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SYSTEM OF HLLW STORAGE TANKS

PHILIPPE M.- MERCIER J.P.- GUE J.P.  
CEA Centre d'Etudes Nucleaires de Fontenay-aux-Roses, 92 (FR)

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# BEHAVIOR OF RUTHENIUM IN THE CASE OF SHUTDOWN OF THE COOLING SYSTEM OF HLLW STORAGE TANKS

M. Philippe<sup>1</sup>, J.P. Mercier<sup>2</sup> and J.P. Gué<sup>1</sup>

<sup>1</sup>Division du Cycle de Combustible  
<sup>2</sup>Institut de Protection et Sûreté Nucléaire

Commissariat à l'Energie Atomique  
Centre d'Etudes Nucléaires  
Boîte Postale 6  
92265 FONTENAY AUX ROSES  
France

## Abstract

The consequences of the failure of the cooling system of fission product storage tanks over a variable period were investigated as part of the safety analysis of the La Hague spent fuel reprocessing plant. Due to the considerable heat release, induced by the fission products, a prolonged shutdown of the tank cooling system could cause the progressive evaporation of the solutions to dryness, and culminate in the formation of volatile species of ruthenium and their release in the tank venting circuit.

To determine the fraction of ruthenium likely to be transferred from the storage tanks in volatile or aerosol form during the failure, evaporation tests were conducted by evaporating samples of actual nitric acid solutions of fission products, obtained on the laboratory scale after the reprocessing of several kilograms of MOX fuels irradiated to 30,000 MWday·t<sup>-1</sup>. A distillation apparatus was designed to operate with small-volume solution samples, reproducing the heating conditions existing in the reprocessing plant within a storage tank for fission products.

The main conclusions drawn from these experiments are as follows:

- ruthenium is only volatilized in the final phase of evaporation, just before desiccation,
- for a final temperature limited to 160 °C, the total fraction of volatilized ruthenium reaches 12%,
- in the presence of H<sub>2</sub>O, HNO<sub>3</sub>, NO<sub>x</sub> and O<sub>2</sub>, the volatilized ruthenium recombines mainly in the form of ruthenium nitrosyl nitrates, or decomposes into ruthenium oxide (probably RuO<sub>2</sub>) on the walls of the apparatus.

Assuming a heating power density of 10 W/liter of concentrate, and a perfectly adiabatic storage system, the minimum time required to reach dryness can be estimated at 90 h, allowing substantial time to take action to restore a cooling source. It is probable that, in an industrial storage tank, the heat losses from the tank and the offgas discharge ducts will cause recondensation and internal reflux, which will commensurately delay dryness and the release of the ruthenium from the solution.

## 1 Introduction

The problems raised by ruthenium in the radioactive offgases of a spent fuel reprocessing plant derive mainly from its complex chemistry and its high specific activity (essentially due to <sup>106</sup>Ru), since this fission product can in fact volatilize significantly during the evaporation or solidification of high-level liquid wastes.

Most of the ruthenium solubilized in dissolution is found in the raffinates of the first extraction cycles, which are then concentrated to a volume of 300 liters/t of uranium reprocessed, and then stored for at least one year before vitrification. These concentrates exhibit very high radioactivity and, due to a considerable heat release (about  $10 \text{ W}\cdot\text{liter}^{-1}$  for a PWR fuel irradiated to  $33,000 \text{ MW}\cdot\text{day}\cdot\text{t}^{-1}$  and cooled for three years before reprocessing), the tanks in which they are stored have to be cooled permanently.

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 analysis of the consequences of such an occurrence was nevertheless conducted as part of the safety analysis of the La Hague reprocessing plant, 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 emergency measures taken in such a situation. Due to the high activities present in the tanks, self-heating of the fission product concentrates, following a prolonged cooling system shutdown, could in fact culminate in their progressive evaporation up to desiccation, with these phases likely to cause the formation of volatile species of ruthenium liable to be released in the tank venting circuit. The evaluation of the activity transfer to the offgas system hence demands the knowledge of the fraction of ruthenium likely to escape from the storage tanks in volatile or aerosol form during the cooling shutdown. To do this, tests designed to simulate the progressive evaporation of a fission product solution in representative conditions were conducted on the laboratory scale with real concentrates, complying in particular with the heating power induced by the fission products.

## **2 Parameters affecting the volatilization of ruthenium in a cooling accident**

The bibliography concerning ruthenium is extremely rich, but the tests conducted are sometimes not very systematic, and usually performed with synthetic solutions [1]. Among the factors governing the volatilization of ruthenium during effluent concentration operations, the following are generally distinguished.

- Solution concentrations in nitric acid and nitrates: while the effect of nitrates is less well understood, the volatility of ruthenium in nitric acid medium generally becomes high between 8 and 13 M, with volatile  $\text{RuO}_4$  being formed by oxidation of the ruthenium nitrosyl complexes in solution.
- The presence of reducing agents: these products inhibit or delay the formation of  $\text{RuO}_4$ . They may be formed by radiolysis of the medium ( $\text{HNO}_2$ ,  $\text{H}_2\text{O}_2$ ), or introduced in the different steps of the process (TBP entrained in raffinates, denitration with formol).
- Solution storage time: the equilibrium of the different chemical species of ruthenium present in the concentrates is often slow to be established, and depends on the age of the solution. Storage also influences radiolysis in solution (production yield of certain species, degradation rate of organic compounds).
- Temperature: during evaporation, the oxidation kinetics of the ruthenium complexes depends directly on the temperature buildup profile. At higher temperatures, thermal decomposition of the ruthenium/nitrosyl complexes may also cause the formation of volatile  $\text{RuO}_4$ .

The large number of parameters involved precludes any precise and reliable prediction of the behavior of ruthenium during an FP tank cooling system shutdown. This nevertheless shows that the simulation tests are only significant if conducted with real solutions containing all the chemical elements likely to alter the behavior of the ruthenium, and in thermal conditions as close as possible to reality, especially the heating power released by the FP. This parameter will be preponderant, because it conditions the temperature buildup profile, the change in acidity of the solution, and the time required to reach dryness.

### 3 Experimental

The tests were conducted in a hot cell in order to:

- determine the liquid/vapor equilibrium curves of a real FP solution, to associate the change in temperature with that of the acidity of the concentrate in the subsequent tests,
- simulate the progressive vaporization of an FP concentrate to dryness, without taking any sample from the apparatus, to avoid disturbing the behavior of the different FP and to be able to compile their balance at the end of the operation.

#### Source of concentrates

The fission product concentrates used for these tests were obtained from the laboratory reprocessing of six MOX fuel rods containing 5% plutonium, irradiated to 30,000 MWday $\cdot$ t<sup>-1</sup>. The raffinates of the first extraction cycle were concentrated to 300 l $\cdot$ t<sup>-1</sup> with continuous denitration by the addition of formaldehyde.

The concentrate was then stored for six months for ageing before conducting the ruthenium volatilization tests. The composition of the FP concentrate is shown in Table 1. The activities are updated to the date of the tests, or after a cooling time of 1550 days (4.2 years).

Table 1  
Composition of fission product concentrate

volume	315 l $\cdot$ t <sup>-1</sup>	
chemical composition:		
• [HNO <sub>3</sub> ] M	1.8	
• [NO <sub>3</sub> <sup>-</sup> ] M	8.1	
• [Mo] g $\cdot$ l <sup>-1</sup>	2.4	
• [Zr] g $\cdot$ l <sup>-1</sup>	6.6	
• [Fe] g $\cdot$ l <sup>-1</sup>	13.8	
• [PO <sub>4</sub> <sup>3-</sup> ] g $\cdot$ l <sup>-1</sup>	0.24	
• [Ru] M	≈0.04	
B/ $\gamma$ activity:	TBq $\cdot$ m <sup>-3</sup>	Ci $\cdot$ l <sup>-1</sup>
• <sup>144</sup> Ce + <sup>144</sup> Pr	5,032	136.0
• <sup>125</sup> Sb	118	3.2
• <sup>106</sup> Ru + <sup>106</sup> Rh	4,603	124.4
• <sup>134</sup> Cs	3,718	100.5
• <sup>137</sup> Cs	11,255	304.2
• <sup>154</sup> Eu	725	19.6
total B/ $\gamma$	25,452	687.9
total $\alpha$ activity	3,800	102.7
calculated residual power (W $\cdot$ l <sup>-1</sup> ):		
• $\alpha$	3.57	
• B/ $\gamma$	3.04	
• total	6.61	

## Apparatus and procedure

The experimental rigs employed are shown in Figures 1 and 2. These systems were designed to operate with small volumes of concentrate (400 cm<sup>3</sup>) and reproduce the actual heating conditions existing in a storage tank with a capacity of several tens of cubic meters.

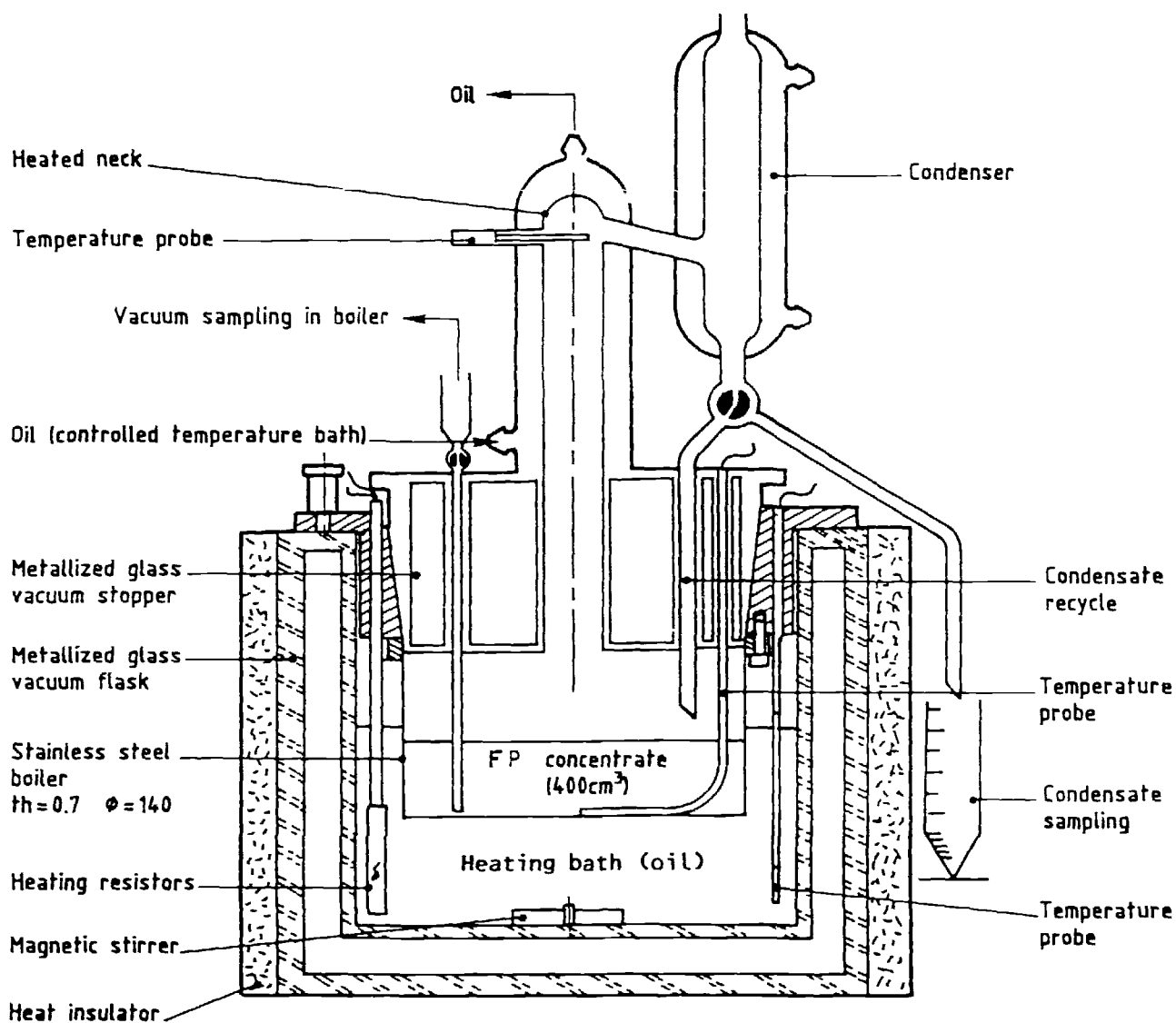


Figure 1 Apparatus used to determine liquid/vapor equilibrium curves

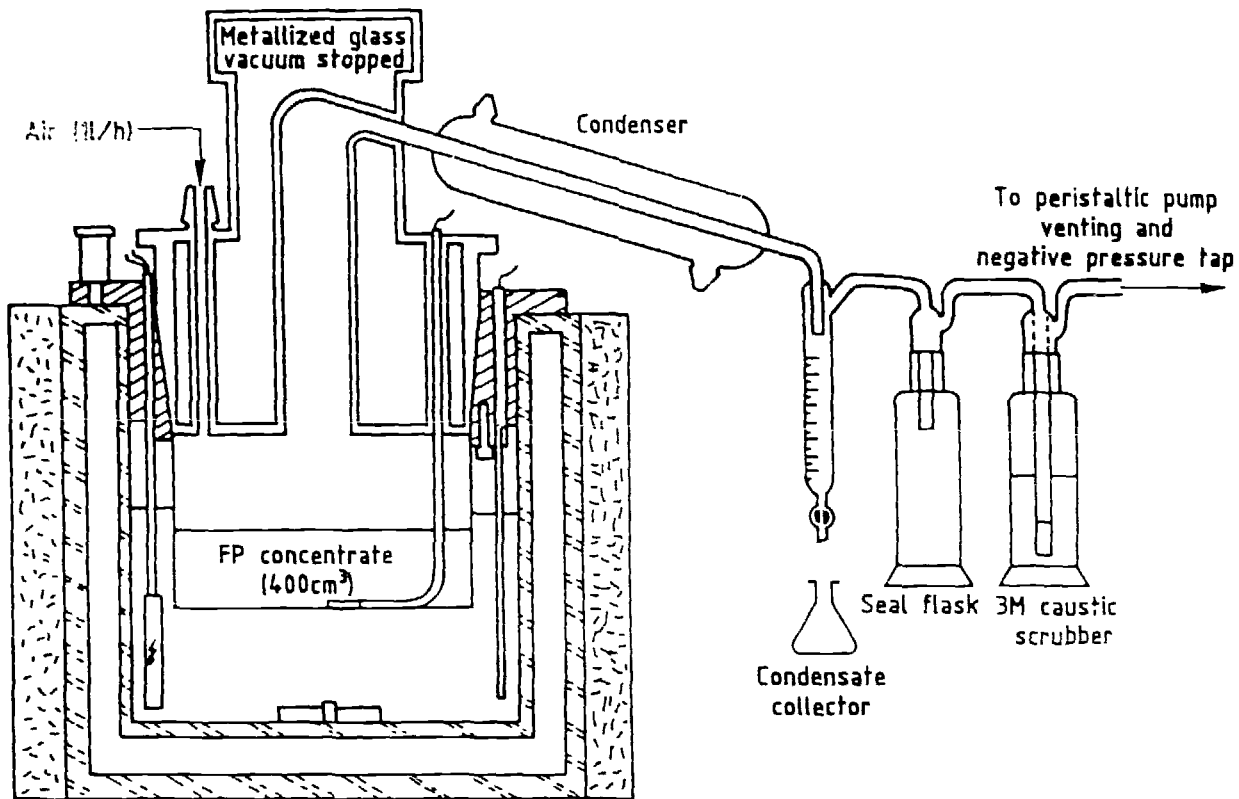


Figure 2 Apparatus used for the test of evaporation to dryness

Given the low heating power densities involved, the apparatus was fully insulated by a double wall of silver-plated glass under vacuum. The boiler tank was of stainless steel. Its cylindrical shape helped to keep the boiling surface area constant and to limit the variation in the heating surface area during evaporation. Heating was provided by oil circulation avoiding local overheating at the boiler wall. The heating power was adjusted in accordance with the heat balance. The heat really absorbed by the solution at any time was equal to the difference between the amount of heat supplied to the system and that lost to the exterior and absorbed by the apparatus. The determination of the mass of water and of the coefficient of thermal conductivity of the system as a function of temperature thus helps to calculate the total energy to be supplied to the system at any time to obtain the desired effective heating power.

During the tests, the heating power used was about  $8 \pm 1.6$  W (or a power density of  $20 \pm 4$  W/l of initial concentrate), and the heat losses reached up to nearly 80% of the total quantity of heat supplied at the end of evaporation.

The system used to determine the liquid/vapor equilibrium curves and shown in Figure 1 is distinguished by the heating of the neck to prevent partial liquid reflux in this zone. The method employed was direct distillation with recycle. Return of the condensate to the boiler ensured a fixed composition and equilibrium temperature in the fraction of solution remaining in the boiler. When equilibrium was reached, the distillate and concentrate were simultaneously sampled, and a larger fraction of the condensate withdrawn. The acidity and temperature of the concentrate then rose progressively until a new equilibrium was reached.

In the second system employed for the progressive vaporization of the concentrate and shown in Figure 2, the heating of the neck was eliminated, but the neck remained insulated by a double wall of silvered glass under vacuum. Only the condensate samples were taken periodically during the test. To avoid overpressures and vapor losses to the exterior, and also to take account of the air circulation in the storage tanks, the apparatus was placed under a slight air blanket ( $1 \text{ l}\cdot\text{h}^{-1}$ ). The ruthenium volatilized in the test was trapped by a caustic scrubber.

## 4 Experimental results and discussion

### 4.1 Variation in acidity and temperature during vaporization of FP concentrates

The rough liquid/vapor equilibrium curves obtained with these FP concentrates are shown in Figure 3. These curves are compared with those of a water/nitric acid system.

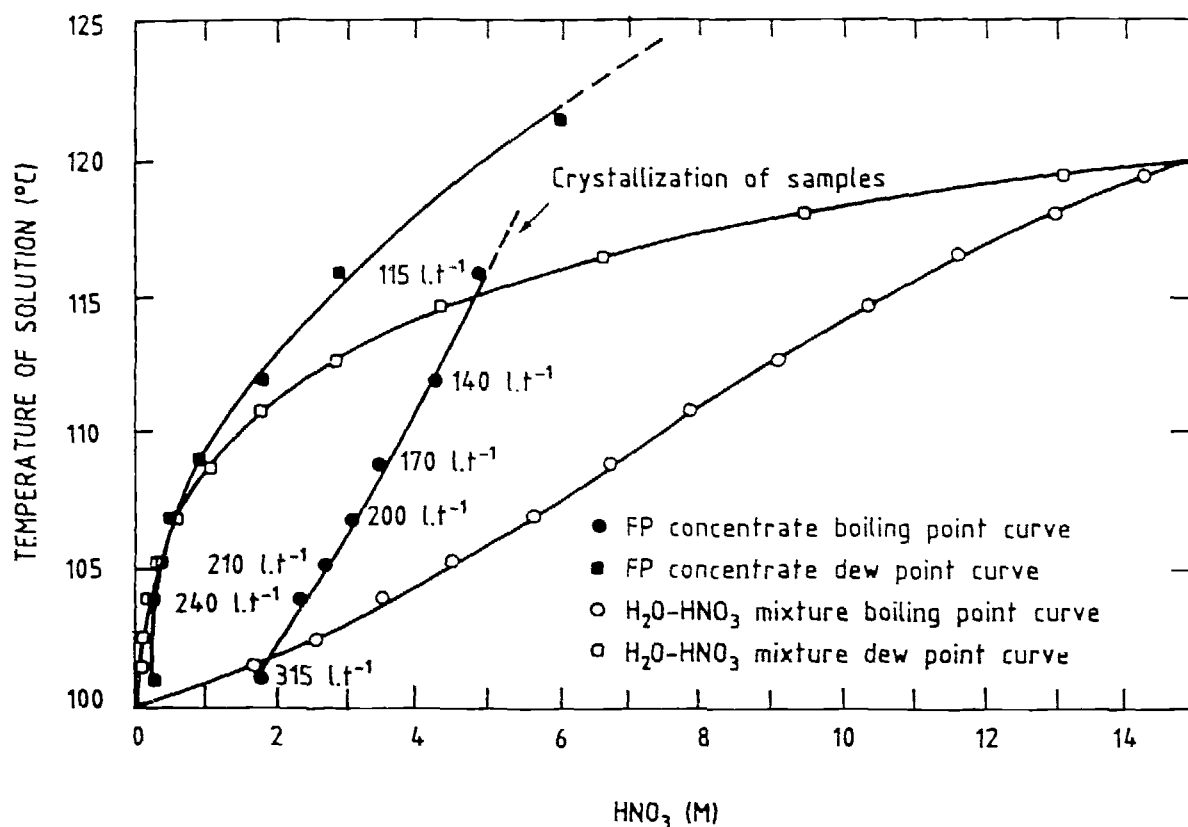


Figure 3 Liquid/vapor equilibrium curves of FP concentrate

As may have been expected, these two systems are quite different. For the same aqueous phase acidity, the boiling point is much higher for a solution containing saline nitrates than for an aqueous nitric acid solution. This is explained by the decrease in the partial pressure of the water due to the salts, causing a rise in the boiling point of the solution.

Above an acidity of 5 M (temperature 116 °C), the nitrate concentration is such that it is impossible to take any samples, because they crystallize at ambient temperature. From 130 °C,  $\text{NO}_x$  is also formed, indicating incipient decomposition of the nitrates. The acid balances that can be determined from the distillates are hence in excess, and no longer serve to estimate the real acidity of the boiler, and the

evaluation of the real volume of the liquid phase is also increasingly difficult due to the growing formation of precipitates. However, concentration was continued to dryness. The final acidity of the condensate was 11.5 M for a boiler temperature of over 150 °C, a much higher temperature than that corresponding to the azeotrope of the water/nitric acid mixture (120 °C).

The first data finally provided by this test can be summarized as follows.

- Variation in the acidity/temperature pair during vaporization is only significant for nitric acid concentrations of 5 M or less.
- The final temperature during the precipitate dryness phase is about 150 °C.
- Incipient decomposition of the nitrates is observed, and the concomitant appearance of NO<sub>x</sub> from 130 °C.

#### 4.2 Behavior of ruthenium during vaporization in the desiccation of FP concentrates

The experiment was conducted this time in a single step, without any samples taken from the boiler. Dryness was reached in 70 h (t = 0 corresponding to the equilibrium temperature of the FP tanks, or 60 °C). This interval was increased by the existence of an internal reflux estimated at 30% of the total flow rate of the vapors leaving the solution. After dryness, the residues were kept at 160 °C (experimental limitation) for nearly 20 h.

The cumulative volume of distillate collected and the change in the concentration of the solution are shown as a function of time in Figure 4. Dryness was reached at a concentration equivalent to 22 l.t<sup>-1</sup>.

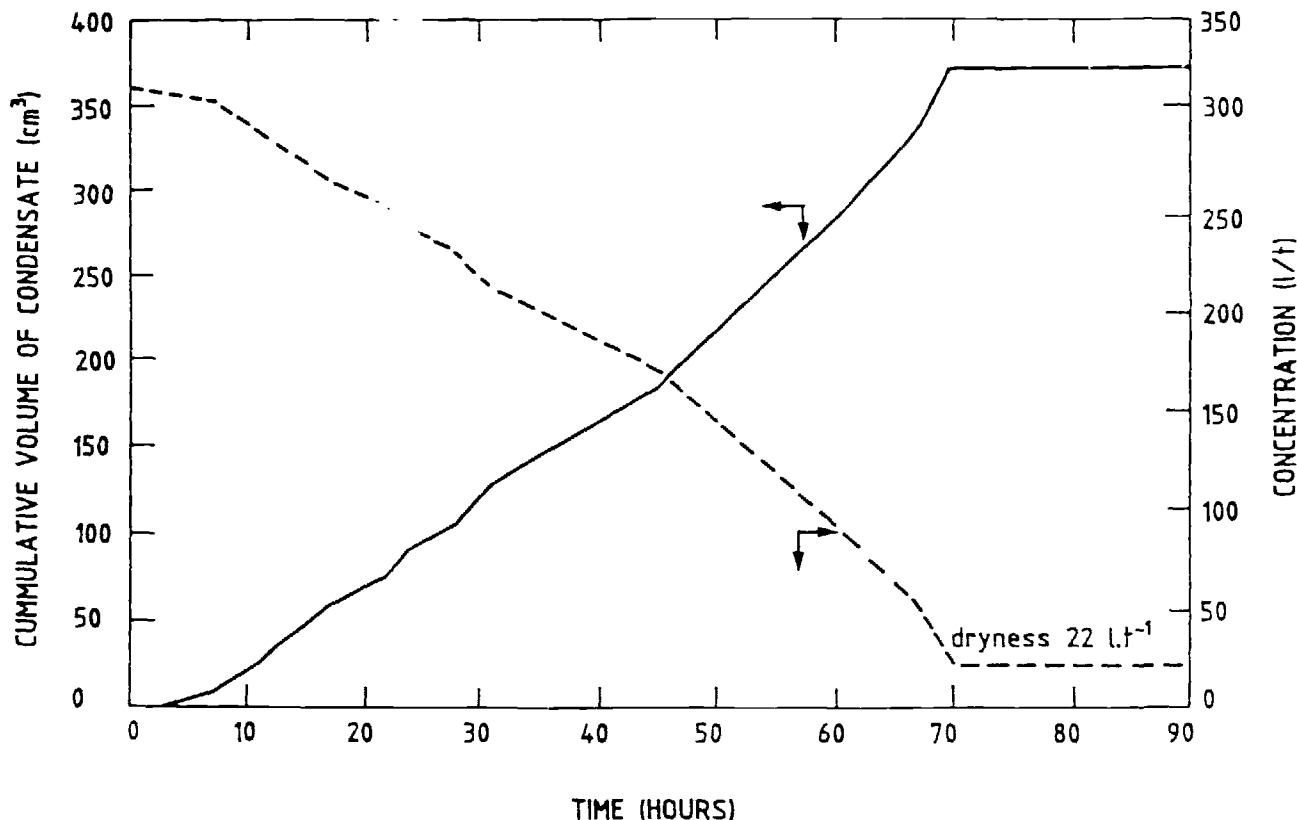


Figure 4 Cumulative volume of condensate and concentration as a function of time



The temperature buildup profiles of the solution and the heating bath are shown as a function of time in Figure 5. During the first 50 h, the solution temperature stabilized at around 102 to 103 °C. It then increased rapidly up to 150 °C before reaching desiccation.

Figure 6 shows the change in acidity of the condensate, and in the total percentage of acid distilled as a function of time. As above, it can be observed that:

- the acidity of the condensate rises suddenly after the distillation of about 75% of the volume of initial solution, to reach a plateau at around 11.5 M,
- the amount of acid recovered in the condensate is more than 20% higher than the number of initial moles (partial recombination of  $\text{NO}_x$  produced by destruction of the nitrates).

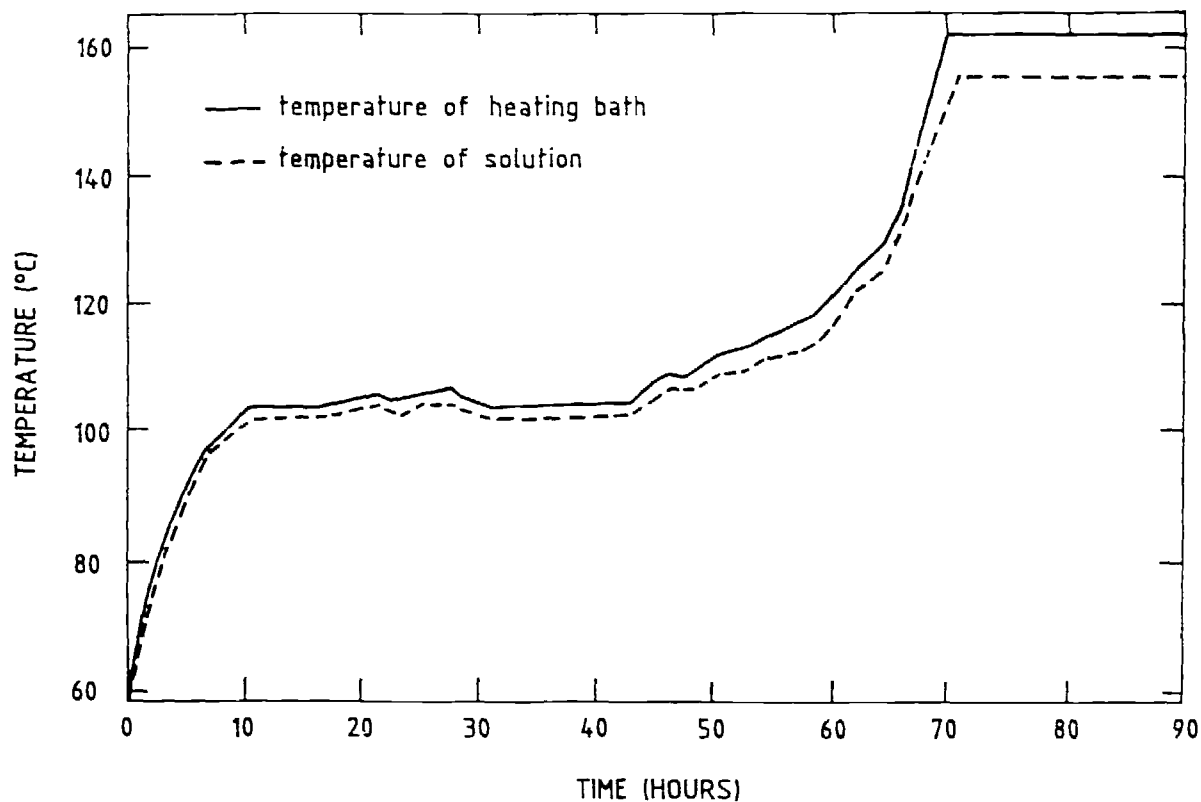


Figure 5 Temperature rise as a function of time

Figure 7 compares the variation in time of the  $^{106}\text{Ru}$  fraction recovered in the distillates with those of  $^{137}\text{Cs}$  and of the  $\alpha$  emitters considered as non-volatile (fractions expressed with respect to the initial activities in the concentrates). Note that the behavior of the other FP measured ( $^{134}\text{Cs}$  and  $^{144}\text{Ce}$ ) is identical to that of  $^{137}\text{Cs}$  throughout evaporation.

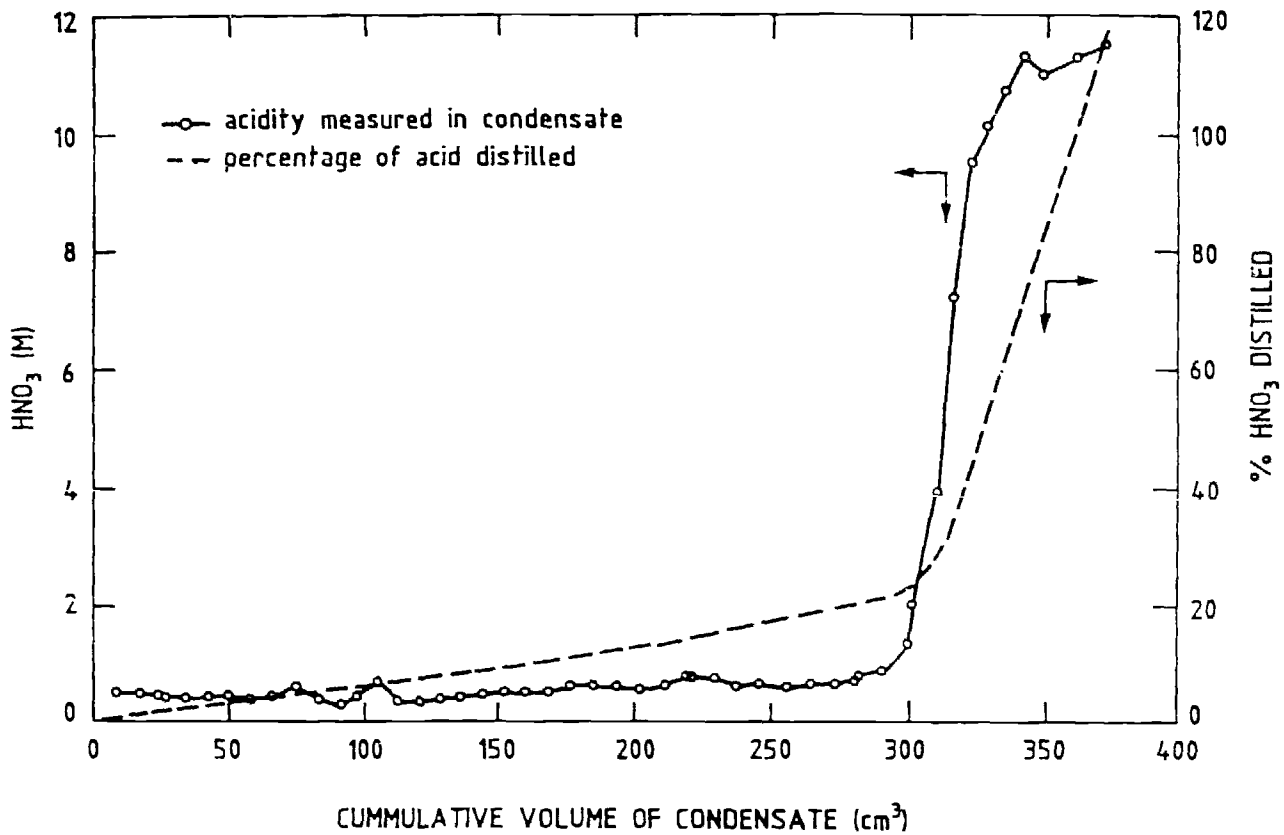


Figure 6 Condensate acidity as a function of distilled volume

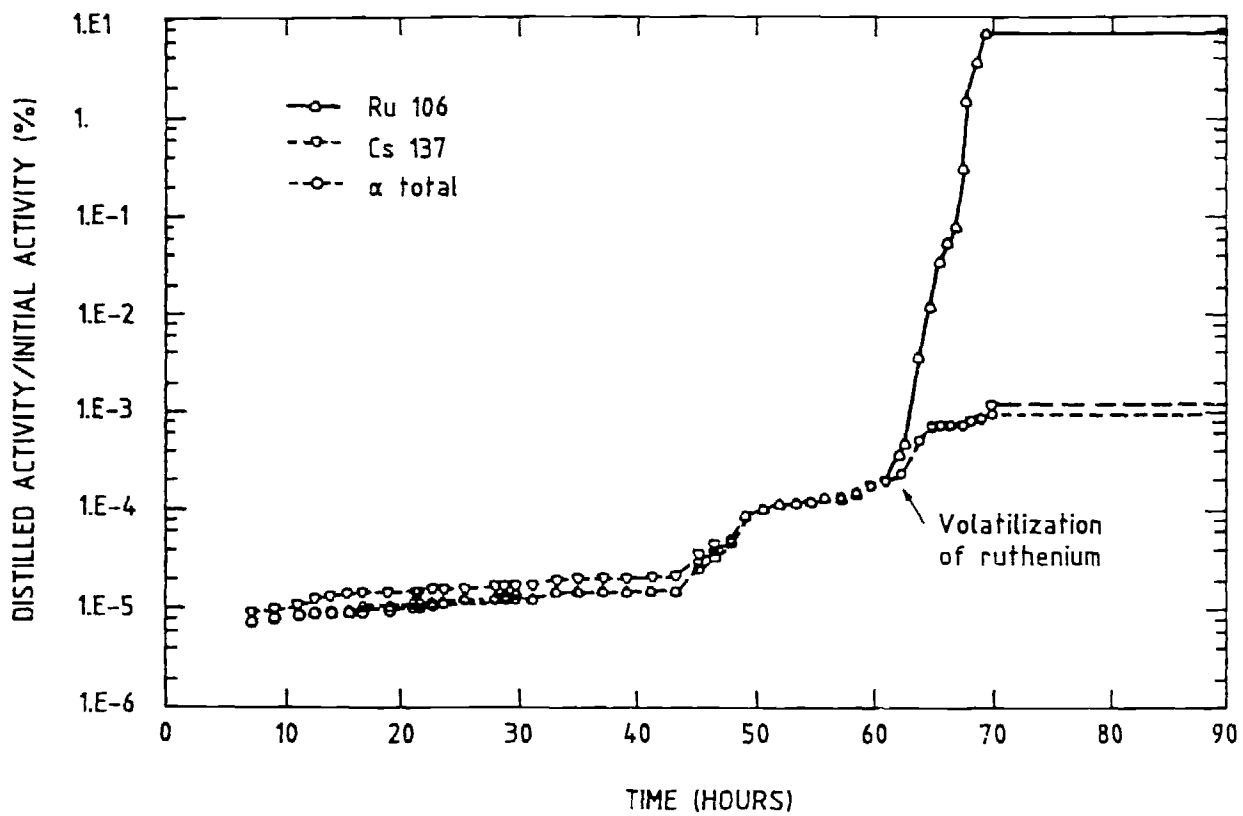


Figure 7 Percentage of distilled activity as a function of time

These curves finally show that ruthenium is volatilized after 60 h (brown coloration of the condensates), together with a sudden increase in acidity of the condensate pointed out above. This volatilization is effective from:

- a concentration of  $85 \text{ l}\cdot\text{t}^{-1}$ ,
- a solution temperature of  $119^\circ\text{C}$ ,
- acidity of about 6 M in the boiler.

The ruthenium thus leaves in the final evaporation phase corresponding to the formation and the desiccation of the residues, thus confirming the results of previous studies conducted on simulated FP solutions [2,3].

Table 2 shows the final balance of ruthenium and of the main radioisotopes transferred from the tank during vaporization. The fractions of activity recovered in the condensate, the caustic trap and the evaporator rinse solution (neck and condenser) are expressed with respect to the initial activities of the concentrate.

Table 2

Balance of main radioisotopes transferred from the tank

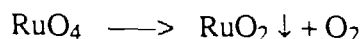
radioisotope	initial activity GBq (Ci)	activity recovered (% of initial activity)					total distilled
		in solution in the condensate	in the caustic trap	in the apparatus rinse solution	in precipitate form		
$^{106}\text{Ru}$	921 (24.9)	7.09	$2.4\cdot 10^{-4}$	3.33	1.68	12.1	
$^{137}\text{Cs}$	4503 (121.7)	$1.12\cdot 10^{-3}$	$7\cdot 10^{-5}$	$2.6\cdot 10^{-4}$	-	$1.45\cdot 10^{-3}$	
$\alpha$ emitters	1520 (41.08)	$9.1\cdot 10^{-4}$	-	$2.2\cdot 10^{-4}$	-	$1.13\cdot 10^{-3}$	

Most of the volatilized ruthenium is found in the condensate (7% of total Ru) and not in the caustic trap ( $\approx 10^{-4}\%$ ). The share due to droplet entrainment is very small, representing a maximum of 0.01% of the total amount volatilized.

Visible/UV spectrophotometry (Figure 8) was used to confirm that the species solubilized in the condensate and the rinse solution were mainly in the form of complexes of ruthenium nitrosyl nitrates [5]. It can therefore be assumed that  $\text{RuO}_4$ , or possibly other volatile species of the  $\text{RuNO}$  type, such as those reported by Klein *et al* [4] are instantaneously recombined in the condenser in the presence of  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{NO}_x$  and  $\text{O}_2$  to form the foregoing complexes. These observations are confirmed by the sudden drop in the nitrous acid content in the condensates, observed from the onset of ruthenium volatilization (Figure 9).

The apparent volatilization rate constant, determined assuming a first-order kinetics, is  $5.3\cdot 10^{-4} \text{ min}^{-1}$  between  $140$  and  $160^\circ\text{C}$ . This figure is higher than the constant determined in 9 to 13 M boiling nitric acid medium for similar Ru concentrations [6,7]. The very clear influence of the nitrates and of the temperature on the ruthenium volatilization process is hence confirmed in these ranges close to dryness.

At the end of the experiment, the walls of the tank and the neck appear to be covered by a black deposit, insoluble in nitric acid. These fine particles, averaging  $7 \mu\text{m}$  in size (measured by sedimentation), represent about 15% of the total quantity of ruthenium volatilized. This implies that part of the volatilized  $\text{RuO}_4$  is thermally decomposed by the reaction:



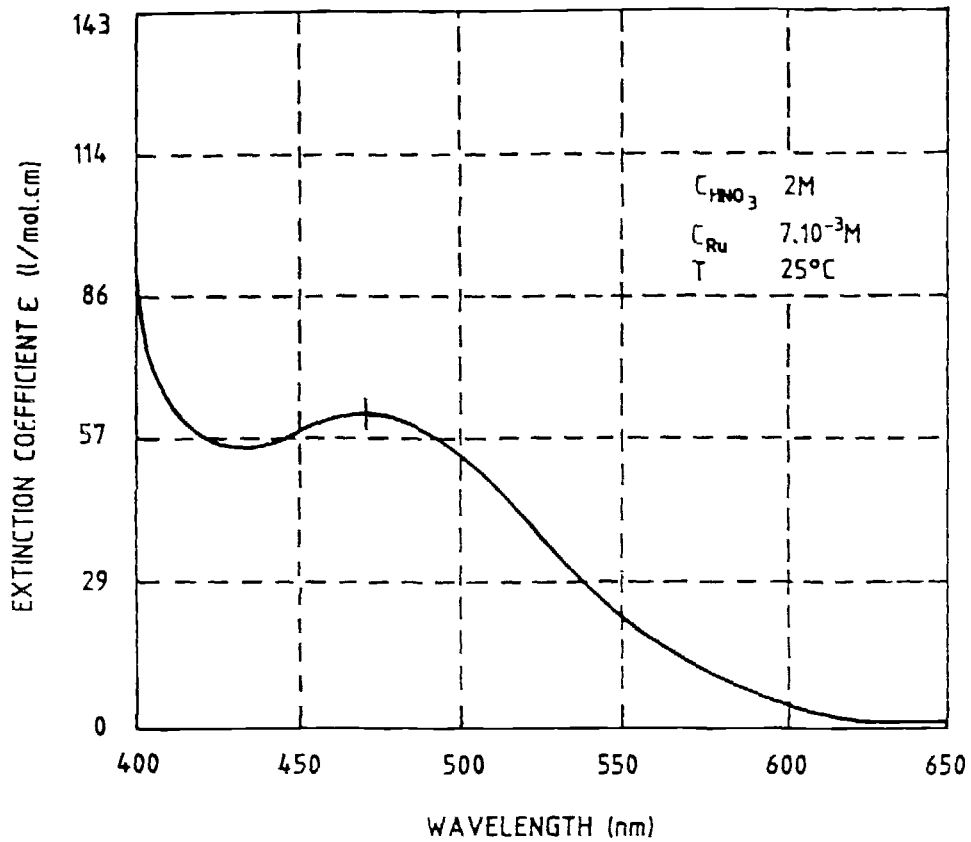


Figure 8 Absorption spectrum of ruthenium in condensate

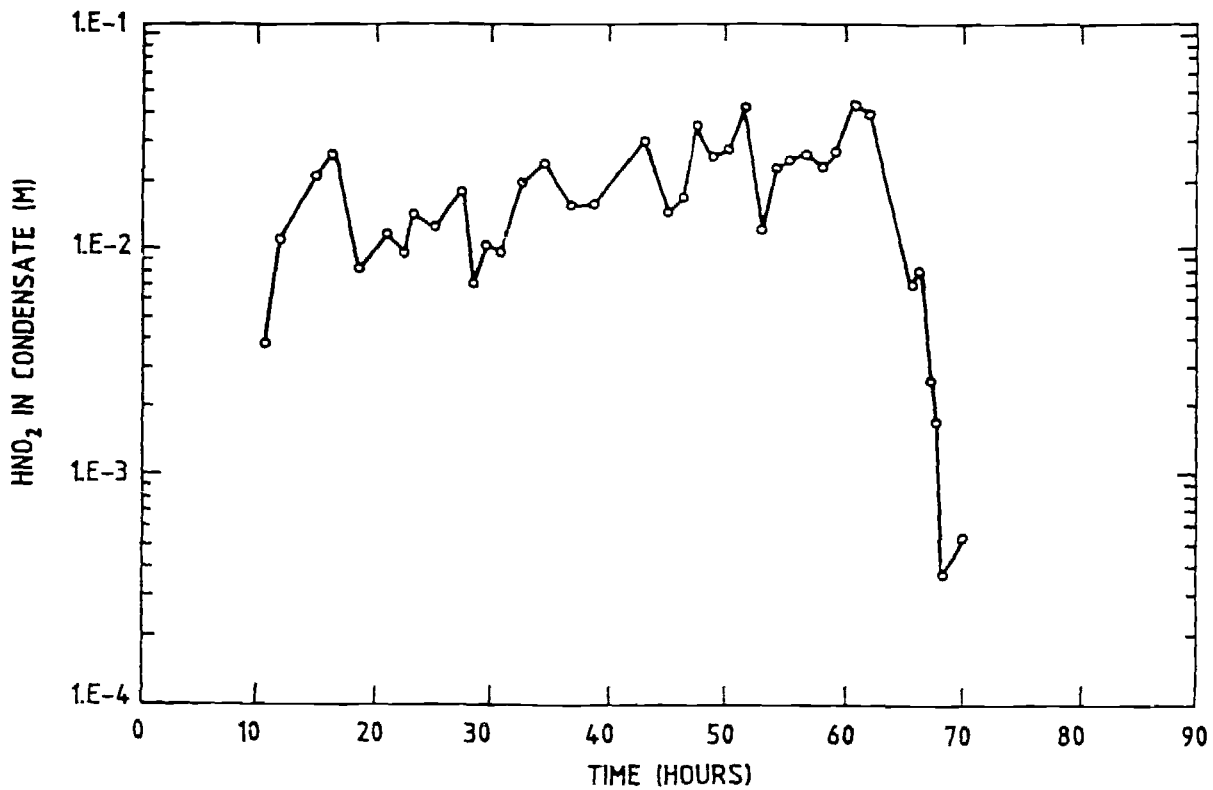
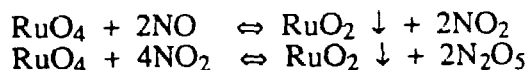


Figure 9 Nitrous acid measured in distillate as a function of time

or could have reacted with the NO<sub>x</sub> present in the apparatus according to reactions of the following type [8]:



However, ruthenium dioxide was not formally identified.

These experiments finally serve to distinguish three phases in the ruthenium release process.

- The boiling phase in which ruthenium transfer from the tank is slight and only occurs through the formation of aerosols entrained by the vapor with the other fission products.
- The phase approaching dryness, when the ruthenium begins to oxidize or to decompose locally, and when the transfer of radioactivity by volatilization of this element predominates over transfer in the form of aerosols with the other fission products.
- The final drying and calcination phase, in which the volatilized RuO<sub>4</sub> is decomposed on the tank walls or reacts with the NO<sub>x</sub> probably to form solid RuO<sub>2</sub>. These fine particles, given the extremely small gas flow rate, tend to redeposit on the apparatus walls.

## 5 Industrial scaling up

These tests finally demonstrated that the risk of ruthenium volatilization, in the case of the prolonged shutdown of the FP tank cooling system, would only exist in the ultimate phase of evaporation approaching dryness. During this final phase, the quantities of ruthenium likely to be transferred to the stack of the plant will depend on local conditions (temperature, NO<sub>x</sub>, scavenging air, wall surface area) and especially on the holdup of the lines and the rate of aerosol entrainment.

Consequently, the time required to vaporize the concentrates completely will determine the maximum time allowed to the reprocessing plant operators to take remedial action. Based on the distillation rates measured experimentally, and assuming a heating power density of 10 W·l<sup>-1</sup>, this period could be about 90 h (including 5 h of rise to boiling point). In these conditions, volatilization of the ruthenium would only become effective after the 75th hour, leaving substantial time to restore a cooling source.

It is also probable that, in an industrial storage unit, the heat losses in the ducts of the offgas discharge system will cause local condensation and hence internal reflux in the storage tanks, which will commensurately delay the release of the ruthenium from the solution.

It is in fact very unlikely that complete evaporation of the stored solutions could occur, rather leaving the possibility of an equilibrium established between the power released by the FP and the heat losses of the tank and its vents.

It is nonetheless the operator's duty to minimize the scavenging air flow rate in the tanks, because this could shift the liquid/vapor equilibrium and accordingly accelerate the evaporation rate of the solution.

## 6 Conclusions

The experiments described in this document were conducted in order to analyze a prolonged accidental shutdown of storage tanks for fission product solutions in a spent fuel reprocessing plant. These tests, performed on a real FP solution, demonstrated very clearly that the volatile species of ruthenium are only formed in the ultimate phase of evaporation, close to dryness. During this phase, the transfer of activity by the volatilization of this element will prevail over simple contamination by aerosols. These volatile species nevertheless prove to be highly unstable, and could recombine mainly in the form of soluble complexes of ruthenium nitrosyl nitrates, or decompose, probably to RuO<sub>2</sub>, depending on local conditions. These experiments also demonstrated that, on the industrial scale, the minimum time

available before the release of the ruthenium from the solution would be more than three days, leaving the plant operators substantial time to restore a cooling source.

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