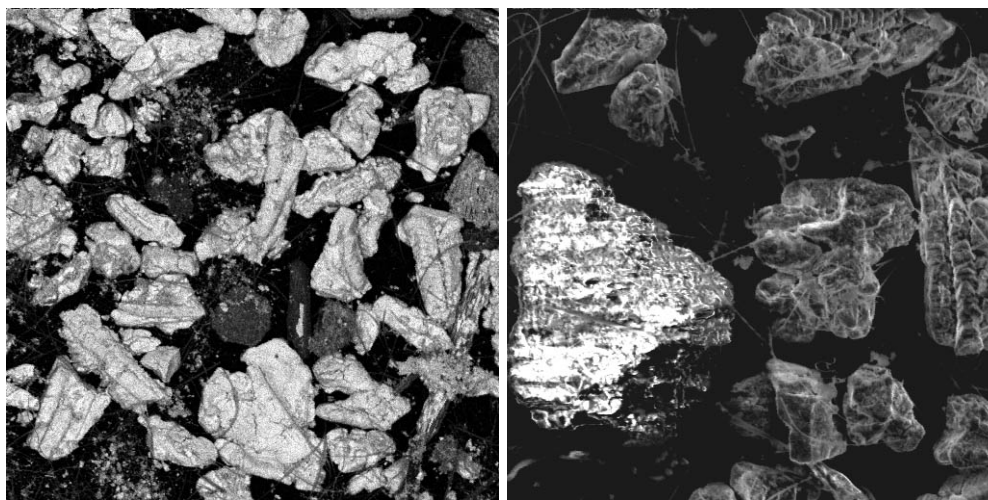


Image area: 1,2 mm x 1,2 mm

Image area: 600 μm x 600 μm

Fig. 39. Digital BEI images for sample 27K

The size of the grains - aggregates varies from a few tenth of micrometer to several hundreds of micrometer. It can be recognised that some aggregates had layered crystallites. On the right hand side of Figure 39 the aggregate which suffered from severe electric charging, was enriched in Al, the material of the tube. Fibres of the filtering material were found in several places on the sample holders. *Most of the grains had U and small amount of Cs content.* Other elements were not found by EDX.

### **Analysis of sample 27**

The size of the grains and aggregates of this sample is much smaller than that of the previous sample. The size of the grains with bright contrast is generally between 1 and 5 μm, the ones with greyish contrast are somewhat larger: 8 – 20 μm. Digital BEI image typical to this sample is shown in Figure 40.

By analysing a lot of grains - aggregates, most frequently U, Sn, Si, Na, Ca and O were detected. Si, Na, Ca and one part of the O came probably from the fibres of the filtering material. At some places of the sample larger sized needle-like grains enriched in Al were found. They are shown in the image pair of Figure 41. Smaller grains with bright contrast were enriched mostly in U and O.

Figure 42 shows two ED spectra: one for a U-rich grain, the other is for Sn-U containing one. Note: Cu and Zn originated from the sample holder.



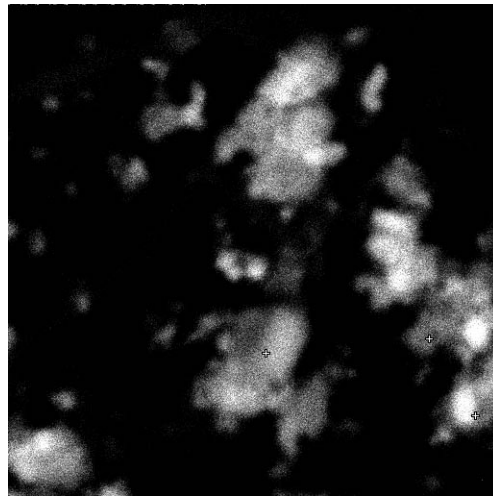


Image area: 120 μm x 120 μm

Fig. 40. Digital BEI image typical for sample 27 taken at 500 times of magnification

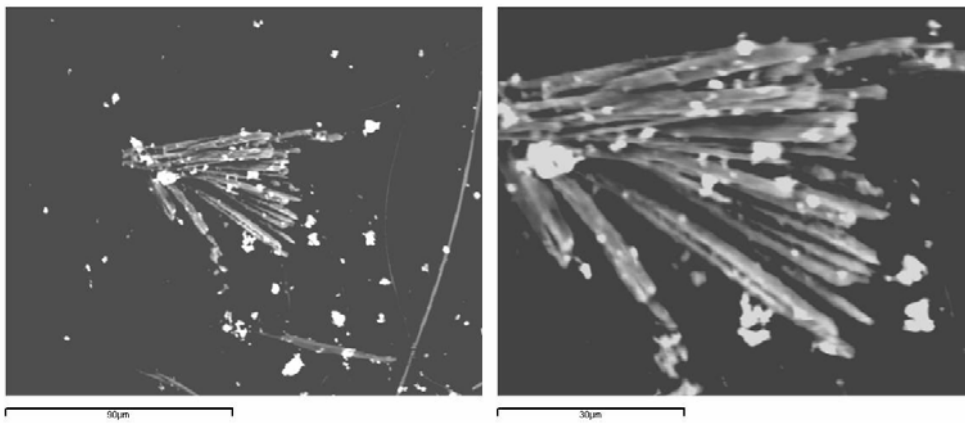


Fig. 41. Image pair taken at 600 and 1500 times of magnification for sample 27

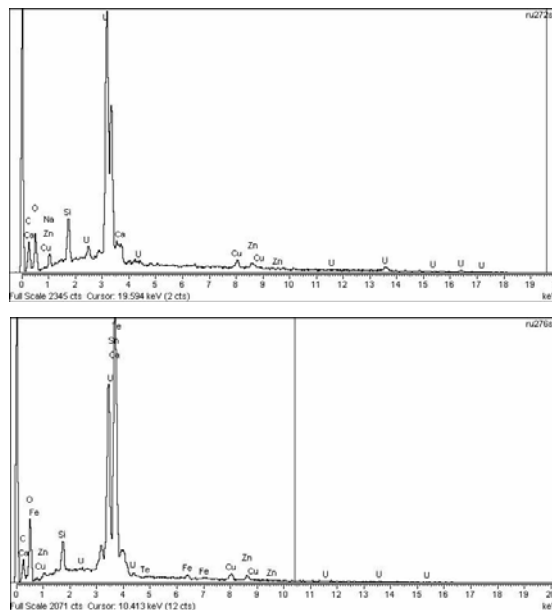


Fig. 42. ED spectra of the U and U/Sn containing grains for sample 27



**Analysis of sample BCS**

This sample also has relatively small grain size – generally a few  $\mu\text{m}$ , the largest grains had 20-30  $\mu\text{m}$  size - shown in Figure 43, where two digital BEI images can be seen. The small grains were almost embedded into the fibres of the filtering material or that of the material of the tube; therefore Si, Na and O were always detected. Only U and sometimes Sn were found, the typical ED spectra are illustrated in Figure 44.

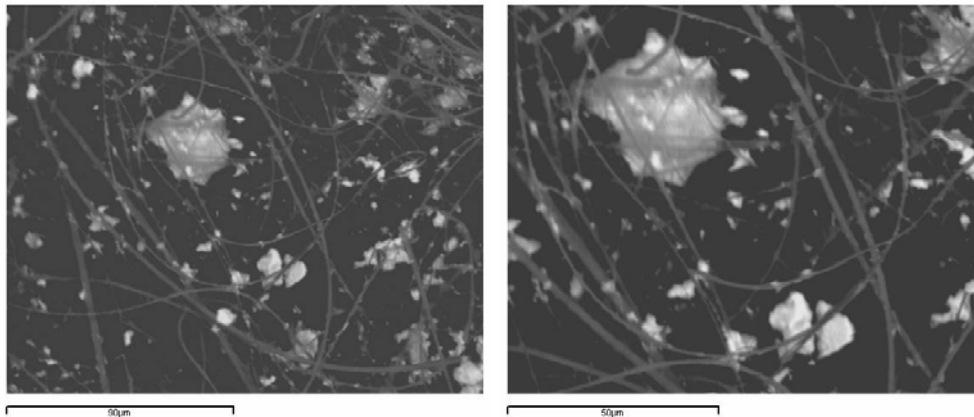


Fig. 43. BEI images taken at 600 and 1000 times of magnification for sample BCS

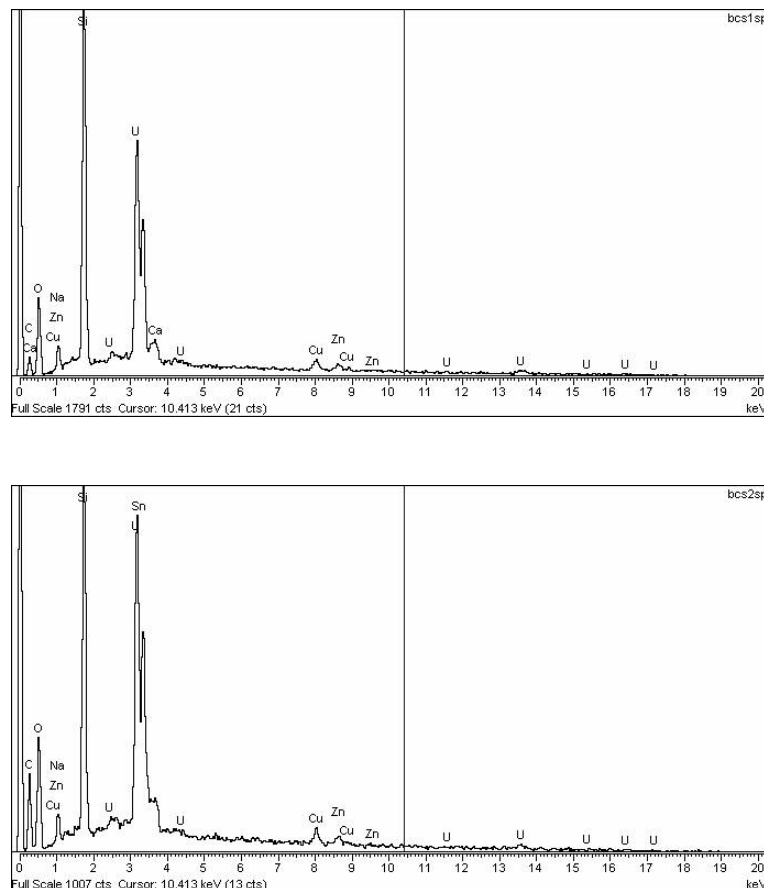


Fig. 44. ED spectra showing U and U/Sn content of the grains for sample BCS

## 7. XRF ANALYSIS OF THE SAMPLING RODS

For the determination of axial distribution of the fission elements deposited along the sampler rod, Micro-beam X-ray Fluorescence ( $\mu$ XRF) measurement has been carried out. During this process the sample was scanned by a silver tube generated X-ray beam, which was focused by a 100  $\mu$ m wide glass capillary. The high voltage was 50 kV and the current 20 mA. For scanning, the sample was fixed to the sample table vertically and was moved in front of the capillary in vertical direction. For moving the sample, Parker stepping motors with 2 mm step resolution were used. Each point was measured for 120 seconds. Spectra were recorded by a Si(Li) X-ray detector and evaluated by the AXIL code.

Axial distribution along the rod could be determined for four elements (Mo, Ru, Te, Cs) that presented in the pellet. From the main components of the pellet, Zr and Nd were detected only in a few measurement points, so axial distributions were not found in these two cases. In Fig. 45 the axial distribution of the detected elements on sample 5-2 is presented. The distance from the first measurement point was marked along the horizontal axes. The first measurement point was taken close to the hottest end of the rod. The XRF methodology has various sensitivity for the different elements, therefore on the vertical axes relative scale was used. The distribution curves of each element were normalised to the maximum count value. Measurement points have been signed by discrete symbols, the continuous lines indicate a 2<sup>nd</sup> degree moving average fit for reducing the statistical noise of the curves.

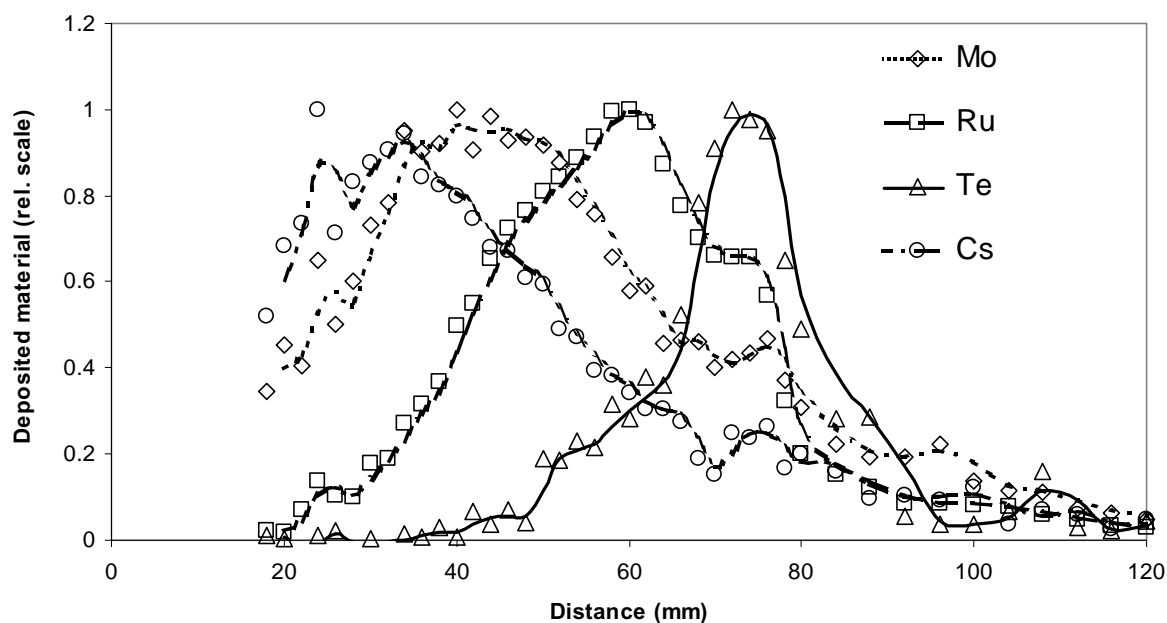


Fig. 45. Axial distribution of fission products on rod sample 5-2.

As it seen on the figure, Cs deposited first on the rod, Mo and Ru were the second and the third and Te the last. Te has the narrowest deposition profile, and Ru has another local deposition maximum following the main maximum point.

The typical temperature distribution along the sampling rod is shown in Fig. 46. This measurement was carried out separately. Similar curves were produced during the tests. It

must be noted that the illustrated temperature distribution can change due to different gas flowrates and composition even for the same furnace temperature.

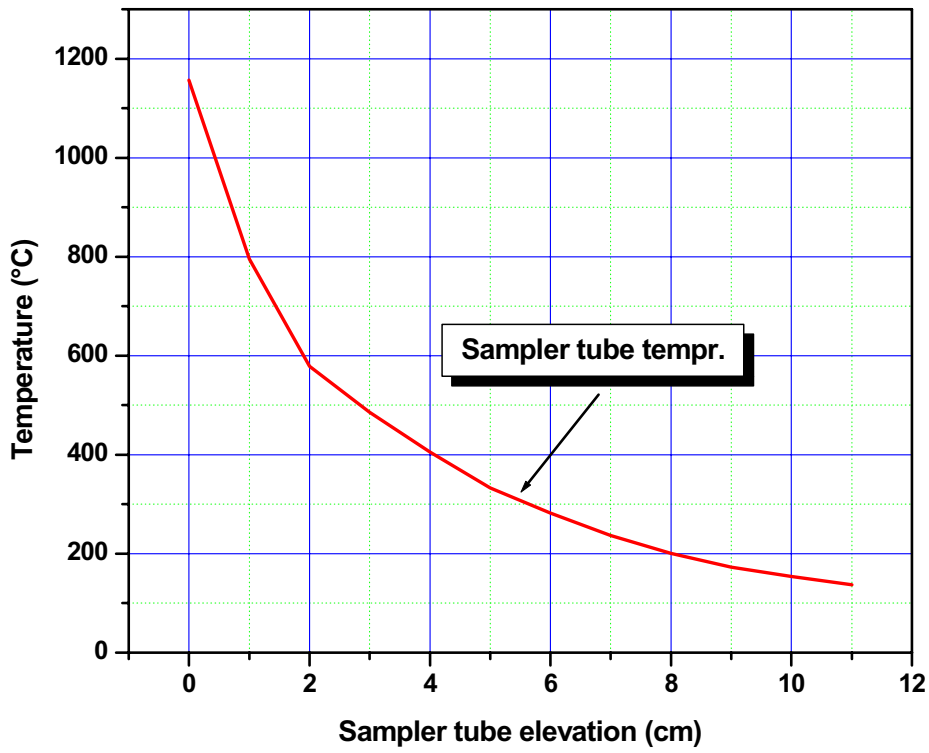


Fig. 46. Typical temperature distribution along the sampling rod

## 8. SUMMARY AND CONCLUSIONS

Experiments have been carried out with short fuel rod samples in order to investigate ruthenium oxidation and release in high temperature air. The temperatures of the tests were 1600, 1700 and 1800 °C. The oxygen content in argon carrier gas was 0.076 bar, about third of atmospheric air. The reduction was necessary, because fast oxidation of Zircaloy cladding raised the temperature of the furnace on uncontrollable way.

All fuel rod samples included a short Zircaloy-4 cladding and a manufactured pellet, that contained inactive fission product simulants. Two tests were carried out in steam and the other five of the current series in air atmosphere. During the tests the zirconium cladding was oxidised and the pellet suffered significant reduction of volume due to densification (sintering).

Samples were collected both as precipitations on an alumina outlet tube from high temperature area to ambient temperature and as absorbed gas escaping with the argon stream. The ruthenium content of precipitation and gas absorber units has been determined. To get some information regarding the time scale of escaping both the alumina outlet tubes and absorber units were changed a few times during the test.

Tests with steam atmosphere did not indicate the formation of any gaseous Ru oxides even at 1700 °C.

Chemical analysis of samples pointed out, that:

- escape of ruthenium oxides delayed with ca 60 minutes in 1100 to 1700 °C temperature interval, slightly less at 1800 °C,
- the partial pressures of Ru-oxides were about two orders of magnitude lower in the presence of uranium oxides and FP components, than if only Ru metal powder was diluted with inert solid component (e.g. ZrO<sub>2</sub>).

The temperature dependence of the deposition of different fission product elements was detected by XRF method applied to the investigation of alumina sampler rods.

The results of electron beam studies indicated that in the selected deposit samples most frequently U containing grains were found. Their sizes varied from a few micrometer to several hundreds of micrometer. Beside U, small amount of Cs was also detected. There were grains enriched also in Sn and rarely Te and Zr, too.

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**OXIDATION AND RELEASE OF RUTHENIUM FROM  
FROM SHORT FUEL RODS ABOVE 1500 °C**

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**Abstract**

The fission product ruthenium is radiotoxic and in oxidized form as ruthenium-tetroxide ( $\text{RuO}_4$ ) also chemical toxic. During fuel element change or in case of a leakage in fuel storages, air flows in the containment or fuel storage. If the circulation pump fails, the fuel elements are heated-up, and at high temperatures gaseous ruthenium oxides are formed and rapidly released from the fuel. Due to the significant higher volatility of  $\text{RuO}_4$  in the Chernobyl Catastrophe the measured concentration of the Ru-isotopes in the fall-outs was comparable to those of iodine and caesium. In order to get more insight in the chemical and physical behaviour of this fission product under severe accident conditions, the Ruthenium release was studied in a series of Separate Effect Tests (RUSSET). In the test short fuel rod segments were used and exposed to air and steam atmosphere at high temperatures. The experiments in air atmosphere showed, that the partial pressures of the released Ru-oxides was two orders of magnitudes lower compared to those measured in previous tests with Ru-powder diluted in a  $\text{ZrO}_2$  matrix. It was found that ruthenium was not released in steam atmosphere in the examined temperature range. Furthermore, the temperature dependence of the deposition was detected by XRF analysis.

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