



**HAL**  
open science

## Volatilization and trapping of ruthenium under a loss of cooling accident on high level liquid waste (HLLW) storage tanks in reprocessing plants

Philippe Nerisson, Marc Barrachin, Laurent Cantrel, Marc Philippe

### ► To cite this version:

Philippe Nerisson, Marc Barrachin, Laurent Cantrel, Marc Philippe. Volatilization and trapping of ruthenium under a loss of cooling accident on high level liquid waste (HLLW) storage tanks in reprocessing plants. GLOBAL 2019 - International Nuclear Fuel Cycle Conference and TOP FUEL 2019 - Light Water Reactor Fuel Performance Conference, American Nuclear Society, Sep 2019, Seattle, United States. pp.659 - 667. irsn-04113171

**HAL Id: irsn-04113171**

**<https://irsn.hal.science/irsn-04113171>**

Submitted on 1 Jun 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

# VOLATILIZATION AND TRAPPING OF RUTHENIUM UNDER A LOSS OF COOLING ACCIDENT ON HIGH LEVEL LIQUID WASTE (HLLW) STORAGE TANKS IN REPROCESSING PLANTS

P. Nerisson<sup>1\*</sup>, M. Barrachin<sup>1</sup>, L. Cantrel<sup>1</sup> and M. Philippe<sup>2</sup>

*Institut de Radioprotection et de Sûreté nucléaire (IRSN)*

<sup>1</sup> BP 3, 13115 Saint-Paul-Lez-Durance Cedex, France

<sup>2</sup> BP 17, 92262 Fontenay-aux-Roses Cedex, France

\* [philippe.nerisson@irsn.fr](mailto:philippe.nerisson@irsn.fr)

*The reprocessing of spent nuclear fuel produces high level liquid waste (HLLW) consisting in concentrated nitric acid solutions containing fission products. Due to the decay heat, these solutions are stored in cooled tanks to prevent their evaporating, boiling and drying out. In case of a total loss of cooling, potential large releases of radioactive materials into the environment, especially volatile species derived from ruthenium, can happen. The loss-of-cooling accident on HLLW storage tanks is one of the accident scenarios identified as a very dreaded situation. An extensive literature review performed at IRSN confirms the rather limited amount of quantitative data on the behaviour of ruthenium in nitric acid solutions, especially on the mechanism of releases and the nature of released species. To go deeper in the understanding of the release process, several aspects, some of them partially studied in the past, have to be considered: ruthenium chemistry in a nitric acid medium characterized by the formation of nitrosyl ruthenium ion  $\text{RuNO}^{3+}$ ; behaviour of volatile ruthenium species in presence of steam, nitric acid vapour and nitrogen oxides (recombination, decomposition, etc.); transfer phenomena and stability of the different gaseous species containing ruthenium through the ventilation network. Subsequently, the efficiency and the performance of various trapping systems that can be used for mitigation (gas/liquid absorbers/traps, steel filters, porous media such as zeolites, MOFs, etc.), or even various means of preventing its volatilization (recombination, addition of reducing agents in situ, etc.) have been assessed by different authors. Previous experimental work performed at IRSN on severe accident scenarios in nuclear power plants allowed to characterize usual filtration devices such as active charcoals or metallic filters, with respect to gaseous  $\text{RuO}_4$ . It showed that these latter do not trap efficiently  $\text{RuO}_4(\text{g})$ .*

*From these findings, IRSN started a research program aiming at improving the knowledge on this topic. A specific test bench has been developed within IRSN experimental platform, in order to study the volatilization of a nitric acid solution containing Ru nitrosyl, simulating a real HLLW in terms of acidity and ruthenium concentration, and to investigate the possible inhibition of Ru volatilization by addition of specific reducing compounds (nitrogen oxides, sucrose, etc.). A first series of tests showed that the quantities of released ruthenium obtained for different temperature levels are consistent with the literature, before testing inhibitors. The experimental setup mentioned before dedicated to gaseous  $\text{RuO}_4$  is also used to study trapping of  $\text{RuO}_4(\text{g})$  by different porous materials: zeolites, rare earth oxides, etc. Decontamination factors (DF) and  $\text{RuO}_4(\text{g})$  retention capacity have been determined for several of these compounds.*

## INTRODUCTION

In the La Hague (France) reprocessing plants, after a period of radioactive decay in pools, the spent nuclear fuel assemblies undergo shearing and dissolution in hot nitric acid. The radionuclides present in the dissolver product solution are separated by solvent extraction (PUREX<sup>1</sup> process) in three types of products and effluents: uranium, plutonium and fission products with minor actinides (designated as FP solutions). FP solutions are concentrated then transferred in dedicated storage tanks (HLLW: high level liquid waste) for an additional radioactive decay time, before being incorporated in vitrified waste. The concentrated FP solutions exhibit a very high radioactivity associated with a considerable heat release (about 10 watts per litre for a PWR fuel irradiated to

---

<sup>1</sup> PUREX: Plutonium Uranium Refining by Extraction

33 000 MWday per ton and cooled for three years before reprocessing), thus the storage tanks need to be permanently cooled. Indeed, due to self-heating, a prolonged shutdown of the tank cooling system could cause the progressive evaporation of the FP solutions to dryness, and culminate in the formation of volatile species of ruthenium and their release in the tank venting circuit up to the environment.

The cooling systems are designed and maintained to perform their function with a very high level of reliability, so that a tank cooling system failure is extremely improbable. The assessment of the consequences of such an occurrence was nevertheless conducted in the design stage (1980s) as part of the safety demonstration of the La Hague plants, especially in order to determine the time interval after which a substantial release of radioactive materials could take place and to evaluate the effectiveness of the measures planned in the on-site emergency plan to get such a situation under control [1]. Nevertheless, this assessment presents several limitations. Firstly, it is based on incomplete data resulting of few studies on the behaviour of the different forms of volatilized ruthenium, the reaction mechanisms in air/H<sub>2</sub>O/HNO<sub>3</sub>/NO<sub>x</sub> medium, the transport behaviour of these materials and the ruthenium chemistry on the basis of local conditions and compositions of gaseous phases. This experimental database, rather limited, needs to be updated by taking into account the more recent results. Secondly, there are uncertainties on modelling calculations as a result of the assumptions adopted for transfer coefficients calculations (air flow, relative humidity, emission rate, size and concentration of aerosols, flow mode, diffusion, sedimentation, etc.). This confirms the need of reassessing the source term and transport behaviour of volatile ruthenium under a total loss of cooling of FP storage tanks accident.

These initial studies have been then reconsidered in the framework of the post-Fukushima complementary safety assessments and the first periodic safety reviews of the La Hague plants, by considering the recent knowledge acquired on this subject, especially in Japan [2].

The behaviour of ruthenium in nitric acid solution has been studied for several decades, focusing on the main following topics:

- general information on ruthenium chemistry in a nitric medium, mechanisms

for the formation of ruthenium tetroxide RuO<sub>4</sub>;

- behaviour of volatile forms of ruthenium in presence of steam, nitric acid and nitrogen oxides (recombination, decomposition, etc.);
- transfer phenomena of the different gaseous ruthenium species, solid or liquid species formed, taking into account the conditions of the considered accidental scenario.

Subsequently, the efficiency and the performance of various filtering systems (gas/liquid absorbers, steel filters, etc.), or even means to prevent the ruthenium volatilization (recombination, addition of reducing agents *in situ*, etc.) have been investigated by different research teams, taking into account the physical and chemical forms expected of this element.

Thus, the literature review performed by IRSN has allowed identifying several areas where additional R&D work is necessary. These areas are listed thereafter:

1. ruthenium chemistry in nitric acid solution;
2. ruthenium chemistry in gaseous phase;
3. volatilization of Ru from nitric solution, means of prevention to avoid ruthenium release;
4. transfer of ruthenium volatile compounds.

After a synthesis of the literature review, the present paper focuses on experimental work performed related to point 3 above.

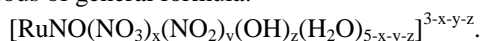
## SYNTHESIS OF LITERATURE REVIEW

### *Ruthenium chemistry in nitric acid solution*

First of all, the chemical equilibrium of nitric acid is rather difficult to study, since including many redox reactions. Besides, if a nitric acid solution is subjected to  $\gamma$  radiation, new radical species may appear in solution under the effect of water and nitric acid radiolysis (H $\cdot$ , HO $\cdot$ , NO<sub>3</sub> $\cdot$ ). These compounds are likely to form secondary harmful species, mainly H<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> [3] [4].

Chemistry of ruthenium in concentrated nitric acid solution ( $10^{-2}\text{M} \leq [\text{HNO}_3] \leq \approx 10\text{M}$  within process streams,  $\approx 2\text{M}$  in HLLW) is very complex, with a potential coexistence of numerous chemical species, especially complex ions. It is mainly characterized by the formation of nitrosyl ruthenium ion (RuNO<sup>3+</sup>), relatively stable. It

consists of a  $\text{Ru}^{2+}$  complex bound with a nitrosonium ion ( $\text{NO}^+$ ). Moreover,  $\text{RuNO}^{3+}$  can form octahedral complexes either nitrated (linker  $\text{NO}^3$ ), nitrous (linker  $\text{NO}^{2-}$ ) or mixed nitrated-nitrous of general formula:



Among these chemical species, nitrated nitrosyl ruthenium complexes have been specifically studied since they are assumed to be responsible for the difficulties in the fission products decontamination of the uranium and plutonium stream [3]. Their general formula is as follows:



Thus, a large diversity of nitrated nitrosyl ruthenium isomers can potentially exist in such solutions [3]. Among these complexes, the predominance of one or more species mainly depends on the concentration of nitric acid and nitrate ions.

In addition to these varied complex ions, minor forms of ruthenium can be found in nitric acid:

- soluble species:
  - soluble oxides, mainly Ru(VIII) in  $\text{H}_2\text{RuO}_5$  i.e. hydrated form of  $\text{RuO}_4$ ;
  - Ru(IV) in ion  $\text{Ru}_4\text{O}_6^{4+} \cdot x\text{H}_2\text{O}$ , from the reduction of Ru(VIII);
- insoluble species:
  - Ru(0) in metallic ruthenium;
  - Ru(IV) in ruthenium dioxide  $\text{RuO}_2$ .

Literature mentions works using high performance liquid chromatography to separate ruthenium species in nitric solution [5], and also UV-Visible spectroscopy to identify ruthenium nitrosyl nitrate [6]. The latter gives significant results only for high concentration of  $\text{HNO}_3$  (>5M).

### ***Ruthenium chemistry in gaseous phase***

The ruthenium species supposed to distil from the nitric acid solutions is  $\text{RuO}_4(\text{g})$ . This assumption is made according to the fact that ruthenium is known to mainly vaporize under this form at low temperatures (below 200°C). Indeed, Nikol'skii [7] determined the vapour pressure above condensed  $\text{RuO}_4$  between 0°C and 91°C, the boiling point being at 130°C according to Koda [8] by assuming a congruent vaporization. In steam conditions, it was recently shown at IRSN by Miradji et al. [9], from thermodynamic equilibrium calculations based on thermodynamic properties of the gaseous species in the Ru-O-H system

calculated by quantum chemistry, that the  $\text{RuO}_2(\text{OH})$  gaseous hydroxide would be favoured at temperature below 1000 K but with pressures well below  $\text{RuO}_4(\text{g})$  pressure. However the composition of the vapour phase above a prototypic waste solution in evaporating/boiling conditions remains largely unknown for different reasons. First of all, the ruthenium release from nitric acid solutions has been mainly investigated up to now by analysing the condensed distillate and such an approach is not really appropriate to identify the speciation of the gas phase. Another reason is linked with the instability of gaseous ruthenium tetroxide, regarding the  $\text{RuO}_2 + \text{O}_2(\text{g})$  decomposition and its high reactivity with surfaces [10] [11] [12] [13] [14]. It is consequently difficult to separate the respective effects of the spontaneous decomposition of  $\text{RuO}_4(\text{g})$  and/or its interaction with surfaces from its interaction with the other gases released from the solution.

An extensive study of ruthenium chemistry in the gas phase was performed by Brittain et al. [15] who used a Knudsen cell coupled to a mass spectrometer in order to assess the impact of  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{NO}$  and  $\text{NO}_2$  on the  $\text{RuO}_4$  vapour pressure between 25°C and 130°C. The main conclusion is that it was never possible to detect other ruthenium gaseous species than  $\text{RuO}_4$  in the presence of the species mentioned above. More precisely, these experiments showed that in the presence of  $\text{NO}$  or  $\text{NO}_2$ , the pressure of  $\text{RuO}_4$  tends to decrease whereas, for its part, the presence of  $\text{N}_2\text{O}$  has no effect. The addition of steam alone leads to a decrease in the  $\text{RuO}_4$  vapour pressure (but to a lesser extent than in  $\text{NO}$  or  $\text{NO}_2$ ) but Brittain indicated that the effect is not reproducible. The addition of  $\text{HNO}_3$  was also evaluated, in a  $\text{NO}_2 + \text{H}_2\text{O}$  atmosphere (equal proportions) with addition of 10% of  $\text{HNO}_3$ . The experiment shows that the reduction of the  $\text{RuO}_4$  signal is of the same amplitude as that observed in the presence of  $\text{NO}_2$  alone. The influence of the temperature is significant on the pressure of  $\text{RuO}_4$  since between 293 and 403 K, the signal decreases by 20% to disappear at 463 K.

Recent studies carried out in a Knudsen effusion cell coupled with a mass spectrometer consisted in a sublimation of a sample prepared from a nitric acid solution, containing  $\text{Ru}(\text{NO})(\text{NO}_3)_3$  dried to 80°C [16]. The sample was then continuously heated up to 480°C. The registered spectrum shows the presence of  $\text{RuO}_4(\text{g})$  between 117°C and 227°C with a maximum at

167°C. The intensity ratios for Ru, RuO, RuO<sub>2</sub> and RuO<sub>3</sub> to RuO<sub>4</sub> (Table 2 in [16]) are significantly higher than those reported by Dillar (Table 1 in [17]) obtained from sublimation of a RuO<sub>4</sub>(c) sample for a similar ionization potential, likely indicating a possible interaction between NO<sub>x</sub> (or other) molecules. In their interpretation, the authors [16] assumed the existence of monatomic oxygen in the gas phase able to promote the formation of RuO<sub>4</sub>(g) from oxidation of Ru(NO)(NO<sub>3</sub>)<sub>3</sub> on the basis of the observation of the O<sup>+</sup> ion pic in the experimental spectrum.

#### ***Volatilization of Ru from nitric acid solutions and means of preventing ruthenium release***

Various experiments related to ruthenium in a nitric acid solution are available in the literature, regarding both ruthenium volatilization rate and trapping efficiency of different methods [4] [5] [18] [19] [20] [21], which can be roughly separated in two main categories:

- gas phase trapping of ruthenium (*a priori* in the RuO<sub>4</sub> form) already volatilized;
- *in situ* trapping in nitric acid solution, by addition of a specific reducing chemical compound, inhibiting the volatilization of ruthenium species from aqueous phase.

#### ***Volatilization of Ru and in situ trapping in nitric solution***

Sato and Motoki [5] focus on the trapping of ruthenium species in real waste nitric solution by means of a decontamination column. The decontamination column consisted of different mixtures of zinc, graphite and active charcoals. Tests carried out with decontamination columns, containing, on the one hand a zinc-active charcoal mixture, on the other hand a zinc-graphite mixture followed by a second purification performed six months later with only activated carbon, put in evidence a good efficiency in terms of ruthenium retention. Indeed, the obtained DFs (Decontamination Factors) were respectively greater than 6500 and 3650~7300 (global DF). Conversely, columns with a zinc-graphite mixture alone and active charcoal alone showed much less efficient purification of Ru ( $5 \leq DF \leq 10$ ), whereas zinc alone seemed to be worse ( $1 \leq DF \leq 2$ ). These results show that pouring the solution in the zinc-graphite mixture transforms the initial ruthenium species into compounds more easily adsorbed on the activated carbon alone.

In the same way, Ishio et al. [18] and Sawada et al. [19] assessed the volatilization rate of Ru in solutions containing fission products and the effect of sucrose addition on these rates. Ishio et al. [18] used 3 mL of a genuine HLLW sample, called high active concentrate (HAC) derived from a liquid waste of the PUREX process. No decrease in the release of ruthenium if the molar ratio  $C_{12}H_{22}O_{11}/HNO_3 = 1/48$  (4% Ru released) was observed, but an important decrease with a sufficient addition of sucrose (i.e. 0.16% Ru released if the molar ratio  $C_{12}H_{22}O_{11}/HNO_3 = 1/24$ , and 0.03% Ru released if the molar ratio  $C_{12}H_{22}O_{11}/HNO_3 = 1/12$ ). This decrease in Ru release is likely due to the decomposition of HNO<sub>3</sub> by sucrose (denitration), leading to the formation of reducing agents such as nitrite ions. The oxidation of Ru by HNO<sub>3</sub> is then inhibited. Sawada et al. [19] also mention the effect sucrose limiting the Ru release, in a study dealing with the influence of sodium nitrate NaNO<sub>3</sub> in a nitric solution of fission products. Tests with sucrose addition in a surrogate HLLW carried out at 180°C showed that, as mentioned before by Ishio et al. [18], sucrose addition appreciably reduces the amounts of Ru released, from 1.33% to 0.11% without NaNO<sub>3</sub> and from 1.71% to 0.18% with NaNO<sub>3</sub>. The explanation proposed by Ishio et al. is also assumed, namely a significant decomposition of HNO<sub>3</sub> by sucrose.

Another way for trapping Ru is the separation by electro-volatilization [4]. The industrial implementation of this method would reduce the purification operations by first eliminating Ru from the dissolution liquors before separation steps of the PUREX process, and thus avoid the addition of chemical species in the nitric solution. The experimental results of the Mousset's study show that electro-volatilization yields obtained depend on many parameters, such as the nature of the nitric solution (real fuel dissolution solution or RuNO<sub>3</sub><sup>3+</sup> commercial solution) and the equipment used for electro-volatilization. For example, the elimination efficiency of Ru from a solution with  $[RuNO_3^{3+}] = 5.10^{-3} \text{ mol.L}^{-1}$  and  $[HNO_3] = 3M$  is about 50% after 18 min.

#### ***Gas phase trapping of ruthenium:***

Igarashi et al. [20] performed tests of ruthenium absorption in water, in order to evaluate the influence of the presence of nitrogen oxides (NO and NO<sub>2</sub>) on the absorbed quantities. When NO or NO<sub>2</sub> concentration increases in the gas flow, quantities of gaseous Ru appreciably decrease.

Analyses performed to determine the nature of ruthenium species trapped in the experimental device suggest that this phenomenon may be due to RuO<sub>4</sub> transformation into nitrated nitrosyl ruthenium complexes, less volatile and more absorbable into water. Thus, RuO<sub>4</sub> trapping is better with NO<sub>x</sub> injection in presence of water.

In the context of spent nuclear fuel reprocessing, Kepak et al. [21] tested trapping efficiency of porous materials with regard to RuO<sub>4</sub>. The main collected data are breakthrough curves of gaseous RuO<sub>4</sub> in a compound derived from zeolite, for several experimental configurations (temperature, duration, etc.).

### ***Transfer of ruthenium volatile compounds***

Literature review does not provide much information about ruthenium transport, deposition (under RuO<sub>2</sub> form for example) and its possible resuspension during accidental situation in nuclear facilities, especially in ventilation ducts, in a scenario without trapping devices. Yoshida et al. [22] performed experiments to evaluate the migration behaviour of RuO<sub>4</sub> in different conditions, assumed to be representative of a loss of cooling accident scenario in terms of temperature and gas composition (air, HNO<sub>3</sub> and steam). They highlighted an influence of gas composition: a majority of Ru is deposited in the experimental duct in conditions of dry air (penetrating fraction about 0,5%), whereas a majority is deposited in air + steam conditions (penetrating fraction about 22%). On the contrary, there is nearly no deposition in air + steam + HNO<sub>3</sub> gas composition (penetrating fraction >99%). This point is important for nuclear safety, notably in terms of radiological protection (accumulation of radioactive Ru deposit in specific areas) and reassessment of the source term released at the main stack of the plant.

## **MATERIAL AND METHODS**

### ***Volatilization of Ru from nitric solutions and in-situ trapping of Ru:***

The objective is to study the ruthenium release, resulting from the heating of a nitric solution containing dissolved ruthenium, with or without additional compound assumed to inhibit its volatilization. Thus, to quantify a potential RuO<sub>4</sub>(g) release from a simplified analytical solution containing ruthenium, representative in terms of acidity and temperature of real HLLW, the experimental setup shown in Figure 1 is considered.

The reactor and the outlet line present a controlled and homogeneous heating device (liquid bath or heating cords according to the configuration test), in order to set a fixed temperature or impose a heating ramp. The initial acidity of the nitric solution is fixed for each test in the range  $1M \leq [HNO_3] \leq 5M$ . Its evolution can be monitored by a pH electrode, as well as redox potential with a specific electrode. The upper-vapour phase of the reactor is continuously swept away by a controlled argon flow, in order to optimize the gas outlet and the bubbling downstream the reactor, up to a potential drying out of the solution.

The entire flow is finally directed to a vapor condenser and then to NaOH bubblers, in order to trap Ru species in aqueous phase, especially RuO<sub>4</sub>(g) dissolving as perruthenate (RuO<sub>4</sub><sup>-</sup>) and/or ruthenate (RuO<sub>4</sub><sup>2-</sup>) in bubblers.

Periodic samplings in the condenser and in the bubblers allow determining Ru quantities trapped at these stages, according to ICP-AES analysis and/or UV-visible spectrometry. An outlet filter is located downstream from the bubblers to trap any compounds in aerosol form.

The difference between quantities of Ru trapped in condenser and bubblers with or without addition of a specific compound (solid or liquid) in the reactor can provide information about the volatilization rate (ratio of Ru released) and the absorption/inhibition efficiency of the compound added. The compounds to be tested in order to assess their potentiality in terms of ruthenium trapping are reducing agents, porous materials, etc...

### ***RuO<sub>4</sub> trapping in gaseous phase:***

The SAFARI<sup>2</sup> test bench has been developed at IRSN for the characterization of RuO<sub>4</sub> retention by different devices, notably the French PWR containment depressurization line devices, namely the sand filter and the metallic prefilter, in the frame of MiRE project<sup>3</sup> [23]. Figure 2 shows an outline of this test bench. This experimental device is subdivided into three modules whose functions are the generation, the filtration and the trapping of gaseous RuO<sub>4</sub> for analysis:

- RuO<sub>4</sub>(g) is generated by oxidation of RuO<sub>2</sub> commercial powder by ozone;

<sup>2</sup> SAFARI: meaSurement of filtrAtion eFFiciency of mARterial with regard to Ruthenium or Iodine

<sup>3</sup> MiRE : Mitigation of outside releases in case of nuclear accident;

- the gas flow is then directed to the filtration module. The filtering medium to characterize for ruthenium tetroxide trapping is located in a glass column. Parameters such as gas flow, temperature, relative humidity (RH) are fitted to be as representative as possible of the studied accidental condition;
- bubblers with NaOH are used for the same function as on the test bench used for Ru

volatilization in  $\text{HNO}_3$  (see Figure 1), i.e. trapping  $\text{RuO}_4$  for ICP-AES and UV-Visible subsequent analysis.

For a filter device tested on SAFARI, these Ru analysis allow to estimate its decontamination factor vs  $\text{RuO}_4$  (DF) and also its  $\text{RuO}_4$  retention capacity.

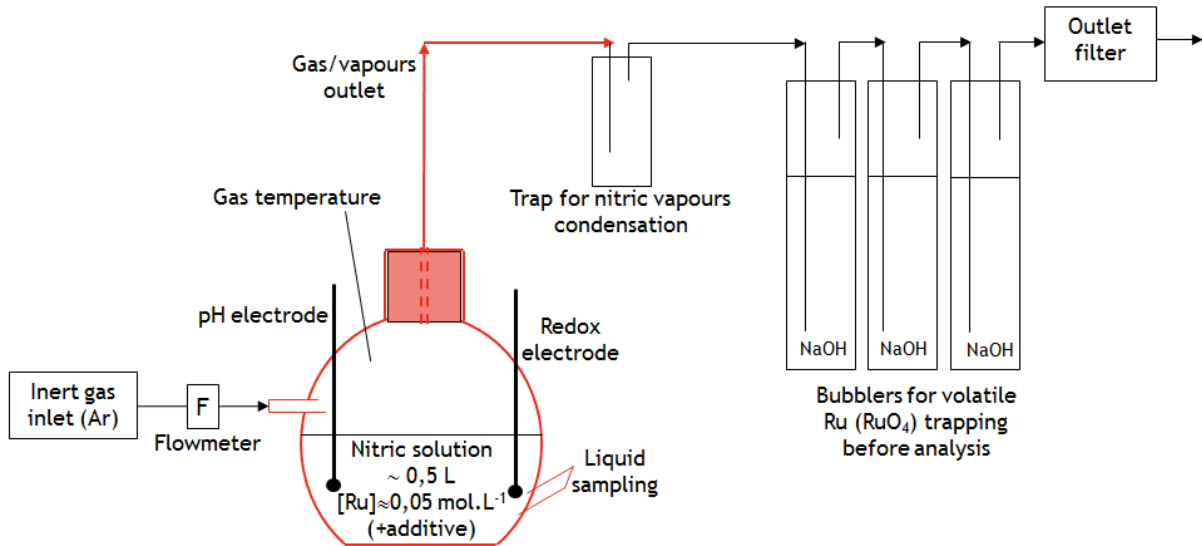


Figure 1: Schematic outline of the experimental test bench designed for characterization of Ru in  $\text{HNO}_3$  solution

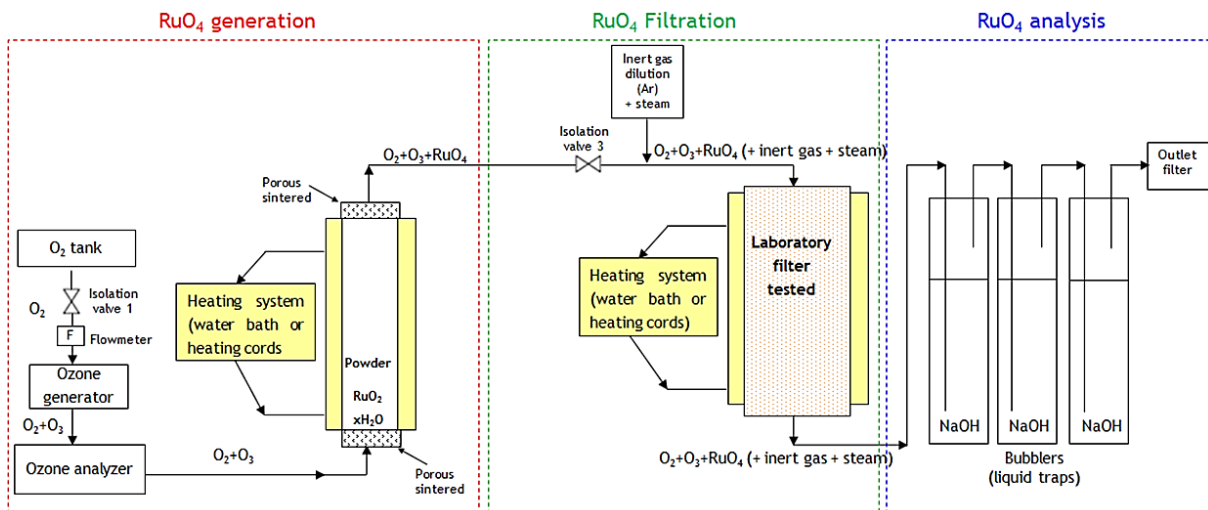


Figure 2: Schematic outline of SAFARI test bench, dedicated to  $\text{RuO}_4$  generation and filtration [23]

## RESULTS AND DISCUSSION

### *Volatilization of Ru from nitric solutions:*

A first series of experiments has been performed with a simplified simulated HLLW, i.e. a nitric solution containing ruthenium nitrosyl nitrate commercially available. Ru concentration and acidity of the initial solution have been determined according to the characteristics of the Ishio et al. experiments [18], namely  $[\text{HNO}_3] = 3.25\text{M}$  and  $[\text{Ru}] = 0.02\text{M}$ . Table 1 shows results obtained for volatilization rates of Ru contained in 700 mL of initial solution.

**Table 1: Ru volatilization from  $\text{HNO}_3$  solution.  $[\text{HNO}_3] = 3.25\text{M}$ ;  $[\text{Ru}] = 0.02\text{M}$**

Temperature of heating fluid	Ratio of initial Ru released after a 6H30 test ( $\pm 12\%$ )	Ratio of initial Ru released after drying (test continued the next day, $\pm 12\%$ )
$\leq 100^\circ\text{C}$	$\leq 0.022\%$	-
$100^\circ\text{C}$	0.04%	-
$110^\circ\text{C}$	0.16%	-
$120^\circ\text{C}$	0.38%	1.62%
$130^\circ\text{C}$	2.03%	2.31%

Results reported in Table 1 are consistent with values obtained by Ishio et al. [18], with 3 mL of genuine HLLW. The test bench proposed is thus validated and operational for such experiments of Ru volatilization. Besides, it allows studying this volatilization/inhibition with more important volumes of nitric solution than Ishio et al. device, which could be interesting eventually for more representative kinetic considerations.

### *$\text{RuO}_4$ trapping in gaseous phase:*

Several porous materials have been tested on SAFARI test bench, with the objective of gaseous  $\text{RuO}_4$  trapping. To perform these tests, operating conditions are dry gas ( $\text{RH} = 0\%$ , no steam injection) and temperature maintained at  $50^\circ\text{C}$ . This temperature is assumed to be enough low to avoid thermal decomposition of  $\text{RuO}_4(\text{g})$  into solid ruthenium dioxide  $\text{RuO}_2$ , usually observed while performing tests above  $100^\circ\text{C}$  [23]. Gas flows are controlled to obtain a filtration velocity about 10 cm/s. Values of decontamination factors obtained, calculated as  $\text{DF} = [\text{RuO}_4]_{\text{upstream filter}} / [\text{RuO}_4]_{\text{downstream filter}}$ , are reported in Table 2.

**Table 2: Gaseous  $\text{RuO}_4$  trapping in porous materials**

Test	Name of compound $\approx 4$ cm beds	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Description	DF vs $\text{RuO}_4(\text{g})$ after 1h ( $\pm 17\%$ )
1	Zeolite Y, Hydrogen	730	Si/Al = 2.5	4
2	Zeolite Y, Ammonium	925	Si/Al = 2.5	4
3	Commercial Zeolite Ag/13X (35%)	369	Si/Al = 1.5	2
4	Standard silica			2
5	Organo-modified silica 1			100
6	Organo-modified silica 2			350
7	Rare earth oxide 1			70
8	Rare earth oxide 2			350
9	Carbon Pleisch	1213	91.4% C – Impregnated with TEDA ( $\text{wt}\% \leq 3$ )	2
10	Carbon Pica not impregnated	1128	91.9% C	2



According to Table 2, tests with zeolites, standard silica or active charcoals, show no significant retention of gaseous RuO<sub>4</sub> (DF ≤ 4 after 1 h of test). On the other hand, some retention of RuO<sub>4</sub>(g) is observed with organo-modified silica and rare earth oxides (70 ≤ DF ≤ 350). Thereafter, a test has been performed with compound n°6, with a thicker bed (≈1 cm). In this configuration, a breakthrough of RuO<sub>4</sub> in the filter is obtained after 25 min of test. It allows to estimate the retention capacity of RuO<sub>4</sub> by the compound, which is about 0.5 g<sub>(RuO<sub>4</sub>)</sub>/g<sub>(compound n°6)</sub>.

## CONCLUSION AND OUTLOOK

In nitric acid solution, literature review shows that chemical properties of ruthenium nitrosyl ion lead to the potential formation of a very large variety of nitrated, nitrous or mixed complexes, whose speciation mainly depends on the acidity and the temperature of the solution. That explains why the accurate inventory of ruthenium species in HLLW storage tanks is difficult to establish. Two kinds of methods are identified in the literature for trapping volatile ruthenium from a nitric solution: *in situ* trapping in nitric solution by addition of a chemical compound inhibiting volatilization of ruthenium species on the one hand, and gas phase trapping for Ru already volatilized on the other hand. Most of these methods have been proved to have significant efficiencies (*in situ* methods in particular). On a basis of a literature survey, IRSN started a R&D program to improve knowledge on these topics. It mainly concerns a qualitative and quantitative characterization of trapping devices, both and in a nitric acid solution and in the gas phase. The first series of tests presented in this paper confirm the vaporization rates of Ru available in the literature. Besides, porous compounds such as organo-modified silica or rare earth oxides present an interesting filtration capacity of gaseous RuO<sub>4</sub>. New series of experiments are currently performed on the two test benches presented in this paper: vaporization of Ru-HNO<sub>3</sub> solution, notably with additives (sucrose, ascorbic acid,...) to evaluate inhibition of gaseous Ru formation, and tests of various porous materials with regard to RuO<sub>4</sub> in different configurations (temperature, RH, gas flow composition).

In parallel, improving the knowledge of thermodynamic properties of the gaseous species is foreseen. For this, different ways could be investigated, such as *ab-initio* calculations to determine thermodynamic properties of condensed

RuO<sub>4</sub>; detailed study of the gaseous phase speciation (RuO<sub>4</sub>(g), nitrates, hydrated compounds...) above dried samples prepared from nitric acid solutions by Knudsen effusion cell spectrometry; tests in open-flow reactor [24] to study chemical reactivity between RuO<sub>4</sub> and mixtures of various gaseous species, including NO<sub>x</sub>. Later on, possible investigations on ruthenium transfer, deposition and its remobilisation could be carried out in such reactor, linked to MEB or XPS surface analyses.

The final objective in the next years is to adapt the SOPHAEROS module of ASTEC code<sup>4</sup> to the issue related to ruthenium release in accident conditions in reprocessing plants.

## REFERENCES

- [1] Mercier J.P. & al., “An example of R&D on safety assessment: study of a prolonged loss of cooling of HALW (beyond design accident)”, Institut de Protection et de Sûreté Nucléaire, OECD/NEA/CSNI Specialist meeting on safety and risk assessment in fuel cycle facilities, Tokyo, Japan, October 1991
- [2] Yoshida N. & al., “Experimental Evaluation of Release and Transport Behavior of Gaseous Ruthenium under Boiling Accident in Reprocessing Plant”, Japan Atomic Energy Agency, CSNI Workshop on Developments in Fuel Cycle Facilities (FCFs) after the Fukushima Daiichi Nuclear Power Station (NPS) Accident, Aomori City, Japan, 15-18 November 2016
- [3] Carron V., “Étude du mécanisme d’oxydation des formes dissoutes du ruthénium dans les solutions d’acide nitrique”, PhD thesis report, Université de Grenoble I, France, December 2000
- [4] Mousset, F., “Électro-volatilisation du ruthénium en milieu nitrique – Influences de la nature des formes chimiques du ruthénium et de la composition des solutions modèles de dissolution”, PhD thesis report, Université

<sup>4</sup> The ASTEC code developed by IRSN is the European reference code for severe accident simulations in Pressurised Water Reactors. Among large number of functionalities, the ASTEC lumped-parameter code can compute thermal-hydraulic conditions, fission product transport and chemistry in reactor coolant systems (RCS) and in the containment. The SOPHAEROS module of ASTEC is based on modelling using control volumes. In each control volume, it can compute vapour speciation assuming a thermodynamic equilibrium.

- Pierre et Marie Curie - Paris VI, France, december 2004
- [5] Sato, T., Motoki, R., "Chemical species of ruthenium in radioactive aqueous waste and decontamination mechanism of ruthenium with zinc-charcoal mixed column", *Radiochimica Acta* 48, pp 101-113, 1989
- [6] Richards J.M. and Mincher B.J., "Selective Partitioning of Ruthenium from Nitric Acid Media," *Solvent Extraction and Ion Exchange*, vol. 35, no. 1, pp. 49-60, 2017
- [7] Nikol'skii, A.B., "Saturated Vapour Pressure of Ruthenium Tetroxide", *Russ. J. Inorg. Chem.*, (Engl. Transl.) 8(5) 541-543, 1963
- [8] Koda, Y., "Boiling Points and Ideal Solutions of Ruthenium and Osmium Tetraoxides", *J. Chem. Soc., Chem. Com.* 17 1347-1348, 1986
- [9] Miradji, F., Virost, F., Souvi, S., Cantrel, L., Louis, F., Vallet, V., "Thermochemistry of ruthenium oxyhydroxyde species and their impact on volatile speciations in severe nuclear accident conditions", *The Journal of Physical Chemistry A* 210 606, 2016
- [10] Mun, C., Cantrel, L. and Madic, C., "Study of RuO<sub>4</sub> Decomposition in Dry and Moist Air", *Radiochimica Acta* 95(11), pp 643-656, 2007
- [11] Cains, P.W. and Barnes, S.J., "Deposition of Volatilized Ruthenium on Stainless Steels", *Journal of Nuclear Materials* 186 83-86, 1991
- [12] Sakurai, T., Hinatsu, Y., Takahashi, A. and Fujisawa, G., "Adsorption of Ruthenium Tetroxide on Metal Surface", *Journal of Physical Chemistry* 89 1892-1896, 1985
- [13] Sakurai, T., Takahashi, A. and Fujisawa, G., "Interaction of Ruthenium Tetroxide with Stainless Steel", *Journal of Nuclear Science and Technology* 20 81-83, 1983
- [14] Eichler, B., Zude, F., Fan, W., Trautmann, N. and Herrmann, G., "Volatilization and Deposition of Ruthenium Oxides in a Temperature Gradient", *Radiochimica Acta* 56 133-140, 1992
- [15] Brittain, R.D. and Hildenbrand, D.L., "Gas Phase Reactions of Ruthenium Tetroxide with Nitrogen Oxides", DOE, Report DOE/SR/00001-T120, 1985
- [16] Kato, T., Usami, T., Tsukada, T., Shibata, Y. and Kodama, T., "Study on volatilization mechanism of ruthenium tetroxide from nitrosyl ruthenium nitrate by using mass spectrometer", *Journal of Nuclear Materials* 479 123-129, 2016
- [17] Dillard, J.G. and Kiser, R.W., "Ionization and Dissociation of Ruthenium and Osmium Tetraoxides", *Journal of Physical Chemistry*, vol 69, n°11, 3893-3897, 1965
- [18] Ishio, T., Shibata, Y., Kodama, T., Kato, T., Tsukada, T., Serrano-Purroy, D., Glatz, J.-P., "Study on radioactive material transport behavior from boiling/drying out high level liquid waste", *Proceedings of Global 2015*, September 20-24, 2015, Paris, paper 5164, pp 1069-1075, 2015
- [19] Sawada, K., Ueda, Y. and Enokida, Y., "Ruthenium release from thermally overheated nitric acid solution containing ruthenium nitrosyl nitrate and sodium nitrate to solidify", *5th International ATALANTE Conference on Nuclear Chemistry for Sustainable Fuel Cycles. Procedia Chemistry* 21 pp 82-86, 2016
- [20] Igarashi, H., Kato, K., Takahashi, T., "Absorption behaviour of gaseous ruthenium into water", *Radiochimica Acta* 57, pp 51-55, 1992
- [21] Kepak F., Koutova S., Kocirik M., Zikanova A., "Removal of RuO<sub>4</sub> vapors on natural clinoptilolite". *Journal of Radioanalytical and Nuclear Chemistry*, VoL 159, No. 2 317-334, 1992
- [22] Yoshida N., Ohno T., Amano Y. and Abe H., "Migration behavior of gaseous ruthenium tetroxide under boiling and drying accident condition in reprocessing plant". *Journal of Nuclear Science and Technology*, 55:6, 599-604, 2018
- [23] Nerisson, P., Hu, H., Paul, J.-F., Cantrel, L., Vesin, C., "Filtration tests of gaseous ruthenium tetroxide by sand bed and metallic filters". *Journal of Radioanalytical and Nuclear Chemistry* 321:591-598, 2019
- [24] Ohnet MN, Leroy O, Mamede AS, "Ruthenium behavior in the reactor cooling system in case of a PWR severe accident". *Journal of Radioanalytical and Nuclear Chemistry* 316:161-177, 2018