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Ruthenium behaviour in severe nuclear accident conditions - progress report

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Abstract

In order to prevent the radioactive ruthenium from spreading in gaseous form in case of an accident in a nuclear power plant it is of interest to know how it is formed and how it behaves. In the experiments the behaviour of ruthenium in oxidising atmosphere at high temperatures is studied.

The methods for trapping and analysing RuO₄ has been studied. It was found that 1M NaOH is capable of trapping RuO₄ totally. The determination of Ru from the solution can be made using ICP-MS (inductively coupled plasma mass spectrometry) and from the reduced precipitates on filters by INAA (instrumental neutron activation analysis).

The results of the experiments carried out so far is reported. A significant difference in the decomposition rate of gaseous RuO₄ depending on the tube material was found. In all experiments only a minor fraction of Ru remained in gaseous form until the bubbler. In order to achieve a better mass balance an experiment using radioactive tracer was carried out. In the decomposition of gaseous Ru needle-shaped RuO₂ crystallites were formed.

Key words

Ruthenium, oxidising atmosphere, high temperatures, experiments

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1. INTRODUCTION

During routine nuclear reactor operation, ruthenium will accumulate in the fuel in relatively high concentrations. In an accident in a nuclear power plant it is possible, although not very plausible that air gets into contact with the reactor core. In this case ruthenium can oxidise and form volatile ruthenium species, RuO_3 and RuO_4 , which can occur in the containment. In contrast to other fission products the oxide forms of ruthenium are more volatile than the metallic form [Jokiniemi and Zilliacus 2001].

In order to prevent the radioactive ruthenium from spreading in gaseous form in case of an accident in a nuclear power plant it is of interest to know how it is formed and how it behaves. In our experiments RuO_2 is exposed to an oxidising atmosphere at high temperatures. The formation and decomposition of gaseous Ru is studied as well as the decomposition products. Experimental parameters are the release temperature, the introduction of seed particles and the oxygen concentration.

2. DEVELOPMENT OF METHODS FOR TRAPPING AND ANALYSING RuO_4

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

2.1 Distillation of ruthenium

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

2.2 Experimental

Ru tracer

The experiments were performed using a ruthenium solution of 1000 mg/l (Accu TraceTM Reference Standard, Ru in dilute HCl). An amount of 5 ml was irradiated for three hours in the Triga Mark II reactor in Otaniemi, Espoo. The neutron flux was $1.2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. Ruthenium has several radioisotopes of which ^{103}Ru was used as the tracer in these experiments. The half life of the isotope is 39.8 days and the measured γ -energy 498 keV.

Distillation of Ru from H_2SO_4

The first experiment was to distill 0.5 mg of Ru from a solution of 12 M H_2SO_4 . Ru was supposed to distill with water. The distillate was collected into 15ml of 6M NaOH solution in a water bath with

ice. After the gamma measurement of the distillate and the distillation residue was done, all ruthenium was still found in the residue. This shows that H_2SO_4 alone was not strong enough to oxidize Ru to RuO_4 . KMnO_4 solution was added into the distilling flask and now the brownish color of the Ru was noticed in the distillate. The reaction was quite violent though it was only gently heated in the beginning of the reaction. Bubbling air through the system and using a higher tube from the flask to the delivery arm was needed to prevent the suckbacks. The Ru yield was 83% in this experiment because of the leak through loosened glass joints caused by the violent reaction. The distillation apparatus is shown in figure 1.

Most of the RuO_2 was precipitated in the tube but the color of the NaOH solution was still brownish. Ethanol was added and the tube was warmed in a water bath. The solution cleared up. The precipitate was centrifuged, washed with water and ethanol and centrifuged again. Then it was dissolved in 1 ml of warm concentrated HCl. The Ru concentration in this solution can be analyzed with ICP-MS or INAA.

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



Figure 1: The distillation apparatus.

If the amount of Ru is small and it is analysed soon after the distillation so that there has been no precipitation, the analysis can be done from the NaOH solution diluted with 1% HNO_3 . To avoid the

large dilution of the analytical solution in experiments containing very small amounts of volatile Ru, the use of more dilute NaOH solution would be better than 6M NaOH

Therefore the next experiments were done using 1M NaOH solution in the receiver. The double experiments were done with 0.5 mg Ru in concentrated H₂SO₄ and by adding 2 ml of 0.04M KMnO₄ as oxidizing agent. The receiver contained 15 ml of 1M NaOH. Both experiments gave 100% yield of Ru showing that 1M NaOH is capable of trapping RuO₄ totally.

3. ANALYSIS OF RUTHENIUM

3.1 ICP-MS

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

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

3.2 INAA

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

4. RUTHENIUM OXIDATION EXPERIMENTS

The system used for the Ru experiments is schematically presented in figure 2. The main component of the system was the tubular flow reactor in which the ruthenium source (RuO₂ powder) was heated. The tubular flow reactor (Entech, ETF20/18-II-L) used was 110 cm long and had two heating zones, each 40 cm long. The ceramic crucible with the RuO₂ powder (about one gram per experiment) was placed over the second heating zone of the reactor. A gas-flow of 5 lpm was passed over the crucible. The flow rate was controlled with a mass flow controller (Tylan General FC-2900M). As the gas exited the reactor it cooled and the gaseous ruthenium oxides decomposed to RuO₂ particles. The RuO₂ particles were filtered out at a point 106 cm downstream of the reactor. At this point the temperature of the gas was ~50 °C. The gaseous ruthenium was trapped downstream of the filter in a 1 M NaOH solution. The bubbler containing the trapping solution was placed in an ice-bath.

In some experiments gas-phase sampling was done at a point 74 cm downstream of the reactor using a j-shaped probe pointing upstream in the flow. The sample was diluted with a porous tube diluter and so minimising the losses during dilution. The number size distribution of the particles was measured with a differential mobility analyser (DMA, TSI 3081) and a condensation nucleus counter (CNC, TSI 3022). The particles are size classified according to their electrical mobility by the DMA and the CNC counts the number of particles in each size class. The system was controlled with the Aerosol Instrument Manager software version 4.0 (TSI). The gas flow in the sampling line was filtered before being vented to the fumed hood. Transmission electron microscopy (TEM) samples were collected on holey carbon coated copper grids using an electrostatic precipitator (ESP).

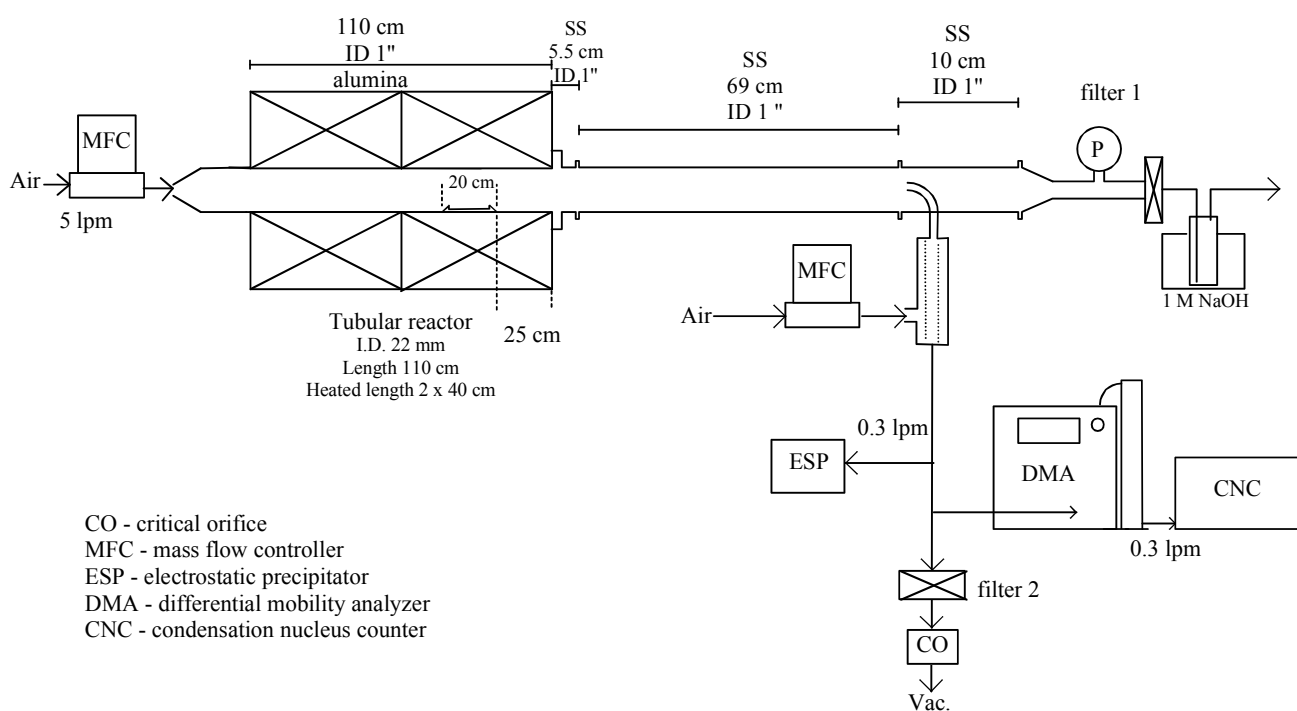


Figure 2: Experimental set-up for Ru-experiments.

So far four of the six planned experiments have been conducted. The details of the experiments can be found in table 1. Experiment #1 was our base case, in which the release temperature was set to 1227°C and a 5 l/min (NTP, NTP conditions 0°C, 101325 Pa) air-flow passed over the crucible containing the RuO₂. The lines downstream of the furnace were stainless steel lines. In experiment #2 the lines downstream were as far as possible ceramic keeping the other experimental parameters as in experiment #1. This experiment was carried out to see the effect of the line material, as RuO₄ is known to react with and deposit on stainless steel.

Table 1: Details of the experiments

Exp #	T release [°C]	Gas	Tube material	Other	Duration of experiment [min]
1	1227	Air, 5 l/min	Stainless steel		60
2	1227	Air, 5 l/min	Alumina		45
3	1227	Air, 5 l/min	Stainless steel	Tracer used	42
4	1427	Air, 5 l/min	Stainless steel		20
5	1227	N₂ + 10 % O₂, 5 l/min	Stainless steel		
6	1227	Air, 5 l/min	Stainless steel	Add seed particles	

As the mass balance in the first experiments was not satisfying, an experiment (#3) was carried out using a radioactive tracer, 103-Ru ($\tau_{1/2} = 39$ days). The experimental parameters were identical to the ones in experiment #1. In the radioactive tracer experiment no sampling of the particles was done. In figure 3 a photograph of the system used in this experiment is shown. In experiment #4 a high release temperature of 1427°C was used.

In experiment #5 the effect of lower oxygen concentration (10%) will be studied and in experiment #6 the effect of seed particles will be studied.

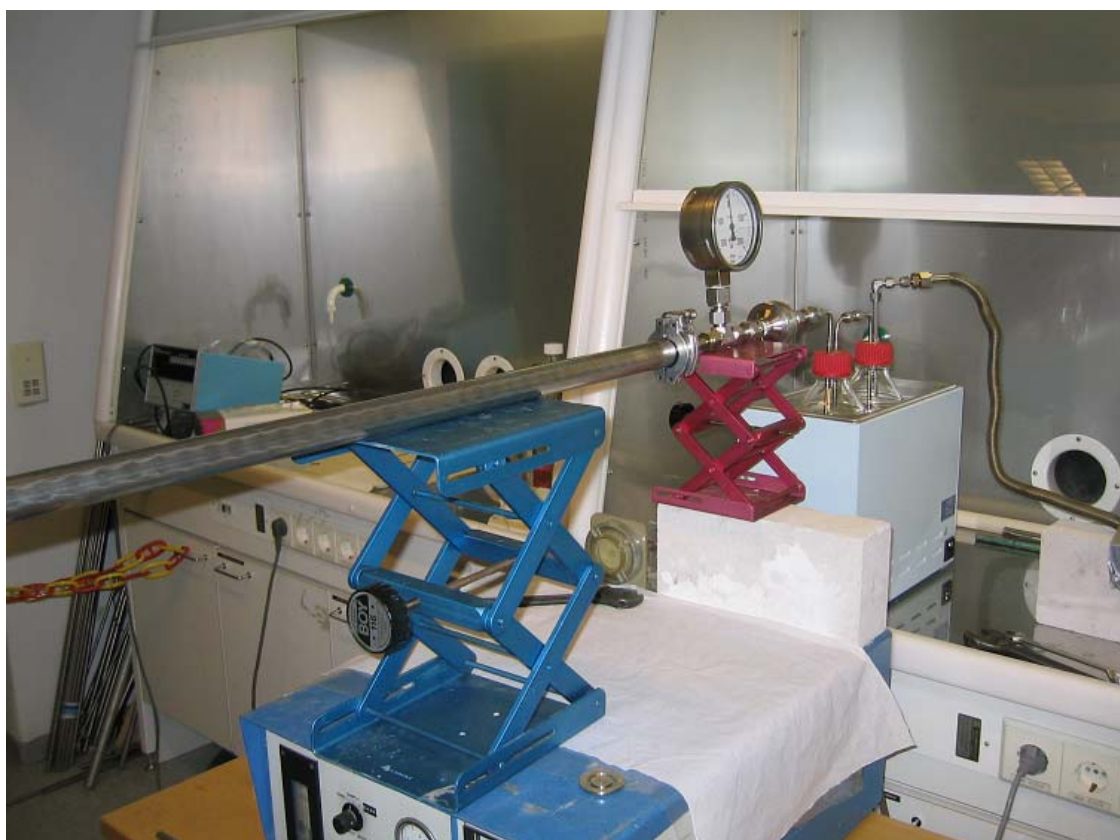


Figure 3: Photograph of experimental setup used in experiment #3.

Analysis of the trapping liquid and filters

The trapping and the tube washing solutions were heated on a sand bath and ethanol was added to reduce ruthenates to RuO₂. The precipitate from the trapping solution was centrifuged and washed twice with water before dissolving it in hot concentrated HCl. After dilution with deionised water Ru-concentration was analysed with ICP-MS. The precipitate that was lost with the solution in centrifugation was filtered and the filter paper analysed with INAA.

The precipitation from the tube washing solution was so small that the solution was filtered through a filter paper. The filter paper was analysed with INAA. The success of the precipitation was proved by analysing the filtered solutions by ICP-MS. The two filters from the experiments were analysed with INAA.

5. RESULTS

Four experiments have been carried out so far. The results are summarised in table 2. In the first experiments a mass balance of only about 40 % was achieved. It was assumed that the rest of the ruthenium remained on the walls of the system. In experiment #3 it was assured that the ruthenium that was missing in the previous experiments is indeed on the walls of the system. In figure 4 the distribution of Ru downstream of the evaporation crucible is shown. This measurement was done using radioactive tracer.

Table 2: Results of the experiments on the behaviour of Ru. Filter 1 is in main line and filter 2 is in sample line.

Experiment #		1	2	3	4
Tube material		SS	alumina	SS	SS
Duration of exp	[min]	60	45	42	20
Flow rate	[l/min] (NTP)	5	5	5	5
Release temp	[°C]	1227	1227	1227	1427
Ru total	[mg]	1117	814	1030	986
% of Ru					
left in crucible	%	31.6	34.4	40	31.3
bubbler	%	0.08	2.70	0.06	0.11
filter 1	%	1.97	6.42	7.11	17.0
filter 2	%	1.93	0.29		0.93
tube	%	6.57	0.91	30.1	10.8
Total	%	42.1	44.7	77.2	60.2

Using stainless steel tubing very little gaseous ruthenium reached the bubbler. This indicates that the gaseous ruthenium reacts more easily with stainless steel than with ceramic material. A major part of the gaseous ruthenium decomposed to RuO₂ in all experiments. Using a higher release temperature

somewhat more ruthenium reached the bubbler. Also more Ru was found on the filter than when using a lower release temperature. The bubbler liquid was colored yellow in the experiments as Ru is trapped (see figure 5).

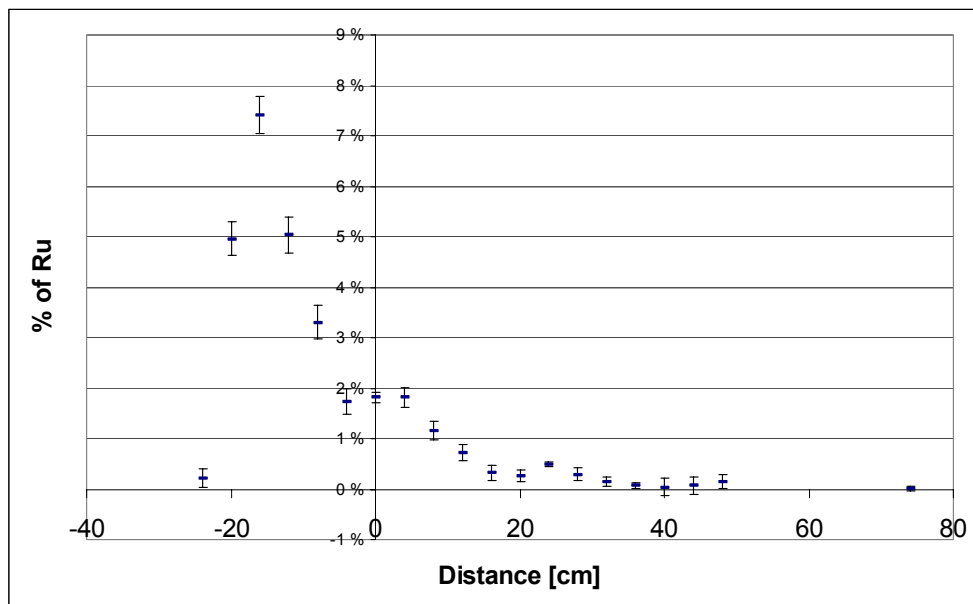


Figure 4: Distribution of Ru downstream of the evaporation crucible. The furnace ends at 0 and the release crucible is located at -25 - -45 cm.



Figure 5: Trapping liquid bottles.

When a release temperature of 1227°C was used the release rate of Ru was 0.15 mg/s. At a higher release temperature, 1427°C, the release rate was 0.42 mg/s.

RuO₂ particles were collected and analysed with the transmission electron microscope (TEM). Representative TEM images is presented in figure 6. From the figures we can see that the RuO₂ particles are needle-shaped and crystalline.

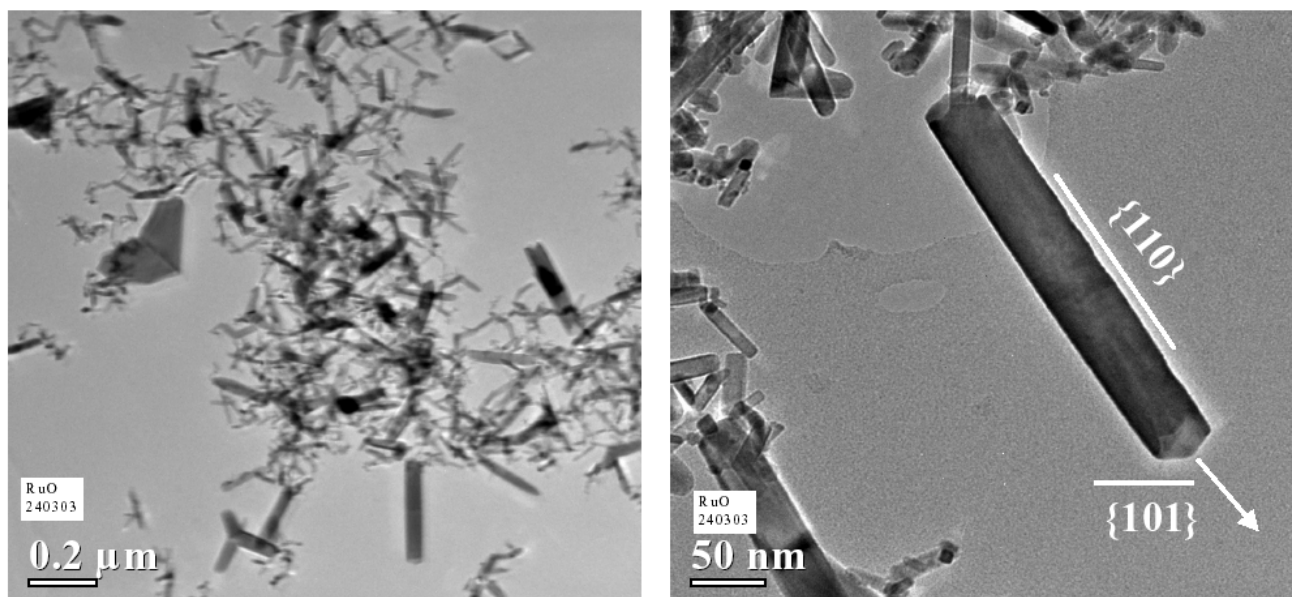


Figure 6: TEM images of RuO₂ particles.

The number size distribution of the particles was measured using a DMA/CNC combination. The number size distribution in all experiments were quite similar. A typical series of size distributions are presented in figure 7.

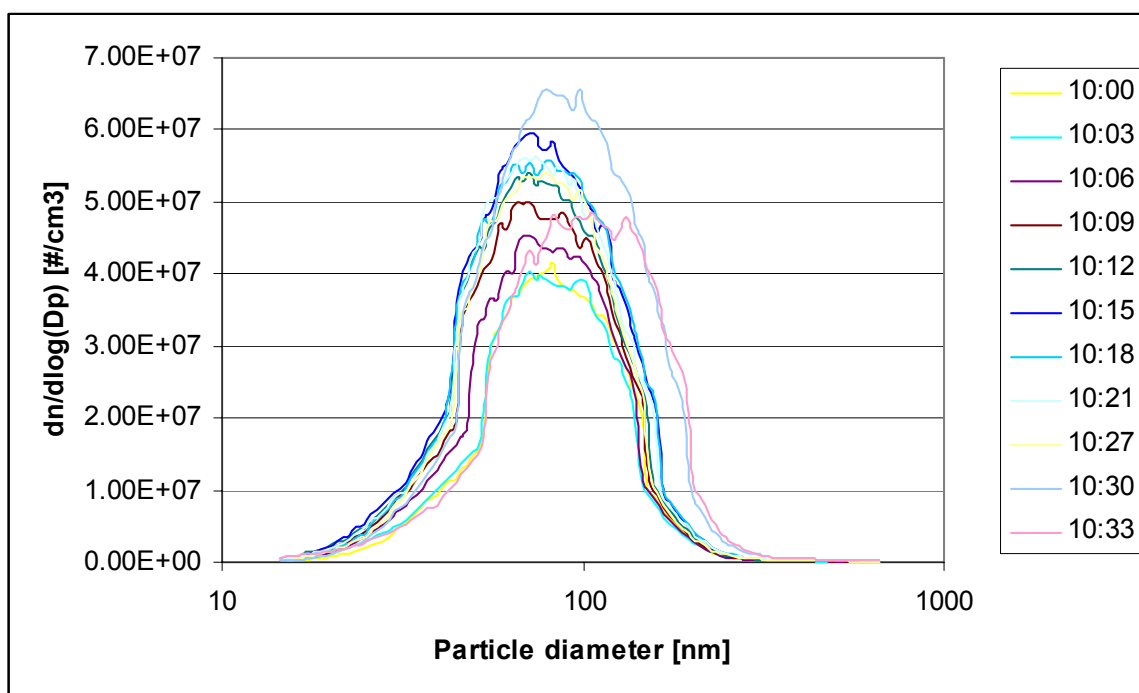


Figure 7: Typical number size distributions of RuO₂ particles (from experiment #2).

7. CONCLUSIONS

The methods for trapping and analysing RuO₄ has been studied. It was found that 1M NaOH is capable of trapping RuO₄ totally. The determination of Ru from the solution can be made using ICP-MS (inductively coupled plasma mass spectrometry). The filters were analysed using INAA.

In the experiments on the behaviour of ruthenium in oxidising conditions at high temperatures a significant difference in the decomposition rate of gaseous ruthenium depending on the tube material was found. This indicate that gaseous ruthenium reacts very easily with stainless steel. In all experiments only a minor fraction of Ru remained in gaseous form until the bubbler.

Using radioactive tracer we were able to reach a mass balance of about 77%. Most of it was on the walls of the system. In the decomposition needle-shaped RuO₂ crystallites were formed.

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