A Literature Review on Ruthenium Behaviour in Nuclear Power Plant Severe Accidents

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ABSTRACT

During an hypothetical severe accident on a Pressurized Water Reactor (PWR), Fission-Products (FPs) are released from the nuclear fuel and may reach the reactor containment building. Among the FPs, ruthenium is of particular interest due to its ability to form volatile oxide compounds in highly oxidizing conditions. In addition, Ru is a very hazardous compound because it is chemically toxic and also because of its radiotoxicity.

The topic of ruthenium is examined in terms of nuclear safety issues. A review of the literature regarding ruthenium oxides properties, gaseous and aqueous chemistry is compiled. The study focuses on the ruthenium tetroxide (RuO_4) which is highly reactive and volatile, and is the most likely gaseous chemical form under the conditions prevailing in the containment. The interactions between ruthenium oxides and containment surfaces, which could be of main importance in the overall Ru behaviour, are also discussed. Finally, an evaluation of the possible revolatilisation phenomena of ruthenium adsorbed on PWR containment surfaces, or dissolved in the sump, under super-oxidizing conditions (radiolysis), is also presented. In this case, ruthenium dioxide (RuO_2) must also be considered.

Knowledge of all these phenomena is required to accurately predict ruthenium behaviour, and to make best estimate assessment of the potential ruthenium source-term.

1   BACKGROUND

A severe accident (SA) would happen in a nuclear reactor if loss of coolant due to an initiating event occurs together with partial or total failure of the safeguard systems, leading to irreversible core dewatering. After the nuclear fuel degradation, FPs released from fuel are transported, in gas, vapour or aerosol form, through the Reactor Coolant System (RCS), partially condensed onto steel surfaces, and reach the containment. Some FPs, still in gas or aerosol form, may leave the containment via different leaks and will lead to radioactive contamination of environment: this is called Source Term (ST).

Among all types of SAs, some happen in a highly oxidizing atmosphere due to possible contact between degraded fuel and air. The different possible air ingress pathways have been studied [1] [2], and three main possibilities have been identified.

The first one corresponds to air ingress during refuelling operations. During this process, the reactor vessel head is removed and the fuel is immersed in water. In the case of possible water loss, the refuelling cavity could be emptied and fuel would come into direct contact with the air [1].

The second possibility is air ingress following lower head reactor pressure vessel melt-through due to molten nuclear fuel (called corium) interaction with steel [2]. Indeed, subsequent to this phenomenon a gas circulation is created between the reactor pit, lower head vessel break and the primary system.

The last possibility is air ingress directly through a break in the primary or secondary coolant system [1].

Other scenarios leading to a contact between fuel and the air are possible, as for example a spent fuel storage pool water draining accident, or a fuel handling accident.

This paper deals with a literature review regarding ruthenium oxides gaseous and aqueous chemistry, in the containment during an oxidizing SA. This study focuses particularly on the ruthenium tetroxide chemistry.

2 RUTHENIUM ISSUE

2.1 DOES RUTHENIUM REPRESENT A REAL ISSUE FOR NUCLEAR SAFETY ?

The study of ruthenium topic by IRSN as well as other organizations devoted to nuclear safety research, in France and other countries, is motivated by several factors.

Firstly, the quantity of ruthenium formed increases with fuel burn-up (BU). With identical BU, it increases with fuel enrichment in ^{235}U; moreover, it is greater in MOX fuel than in UO_2 fuel. As a consequence, the amount of ruthenium formed during fuel life will continuously rise in the future, because utilities tend to optimise fuel performances.

Secondly, ruthenium is a high specific activity fission-product. The graph in Figure 1 shows the evolution, during the first 2 years after an emergency scram, of the important part of ruthenium activity with respect to the total activity of all the FPs released (^{131}I, ^{133}Xe, etc.) [3] [4], it has been assumed that 50% of the bundle inventory is released.

Finally, ruthenium has, in addition to its chemical toxicity, which was already known through toxicological studies [5] [6] [7], a high radio-toxicity, essentially through its isotopes ^{106}Ru ($T_{1/2} = 369$ days) and ^{103}Ru ($T_{1/2} = 39.3$ days). It is therefore an important short and middle term radio-contaminant.

In radiological protection four groups of radionuclides were defined [8], and ^{106}Ru was ranked in group 2 « high radio-toxicity », in the same way as ^{131}I, and ^{103}Ru in group 3 « moderate radio-toxicity », as ^{137}Cs.

The danger of ruthenium particles is their specific activity and the high associated risk of irradiation and internal contamination (inhalation, ingestion). For example, a 8 µm diameter particle which has a 1500 Bq activity (calculated for RBMK fuel [Chernobyl], with an average burn-up), may induce more than 1.6 mGy.cm^{-2}.h^{-1} to skin (external irradiation) [9].

Under the action of oxidizing agents, which may be produced either from sump water radiolysis or from air radiolysis, ruthenium metal or dioxide, could be oxidised, up to +VIII oxidation state. Its volatile compounds (essentially RuO_4) may be present in the containment in the case of a severe accident and could represent a high potential risk for nuclear safety.

2.2 RUTHENIUM RELEASE FROM DEGRADED FUEL AND TRANSPORT IN RCS

Metal ruthenium is considered as a moderately volatile species; then the fraction emitted, from UO_2 fuel heated to 2573 K, varies between 1 and 10% [10]. Indeed, according to Ellingham diagram, to obtain Ru oxides, it is necessary to have preliminarily oxidised most of the other elements, especially uranium, plutonium and molybdenum. The presence of volatile ruthenium species is possible only if the fuel is subject to strong oxidation, such as the one resulting from an air ingress in the reactor pressure vessel. Affinity for oxygen is in decreasing order: $Zr > UO_2 > Ru$. So oxygen availability for Ru depends strongly on the UO_2 matrix oxidation state [1]. As indicated by Hunt [11], some elements can become oxidised (Ru extreme case) only if UO_2 has previously be oxidised in UO_{2+x}. Oxygen potential is of prime importance for the ruthenium release rate.

Ruthenium release from fuel matrix (or simulant), under air atmosphere, has been highlighted by various experiments.

Atomic Energy of Canada Limited (AECL) carried out some tests which consisted of heating pieces of irradiated fuel pellets, under different atmospheres. The fuel BU of the test called H02 was 10 GWd/tU. This test was performed under Ar/H_2 atmosphere, and next in air. The maximum temperature reached was 2163 K. Figure 2 shows that, as soon as an oxidizing atmosphere is present (transition from Ar/H_2 mixture to air atmosphere), ruthenium release increases drastically to reach a value close to that of ^{133}Xe, which is a very volatile compound, released at nearly 100%. It is worth noticing the presence of an induction time (approximately 5000 seconds) assumed to correspond to time necessary for oxidation of the UO_2 matrix by air, next Ru release is extremely quick [12].

In the frame of the PHEBUS–RUSET programme, in 2002 the Hungarian research organization (AEKI) studied the ruthenium release at high temperature in oxidising environment. These tests confirmed the presence of a gaseous type of ruthenium [13].

Once released out of fuel matrix, ruthenium can be transported through the RCS, under various physico-chemical forms: ruthenium trioxide ($RuO_3(g)$), ruthenium tetroxide ($RuO_4(g)$), RuO_2 aerosol (ruthenium dioxide) and ruthenium mixed aerosols (Cs_2RuO_4…), before reaching the containment via the RCS break.

The British technology company AEA-Technology and VTT Processes (Finland) have studied ruthenium transport. It has been observed that RuO_4 partial pressure measured is far higher than the predicted thermodynamic equilibrium calculation; so ruthenium tetroxide decomposition may have been limited [14] [15]. Similar results were obtained in other experiments [16].

Interesting information can also be drawn from the Chernobyl accident even if this accident is not strictly a PWR severe accident; nevertheless a strong ruthenium release occurred. Indeed, total releases of [103]Ru were higher than those of ^{137}Cs, 9.3×10^{16} versus 4.7×10^{16} Bq [17], corresponding to about 2.9 % of the Ru initial inventory [18], so it confirms the possibility that ruthenium can be released outside the fuel matrix.

Many radioactive particles emitted contain ruthenium, essentially under metal form [17]. Various authors have tried to explain the origin of this metal form but assumptions vary from one author to another. Nevertheless Broda *et al.* [19] have formulated a pertinent hypothesis, they postulated that some radioactive compounds, emitted in gas form, precipitated and condensed when they reached the airborne plume. Ru and Mo volatile oxides, formed due to heating from graphite combustion, reduced or decomposed at high temperature, are probably the main compounds of such precipitates. This scenario has been suggested subsequently as the origin of the very high purity of radioactive ruthenium and of to the fact that many particles have been found incorporated in large fragments of non-radioactive material. In addition, the formation of volatile compounds is also confirmed because the condensed Ru particles showed a constant [103]Ru/[106]Ru isotopic ratio.

This is only possible if they come from an initial gaseous release form, because this ratio depends on BU, so variable according to the Ru location in fuel matrix.

In the case of release of solid particles from fuel, this ratio could not be identical, it would change according to the fragments analysed [20].

All these experimental observations indicate that ruthenium can be released from fuel in large quantities according to conditions, and next transported through the RCS. But then, how do emitted ruthenium compounds behave in the containment ?

2.3   RUTHENIUM BEHAVIOUR IN THE REACTOR CONTAINMENT

Ruthenium behaviour is directly linked to the nature of the Ru compound. $RuO_3(g)$ is unlikely to reach the containment because it is unstable thermodynamically in the temperature range of the containment SA conditions [21] [22]. In the gas phase, mixed aerosols are not the major risk from a source-term point of view, because after aerosols settling in aqueous phase (sump), ruthenates will be formed. The two essential species are RuO_4, the most stable gaseous form in containment conditions, and the little soluble aerosol RuO_2, which can have an impact in terms of potential revolatilisation under RuO_4 form.

In the aqueous phase, ionic compounds of ruthenium essentially (RuO_4^-/RuO_4^{2-}), have to be taken into account, because they can be involved in reactions leading to the formation of either gaseous RuO_4 or RuO_2.

The potential reactivity of ruthenium onto surfaces is important. Therefore, the important surfaces present inside the PWRs containment have to be considered in terms of reactivity; these surfaces are made of painted steel and stainless steel surfaces (316L and 304 L) [23]. Ruthenium tetroxide seems to have a certain affinity for iron oxides [22] [24] and for organic compounds [25] [26]. Reactions involving RuO_4 with internal surfaces of containment can be expected to occur, especially as the developed total surface is very large - several thousands of m^2.

During a SA, there is a high dose rate in the containment, in gaseous and aqueous phases, resulting from the large amount of FPs present in the containment. Radiolytic reactions occur in the atmosphere and the sump leading to the formation of oxidants which might oxidise ruthenium up to +VIII oxidation state.

3   GENERAL PROPERTIES CONCERNING RUTHENIUM OXIDES

Although it is an iron homologue, ruthenium has neither the same reactivity nor the same chemistry. Ruthenium chemistry is extremely complex, lots of compounds are known - inorganic as well as organic forms. Its external electronic structure is $4d^7 5s^1$, which gives it 9 stable oxidation states lying between 0 and +VIII, and even a –II oxidation state, $(Ru(CO)_4^{2-})$ [25]. Our talk is limited to compounds which could be involved in nuclear safety issues.

With alkali metals and alkali earth metals present in large quantity as FPs, ruthenium can form mixed compounds, Cs_2RuO_4, $SrRuO_4$, $BaRuO_3$, etc.

Ruthenium halides can also be quoted: RuF_6 to RuF_3, $RuCl_3$, $RuCl_2$, RuI_3, RuI_2,…[27]. The last two compounds present particular interest, because iodine is a very hazardous FP [28]. In aqueous phase, oxidation states +VI, +VII, and +VIII, give essentially tetraedric oxo-complex: ruthenate ions (RuO_4^{2-}), and perruthenate ions (RuO_4^{-}), as well as ruthenium tetroxide and its hydrolysed form H_2RuO_5.

The possible existence of ruthenium hydroxides and also ruthenium oxy-hydroxides is mentioned in the literature even if the data are scarce.

Besides metal ruthenium, ruthenium aerosols (type Cs_2RuO_4), and possibly ruthenium hydroxides, ruthenium oxides are the main compounds supposed to be formed during a severe accident. The four main ruthenium oxides are: RuO, RuO_2, RuO_3, RuO_4 [29].

Table I lists all Ru compounds that may be concerned in this topic; they are classified according to their oxidation states. Letters (g), (aq), and (c) refer respectively to gaseous, aqueous and condensed phases.

The main characteristics of ruthenium oxide compounds are detailed hereafter.

✓ RuO

This oxide is only gaseous. According to Shäfer *et al.*, when the temperature is over 1273 K, the three oxides RuO_4, RuO_3 and RuO_2 are decomposed into RuO [30]. However, various authors, such as Rard [31] or Bell [21] have doubts concerning its existence. After experimental works, Eichler *et al.* [29] claims that RuO monoxide only exists when temperatures are over 1900 K. Enthalpy of formation has been established by Norman and Staley [32] at 1900 K.

✓ RuO_2

Ruthenium dioxide is the most stable Ru oxide. It appears under brown-black powder with a tetragonal rutile structure, type TiO_2. A mean of production is to roast Ru_{metal} in an oxygen stream in a very high temperature muffle furnace [25], another is to dehydrate $Ru(OH)_3$ hydroxide at 723 K [33].

By heating RuO_2 under an oxygen flow, volatilisation takes place, indicating the formation of higher oxidation state oxides.

These oxides, which are thermodynamically unstable, decompose on cooling to form anhydrous RuO_2 blue crystals, this phenomenon has been experimentally confirmed by Rard [31]. In anhydrous form, dioxide is insoluble, but a hydrated form exists (RuO_2,xH_2O with 2<x<3), so its dissolution becomes possible [33] even if this is quite difficult. RuO_2 is also assumed to exist under gaseous form but solely at very high temperatures, superior to 2000 K [34], like in the reactor core in SA conditions.

✓ RuO_3

Very little information are available in the literature concerning this oxide. Its existence in gas form was questioned for a long time, but Schäfer's [30] and Bell's teams [21] in 1963 proved its existence. According to these authors, the partial pressures of ruthenium trioxide and ruthenium tetroxide are equal in ($RuO_2 + O_2$) environment at 1 atm and at 1327 K. RuO_3 predominates in gaseous phase above this temperature up to 2000 K, and RuO_4 below this temperature (1327 K).

Eichler *et al.* [29] indicate that ruthenium trioxide in gaseous phase can condense in dioxide form. Moreover, $RuO_3(g)$ could also be transformed in solid RuO_3 form [35] even if this hypothesis is not accepted by all the scientific community.

✓ RuO_4

Ruthenium tetroxide can exist in gaseous state or in condensed state. The properties of this compound are extensively detailed later. An important characteristic is that this oxide is very volatile with very toxic vapours.

To illustrate this last point, the liquid-vapour equilibrium constant of ruthenium tetroxide has been calculated with GEMINI 1 [36] and the thermodynamic databank associated COACH:

RuO_4 (aq) $\Leftrightarrow$ RuO_4 (g) K=8.8$\times10^{-2}$ at 360 K
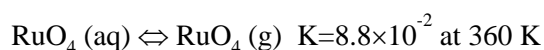
The constant of this reaction represents the RuO_4 vapour pressure in the standard reference state.

4 RUTHENIUM OXIDE CHEMISTRY IN SEVERE ACCIDENT CONDITIONS

4.1 RUTHENIUM REACTIVITY IN GAS PHASE

From a nuclear safety point of view, ruthenium compounds can be split into two categories, the gaseous forms, and the aerosol forms, amounts of which are very much predominant. Possible gaseous forms can only be RuO_3 and RuO_4 oxides. However, the maximal temperature in the containment in the case of SA will very likely remain below 413 K, value not compatible with the thermodynamic stability of trioxide [22] [21], as already mentioned.

The Figure 3, obtained by means of thermodynamic code COACH-GEMINI 1 [36] indicates clearly that RuO_3 decomposes at about 1500 K to form RuO_2 and RuO_4.

Even if thermodynamic equilibrium calculations also show $RuO_4(g)$ instability at low temperature and all the more in the temperature range of the containment (313 K/ 413 K), several arguments favour a more complete study of the reactivity associated to this species.

Firstly, recent experimental data [14] [13] tend to prove that RuO_4 would be formed in RCS in non negligible amount. Secondly, RuO_4 has a very high saturation vapour pressure, so its volatility makes it hazardous for the populations. Thirdly, in the reactor containment conditions (oxidizing medium), this high oxidation state (+ VIII) could be stabilised.

Concerning aerosols, there are mixed ruthenium aerosols, and ruthenium dioxide RuO_2(s). Mixed aerosols are water soluble and ruthenium dioxide, on first analysis, does not represent a major danger under this form, except in the case of early containment failure, but it can be a possible source of RuO_4(g) formation by oxidation of aerosols deposits on the walls. To sum up, in order to be able to make an accurate estimation of the Ru source-term, a better understanding of tetroxide and dioxide behaviour is needed.

4.1.1 *RUTHENIUM TETROXIDE*

For several authors [24] [37], ruthenium tetroxide appears in two forms in solid state. The first condensed state is brownish globules, which are little soluble in water, and seem to constitute a crystalline state. They are produced by solidification of liquid tetroxide below 300 K. The second state corresponds to very unstable yellow needles, which are obtained by condensation of tetroxide in the vapour state. These needles melt at approximately 298 K. This form is more soluble in water and produces a golden yellow solution; its solubility in water is estimated at 17.1 g.L^{-1} at 273 K, and 20.3 g.L^{-1} at 293 K [26]. It is also very soluble in tetrachloromethane and produces an orange red solution. Its sublimation can be observed at 280 K with a pressure of about 4 mbar [24]. This crystalline form can be obtained with sublimation and next condensation of the brownish form.

However, a study by Nikol'skii [38], focused on determining the melting point, vapour pressure, and solubility in water, refutes this hypothesis of ruthenium tetroxide polymorphism.

Tetroxide vapours are yellow, toxic and smell strongly like ozone. They are reactive, particularly with organic materials and reducing agents. Sensitivity to photolysis has also been demonstrated [35]. Indeed, in a dark place, in dry atmosphere and in a sealed tube, ruthenium tetroxide can be stored for several years. On the other hand, with light and humidity, its decomposition happens quickly.

The duration was not indicated. RuO_4 is also supposed to decompose in an explosive way into RuO_2 when temperatures are near 381 K [39]. This last point is not mentioned in any other article nevertheless it is worth noticing that only these authors have manipulated about one hundred grams of tetroxide which represents a huge amount - never handled again.

4.1.1.1 Thermal stability of RuO_4 (g)

RuO_2 stability and RuO_4 volatility can be easily explained with covalent bonds. Binding energy between tetroxide atoms is low because they are perfectly saturated, and the structure is symmetrical, this is the reason why this compound can be easily melted, sublimated and volatilised.

Few experimental studies on ruthenium tetroxide stability in gaseous phase have been performed. Ruthenium tetroxide decomposition mechanisms and the associated kinetics are still unknown. According to Leudet [40], tetroxide decomposition, at low temperatures, takes place according to the following reaction:

$$RuO_4(g) \Leftrightarrow RuO_2(s) + O_2(g) \qquad K= P_{O2}/P_{RuO4} \qquad\qquad \text{Eq. 4-1}$$
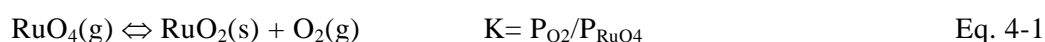
The relation below gives the equilibrium constant:

$$\text{Ln K}= \frac{14880}{T} - 11.53 + 1.135 \ln T \qquad\qquad (T \text{ in K})$$

$RuO_4(g)$ stability rises with temperature. The equilibrium constant calculated (7×10^{19} at 293 K and 2×10^{15} at 373 K) indicates an almost complete decomposition if equilibrium is reached.

Ortner [41] introduced gaseous tetroxide in a sealed tube (Carius tube), maintained at a constant temperature for some time, and then rapidly cooled to stop the reaction; but the precise boundary experimental conditions were not provided.

They noticed that in the presence of wet air, decomposition happens only after an induction time, the duration of which depends on steam concentration and temperature. But, after adding a drying agent, the induction time has been shortened. No hypothesis was formulated.

The decomposition seems to be initiated by ruthenium deposition on glass walls; this would indicate an auto-catalytic reaction, all the more that in introducing RuO_2 into the tube, induction time was also reduced. The decomposition kinetic was studied between 383 K and 413 K, with an RuO_4 initial pressure of about 0.3 atm, in the presence of 25 mg to 150 mg of RuO_2. The kinetic rate law determined is of first order with respect to RuO_4. An Arrhenius law expressed the rate constant:

$$k \ (\text{min}^{-1}) = 7.12 \times 10^{14} \exp(-128 \times 10^3/(RT)) \qquad \text{(T in K)}$$

Corresponding reaction half-lives, calculated at different temperatures, are reported in Table II.

The kinetics of the RuO_4 decomposition is very slow at room temperature, which may justify the existence of $RuO_4(g)$ even if it is not thermodynamically stable. The temperature range ($\Delta T = 30$ K), where the kinetic data were determined, is limited and, above 373 K, extrapolation is uncertain. Moreover, the possible explosive decomposition of tetroxide at temperatures around 381 K, noticed by Sainte Claire Deville and Debray [39] is not consistent with this study even if the possible explanation is that the amount of the tetroxide amount involved in these tests was weaker. The influence of the presence of metal ruthenium, in powder form, on the decomposition rate, has also been studied. The results obtained for different concentrations of tetroxide indicate that 54% of RuO_4 is decomposed after 3h, at 383 K, and after 2h, at 413 K, it is 100%. Nevertheless, the lack of information about the precise conditions of experimentation limits the interest of these results.

At the end of the 19th century, Debray and Joly [42] had already pointed out the impact of water steam on ruthenium tetroxide stability. Indeed, RuO_4 can react with water steam to form a black coating of lower oxide. This black amorphous precipitate, dried in an oven at 383 K, consists of $Ru_2O_5,2H_2O$; and even after drying, it remains partially hydrated. Tetroxide decomposition, which is slow in the dark, is accelerated with sunlight especially with ultra-violet rays. According to Wöhler *et al.* [43], dioxide hydrates would be formed.

Ortins de Bettencourt and Jouan [24] have also investigated RuO_4 decomposition kinetics. Even though they had great experimental difficulties, particularly in tetroxide generation and its transfer into reactor vessel, they confirmed that the reaction is of first order.

More recently, Zimmerman *et al.* [35] have again shown interest in RuO_4 decomposition and the resulting products. Their study is based on irradiation of $RuO_4(g)$, by a mercury arc lamp, or by a photolytic flash. Photolytic decomposition was observed in measuring the absorbance decrease of RuO_4.

4.1.1.2 $RuO_4(g)$ reactivity under radiation

The formation of air radiolysis compounds has been extensively studied [44] [45] [46]. Willis and Boyd [47] published all the radiolytic yield values (G-values) of primary compounds coming from air radiolysis, as well as the reactions between these different species. The set of thermal and radiolytic reactions can be solved by the Facsimile software [48] in order to predict the gas mixture composition as a function of boundary conditions. By way of illustration the main compounds generated by radiolysis are shown on Figure 4, for prototypical conditions (10 $kGy.h^{-1}$ dose rate, 373 K, steam mass fraction = 30%, and no potential sorption of radiolysis compounds on surfaces).

The main radiolytic compounds present in the containment in the case of SA are NO_2 and N_2O and O_3, which are oxidants.

The ruthenium tetroxide concentration in containment atmosphere is quite difficult to evaluate in the case of SA, it will nevertheless be extremely low with respect to atmosphere compounds. It is then legitimate to assume that most of the energy released by ionising radiations is distributed between N_2, O_2 and H_2O molecules and the influence of radiation on ruthenium species will be rather due to chemical reactions with air radiolysis compounds than to direct radiations. $RuO_4(g)$ stability under radiolysis is legitimately questionable**.** The few experimental tests from literature are summarized below.

Igarashi's team [49] has studied NO_x action on $RuO_4(g)$ stability. The addition of NO and NO_2 facilitates ruthenium absorption in water. This effect is even stronger in the case of monoxide. Addition of NO_2 with an NO_2/RuO_4 molar ratio of about 189 reduces the proportion of tetroxide in the gas phase by a factor 168, and the addition of NO with a 22 ratio, reduces it by 1180.

This phenomenon could be due to tetroxide transformation into a nitrosylruthenium complex, which is less volatile and more soluble in water.

Fletcher *et al.* [50], in 1955, demonstrated the formation of a species of bi-nuclear ruthenium. This species is obtained via the reaction:

$$2\ RuO_4 + 8\ NO\ \rightarrow\ Ru_2N_6O_{15} + N_2O \qquad\qquad\qquad Eq.\ 4\text{-}2$$

In the presence of water, the final compound is not only $Ru_2N_6O_{15}$ form - aquo-nitrato-$RuNO^{3+}$ forms are also generated [51].

4.1.2 THERMAL AND RADIOLYTIC REACTIVITY OF RUTHENIUM DIOXIDE

If $RuO_2(c)$ reactivity with air is reasonably limited because of its thermodynamic stability, a possible release of $RuO_4(g)$, at 600 K, has been shown experimentally [13] coming from $RuO_2(c)$ deposit, the RuO_4 partial pressure measured is of about 10^{-6} bar. Maas and Longo [52] also suspected the possibility of re-oxidizing ruthenium dioxide with air at low temperatures.

From a theoretical point of view, the equilibrium constant calculated [36] for the reaction: $RuO_2(s) + O_2(g) \leftrightarrow RuO_4(g)$, is equal to 5.10^{-17} at 373 K. For an oxygen partial pressure of approximately 0.2 bar, the resulting tetroxide concentration is about 3×10^{-19} mol.L^{-1}. This reaction cannot form tetroxide in great proportion. RuO_2 reactivity seems to be limited with oxygen, but for radiolysis products it is no longer the case.

Reactivity with ozone: $RuO_2(s) + 2/3\ O_3(g) \leftrightarrow RuO_4(g)$, is much higher, indeed K=0.2 at 373 K. For prototypical ozone concentration, estimated at approximately 10^{-8} mol.L^{-1} or 3×10^{-7} bar, the tetroxide partial pressure obtained is about 2×10^{-7} bar, or 6×10^{-9} mol.L^{-1} in terms of concentration.

Reactivity with nitrous oxide is also enhanced, as indicated by the reaction follow:

$$RuO_2(s) + 2\ N_2O(g) \leftrightarrow RuO_4(g) + 2\ N_2(g) \qquad\qquad K=2.6\times10^{14}\ at\ 373\ K.$$
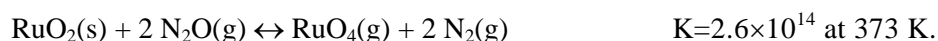
According to air radiolysis model, for an N_2O concentration of about 10^{-6} mol.L^{-1}, corresponding to 3×10^{-5} bar, the consumption of all $N_2O(g)$ will lead to the production of RuO_4 with a $1.5.10^{-5}$ bar partial pressure once equilibrium has been reached.

Another reaction between ruthenium dioxide and nitrogen dioxide is also possible by the following reaction: $RuO_2(s) + 2\ NO_2(g) \leftrightarrow RuO_4(g) +\ N_2(g) + O_2(g)$ K = 0.2 at 373 K

If the NO_2 concentration is identical to that of N_2O, equilibrium is not moved a lot to $RuO_4(g)$ formation. For a NO_2 partial pressure equal to 10^{-6} mol.L^{-1}, P_{RuO4} should not be over 10^{-10} bar when equilibrium is reached. This reaction does not constitute a potential source of gaseous tetroxide formation.

Even if RuO_2 and RuO_4 are the species of main interest, ruthenium hydroxides or oxy-hydroxide species in gaseous state can also exist. Unfortunately, very few data in literature are available on this subject, insofar as no experimental evidence has been published yet; only a few authors have mentioned them because they have demonstrated their thermodynamic stabilities in gaseous phase. Two compounds might exist, RuO_3OH and $RuOH$. In our conditions, only $RuO_3(OH)$ could come up since it would be stable when temperatures are low. Its partial pressure is supposed to be close to 10^{-7} bar at 500 K according to FACT thermodynamic code [53].

In absence of references, all previous equilibrium constants were calculated with COACH, the database associated to GEMINI 1 [36].

The study of previous reactions, associated with the few experimental results highlights that RuO_2 deposits could be oxidised to a significant extent leading to gaseous ruthenium tetroxide formation, with partial pressures that may reach 10^{-7} to 10^{-5} bar in the containment.

4.2 RUTHENIUM THERMAL REACTIVITY IN AQUEOUS PHASE

A severe accident leads to the formation of an aqueous phase in the containment (with a minimum volume of about 200 m^3 corresponding to the water volume of the RCS for a French PWR 900 MWe, for example).

Ruthenium behaviour in aqueous solution has to be considered for an accurate source-term evaluation. Indeed, the aqueous reactions could either trap ruthenium in solution through stabilisation, or produce volatile ruthenium tetroxide.

Possible forms in solution are mainly RuO_4 transferred from the gaseous phase, RuO_2 coming from the soluble aerosol settling, and ruthenate and perruthenate coming from the settling of mixed aerosols. Sump pH may vary from 4 to 10, according to the availability of the spray system.

4.2.1 BEHAVIOUR OF DISSOLVED TETROXIDE

Ruthenium tetroxide is a soluble molecule in water as reported in Table III. According to the pH solution, it can be present in H_2RuO_5 acid form, known as "hyperruthenic", and it is an amphoteric species. Martin [54] suggested that RuO_4 could act as a weak acid and as a weak basis, as shown with the following equilibria:
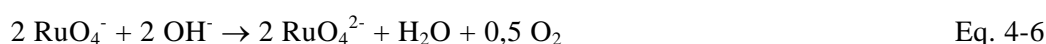
weak acid:

$$RuO_4 + H_2O \Leftrightarrow H_2RuO_5$$
$$H_2RuO_5 + H_2O \Leftrightarrow HRuO_5^- + H_3O^+ \qquad pKa= 11.2 \text{ at } 298 \text{ K} \qquad \text{Eq. 4-3}$$

weak basis:

$$H_2RuO_5 \Leftrightarrow HRuO_4^+ + OH^- \qquad pKa = 14.2 \text{ at } 298 \text{ K} \qquad \text{Eq. 4-4}$$

Zoubov *et al.* [55] have specified that tetroxide decomposes rapidly with light, forming a black deposit of $RuO_2,2H_2O$ hydrated dioxide. Hydrochloric acid reduces RuO_4 in tetra- and trivalent complex forms, becoming oxidised into chlorine.

The analysis of pH-potential diagram [33], and that of redox potential values, indicated in Table IV, show that in pH range of interest (4-10), tetroxide is not stable, at 298 K, in aqueous solutions without oxidizing and complexing agents. Reduction to hydrated ruthenium dioxide or into Ru metal occurs. In a sodium hydroxide solution, tetroxide is reduced in perruthenate (Ru-VII) and ruthenate (Ru-VI) ions [26]:

$$2 RuO_4 + 2 OH^- \rightarrow 2 RuO_4^- + H_2O + 0,5 O_2 \qquad \text{Eq. 4-5}$$
$$2 RuO_4^- + 2 OH^- \rightarrow 2 RuO_4^{2-} + H_2O + 0,5 O_2 \qquad \text{Eq. 4-6}$$
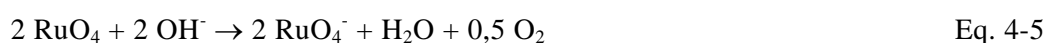
Nowogrocki *et al.* [56] have studied Eq. 4-6 reaction in a RuO_4^- concentration range of about 10^{-2} mol.L^{-1} and the following kinetic rate law was determined:

$$\frac{-d[RuO_4^-]}{dt} = k\,[RuO_4^-]^2.[OH^-]^3 \qquad \text{with k= 20 L}^4\text{.mol}^{-4}\text{.h}^{-1} \text{ (at room T)}$$

Nikitina *et al.* [57] have also studied kinetics of perruthenate reduction into alkaline solution, but in much lower concentration ranges ($10^{-4}/10^{-6}$ mol.L^{-1}). With constant ionic strength, the kinetic rate law of RuO_4^- reduction was established:

$$\frac{-d[RuO_4^-]}{dt} = k_1\,[RuO_4^-]^2.[OH^-] + k_2\,[RuO_4^-]$$

with k_1= 0.41 ± 0.08 L^2.mol^{-2}.s^{-1} and k_2= (1.2 ± 0.3).10^{-4} s^{-1} at 293 K

These two kinetic rate laws provide very significant differences in the perruthenate disappearance rate.

As shown on potential-pH diagram, at room temperature, orange solutions of ruthenate are stable in very alkaline medium. If the pH is sufficiently decreased, below 12, ruthenate disproportionates into green perruthenate, and $RuO_2,2H_2O$, as indicated in Eq 4-7:

$$3\,RuO_4^{2-} + 4\,H^+ \rightarrow RuO_2,2H_2O + 2\,RuO_4^- \qquad\qquad \text{Eq. 4-7}$$
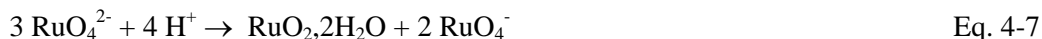
This ruthenate disproportionation reaction was checked experimentally by Connick and Hurley [58], who worked with quite low Ru concentrations, approximately 10^{-5} mol.L^{-1}. However, they suggested the following general reaction:

$$3\,RuO_4^{2-} + (2+x)\,H_2O \rightarrow 2\,RuO_4^- + RuO_2,xH_2O + 4\,OH^- \qquad \text{Eq. 4-8}$$
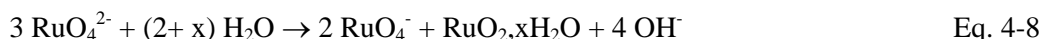
The precipitate obtained was analysed with X-ray diffraction (before and after heating at 413 K and next at 973 K), and the results confirm the $RuO_2,2H_2O$ form.

For pH lower than 12, perruthenate can now be reduced into hydrated dioxide as follows:

$$4\,RuO_4^- + 4H^+ + 6H_2O \rightarrow 4\,RuO_2,2H_2O + 3\,O_2 \qquad\qquad \text{Eq. 4-9}$$
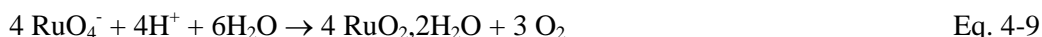
Nevertheless, the degree of hydration of the ruthenium dioxide is still uncertain. Zoubov *et al.* [55] are inclined to favour $RuO_2,2H_2O$ formation, while other authors, like Nowogrocki [56] or Rard [31], proposed the generic Ru_2O_5, xH_2O compound formation instead.

Zoubov *et al.* [55] indicated that when pH is lower than 7.5, ruthenate ion decomposition can lead to the formation of RuO_4 or H_2RuO_5 ("hyperruthenic acid"). This statement was also confirmed by Nowogrocki and Tridot [59] who performed ruthenate and perruthenate solution acidification tests, by making measurements with spectrophotometry, pH-metry, and conductimetry. Ionic equilibria and redox equilibria make it possible to confirm Zoubov's results. They suggest a reactional mechanism, which is slightly different from the previous ones, in particular due to the formation of a pentavalent ruthenium hydrated oxide instead of hydrated dioxide such as:

$$2\ RuO_4^{2-} + 3\ H^+ \xrightarrow{\ H_2O\ } RuO_4^- + RuO_x\ (aq) \hspace{3cm} \text{Eq. 4-10}$$

$$3\ RuO_4^- + 3\ H^+ \xrightarrow{\ H_2O\ } 2\ RuO_4 + RuO_x\ (aq) \hspace{3cm} \text{Eq. 4-11}$$

It can be summarized as: $3\ RuO_4^{2-} + 6\ H^+ \xrightarrow{\ H_2O\ } RuO_4 + 2\ RuO_x\ (aq)$ \hspace{1.5cm} Eq. 4-12
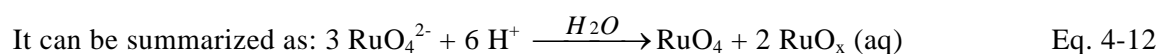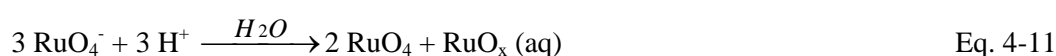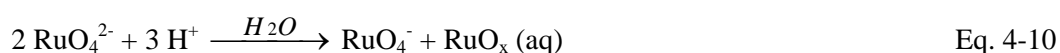
Nowogrocki *et al.* [56] demonstrated the possible formation of volatile ruthenium tetroxide from a 0.5 N sodium hydroxide solution containing perruthenate ions in the presence of an oxidizing agent of hypochlorite type.

This information is important in terms of nuclear safety because these boundary conditions are probable. Ruthenium ionic species [(+VII) and (+VI)] can be present in acid or in alkaline sump, oxidizing agents (due to radiolytic compounds) can be also there. To sum up, the aqueous phase could be a potential source of volatile ruthenium. Table V recapitulates the stability domain of the main ruthenium compounds as a function of pH conditions.

4.2.2   *RuO$_4$ VOLATILITY*

In studying RuO_4 partition coefficients between the organic phase and aqueous phase, for different acidities, Martin [54] noticed that ruthenium tetroxide in water and in CCl_4 made an ideal mixture (for dissolved RuO_4 concentration lower than 0.2 mol.L^{-1}; RuO_4 vapour pressure in equilibrium with CCl_4 solution at 303 K obeys Henry's law).

Nikol'skii [38] measured RuO_4 saturation vapour pressure between 1 K and 364 K. Two empirical equations were recommended in order to calculate $P_{SatRuO4}$ as a function of temperature (lower or upper than 298 K corresponding to the tetroxide melting point). Sublimation, vaporization and fusion enthalpies were also calculated, as well as theoretical melting (298 K) and boiling points (364 K).

For 273 K < T < 298 K:

$$\log P = \frac{2880.3}{T} + 10.673 \quad \text{(T in K and P in mm Hg)}$$

The uncertainty associated to P is approximately 5%.

For 298 K < T < 364 K:

$$\log P = \frac{-2847.9}{T} + 1.75\log T - 0.008406T + 8.737 \quad \text{(T in K and P in mm Hg)}$$

The uncertainty associated to P is approximately 2%.

By comparison between Nikol'skii's values and those of the COACH thermodynamic database [36], it is obtained at 300 K and at 360 K respectively, 1.5×10^3 and 2.5×10^4 Pa with Nikol'skii relationships, 4.9×10^2 and 8.8×10^3 with COACH database. Uncertainties concerning vapour pressure is quite large.

4.2.3 SOLUBLE RUTHENIUM DIOXIDE

Ruthenium dioxide in its hydrated form, RuO_2,xH_2O with 2< x <3, may be soluble in aqueous phase, even if solubility turns out to be difficult, especially in a non complexing acid medium [33].

Solubility is due to the formation of the following specific compounds (monomer or polymer):

$RuO_2, 2H_2O$ (c) $\rightarrow Ru(OH)_2^{2+}$(aq) + 2 OH$^-$ Eq. 4-13

$K_S = [Ru(OH)_2^{2+}$(aq)] $[OH^-]^2 = 8.5\times10^{-28}$

and: 4 $Ru(OH)_2^{2+}$ + 4 $H_2O \rightarrow Ru_4(OH)_{12}^{4+}$(aq) + 4 H^+ Eq. 4-14
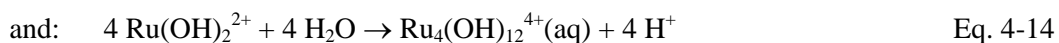
$K_S = 7\times10^{-46}$

There is a slow polymerisation of Ru(IV) monomer, which makes thermodynamically stable tetramer [60] [61]. This species was observed experimentally by Bremard *et al.* [62], they also showed that this tetramer can precipitate into an hydroxide according to Eq. 4-15.

$$Ru_4(OH)_{12}{}^{4+} + 4\ OH^- \rightarrow 4\ Ru(OH)_4 \qquad\qquad Eq.\ 4\text{-}15$$

Equation 4-15 writing is purely formal for ion precipitate because it is probably hydrated.

Finally, even if according to pH-potential diagram, $RuO_2,2H_2O$ is insoluble in non complexing acid solutions, it can be dissolved partially in mono or polynuclear forms. It could even appear in hexavalent state in ruthenate form in the presence of oxygenated alkaline solutions [55].

4.2.4   *RUTHENIUM HYDROXIDES*

$Ru(OH)_3$ hydroxide is stable in aqueous phase, whatever the pH and for a certain range of potential. Otherwise, it is likely to be oxidised into hydrated dioxide $RuO_2,2H_2O$ or $Ru(OH)_4$ even into RuO_4; it can be also easily reduced into elementary ruthenium [55].

4.2.5   *SOLUBLE RUTHENIUM AEROSOLS*

When soluble ruthenium aerosols are dissolved, they liberate either ruthenate or perruthenate anions, as a consequence the chemistry involved is the same than already described for these compounds.

4.3   RUTHENIUM REACTIVITY UNDER RADIOLYSIS IN AQUEOUS PHASE

The presence of radionuclides in sump, in severe accident conditions, will produce a large dose rate (up to 10 kGy/h) in this phase, and will then lead to aqueous solution radiolysis phenomenon. As the main compound in this phase is water, we can easily go back to a water radiolysis issue. Sodium hydroxide introduced via the containment spray system does not question this hypothesis, nor initial presence of boric acid (H_3BO_3) in primary system. Water radiolysis produces molecular, ionic and radical species, which may be either oxidizing or reducing agents. Redox reactions, involving ruthenium dissolved species into solution, may take place.

Ruthenium can react with radiolytic compounds. The most numerous free radicals are $e^-_{(aq)}$ and $OH^\bullet$, $H^\bullet$ is present in lesser extent [63].

Hydrated electron is a powerful reducing agent, while $OH^\bullet$ is a strong oxidizing agent. Rate constant for radical reactions are often high, approximately 10^9-10^{10} L.mol^{-1}.s^{-1}, close to the diffusion limit.

The analysis of redox potentials of $O_2/O_2^{\bullet-}$ (-0.33V) and $(O_2 + 2H^+)/H_2O_2$ (1V) show that $O_2^{\bullet-}$ can be either oxidizing or reducing agent. It is a weaker oxidizing agent than $OH^\bullet$, but able to reduce metallic ions ($HO_2^{\bullet-}$, its conjugated acid, is stronger than $O_2^{\bullet-}$). In acid medium, when there is no reactant, $O_2^{\bullet-}$ reacts preferentially with $HO_2^{\bullet-}$ to give hydrogen peroxide.

Generally H_2O_2 is not very reactive, but its action should not be omitted, it is both an oxidizing and a reducing agent. Indeed, concerning iodine for example, H_2O_2 is able to reduce I_2 into I^-. Finally, hydrogen radical $H^\bullet$, which corresponds to conjugated acid of aqueous electron, is also a strong reducing agent.

For the ruthenium safety issue, our interest is limited to the potential role of oxidizing agent on ruthenium behaviour. The redox potential reported in Table VI [64] [65] show us that the presence of hydroxyl radical $OH^\bullet$ could stabilize $RuO_4(aq)$ due to the very high redox potential of $OH^\bullet/H_2O$ couple and this is also true for H_2O_2/H_2O couple.

So in severe accident conditions, ruthenium tetroxide could be stable in the sump. Table VII is the update of Table V taking into account the radiolytic conditions and not only the thermal conditions.

Haïssinsky *et al.* [66] have performed ruthenate ions radiolysis experiments in sodium hydroxide aqueous solution. The radioactive source was ^{60}Co with an activity of 1700 Ci (max. dose rate 4.8 kGy.h^{-1}). Sodium ruthenate was reduced into Ru-IV hydroxide precipitate. Nevertheless, perruthenate ions, RuO_4^-, are supposed to be formed transitorily due to the following oxidation reaction:

$$RuO_4^{2-} + O^{\bullet-} + H_2O \rightarrow RuO_4^- + 2\ OH^- \qquad\qquad\qquad \text{Eq. 4-16}$$
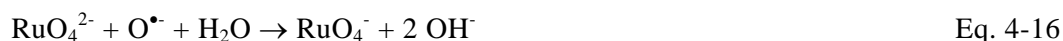
Ruthenate reduction yield falls when its concentration rises, which is directly attributed to the reaction with radical-ions $O^{\bullet-}$. Ruthenate disappearance and Ru(IV) hydroxide formation increase in aerated solution and at low concentration in Ru(VI) (approximately 10^{-4} M), but the reduction is not complete even for long irradiations (100 h, corresponding to 480 kGy).

No specific study of reactions between ruthenium compounds and hydrogen peroxide (H_2O_2) is available in literature.

5   INTERACTIONS BETWEEN RUTHENIUM OXIDES AND CONTAINMENT SURFACES

For example, in French PWR 900 MWe, the internal wall of reactor containment building is covered with a 6 mm thick metal "skin", made of steel [67], which ensures leak tightness. This metallic "skin" is painted to improve leak tightness, protect against corrosion but also for easier decontamination in case of incidents or accidents. The paint which is most often used in the containment is a waterbased polyamide epoxy type. Its chemical structure was established during Aujollet's PhD [68]. Concerning PWR 1300/1450 MWe, there is no metallic skin; but the concrete wall is also painted in the same way.

Inside the containment, there are also lots of other elements made of steel but not painted, for example the steam generators and all the hoopings that maintain the heat insulator. Most of these surfaces are made of stainless steels of the 316L and 304L types [23].

5.1   REACTIVITY OF RUO$_4$ WITH SURFACES IN GASEOUS PHASE

No experimental study of the interaction between gaseous ruthenium tetroxide and paints (epoxy) has been carried out yet. However, it is well known that RuO$_4$(g) is very reactive with organic compounds [25] [27] [26]. Tetroxide is used in organic chemistry as an oxidizing agent. Table VIII gathers the various organic compounds which can be oxidised by RuO$_4$. A strong reactivity of tetroxide vapours with the painted surfaces of the containment can be expected.

On the other hand, ruthenium tetroxide affinity for iron oxides has already been studied [52] [69]. Besides, ruthenium was also found on structure material particles (Fe and others) after the Chernobyl accident. Kashparov *et al.* [70] think that the origin of these particles is linked to the following process: firstly, Ru seems to have been oxidised in the fuel particle surface, and secondly, RuO$_4$ seems to have been vaporized and finally these vapours seem to have condensed onto aerosol particles formed by structure materials.

Maas *et al.* [52] mentioned that ruthenium trapping by iron oxides is very efficient, at about 99.9 %. The following deposition mechanism was proposed: RuO$_4$(g) $\rightarrow$ RuO$_2$(s) + O$_2$(g) (Eq. 4-1).

The large specific surface of iron oxides and the variability of iron oxidation states are supposed to promote the reduction of RuO$_4$ onto the surface. Even if RuO$_2$ is often considered as "fixed" irreversibly by iron oxides, so avoiding any later re-volatilisation, the deposition mechanism is not really understood, no existence of mixed ruthenium/iron oxides has yet been mentioned.

Holdoway [69] performed various tests in order to study ruthenium volatilisation and RuO$_2$ deposition phenomena. One of them consisted in heating ruthenium dioxide which had been previously activated (^{103}RuO$_2$(s)), up to 1323 K under an O$_2$ stream, and then follow the vaporised ruthenium dioxide progressively deposited along the stainless steel thermal-gradient tube located downstream the furnace.

The measured deposits are distributed as shown in Table IX. The results obtained clearly indicate the existence of a volatile ruthenium compound, even at low temperature, contrary to thermodynamic predictions. The most probable candidate is ruthenium tetroxide.

Deposition reactions considered by Holdoway are:

$$RuO_3 \text{ (g)} \leftrightarrow RuO_2 \text{ (s)} + 1/2\ O_2 \qquad\qquad \text{Eq. 5-1}$$

$$RuO_4 \text{ (g)} \leftrightarrow RuO_2 \text{ (s)} + O_2 \qquad\qquad\qquad \text{Eq. 4-1}$$

Ruthenium deposits on steel are apparently not uniform, because deposits take place in priority on already deposited RuO_2 and not on still available surface sites. The presence of RuO_2 would then catalyse RuO_4(g) condensation. Moreover, this self-catalytic reduction phenomenon is also mentioned by various authors [35] [24] [52].

Ortins de Bettencourt and Jouan [24] have observed that the nature of the ruthenium deposits varies as a function of the temperature deposition. Around 773 K, ruthenium is deposited in an irreversible way; but at 423 K, the crystals obtained disappear completely when the tube is rinsed. The latter are assumed to be hydrated RuO_2, or Ru_2O_5, whose existence has already be mentioned by Debray and Joly [42].

The Eichler's German team [29] also studied adsorption of ruthenium tetroxide onto stainless steel substrates. During thermochromatography tests carried out between 1500 and 300 K, a large proportion of the ruthenium was volatilised under an oxygen stream, and some of it settled in the column around 800 K, a weak part, probably in RuO_4 form, was able to reach the active charcoal trap set at the outlet at room temperature. When quartz powder was added, ruthenium volatility was strongly reduced and the fraction which reached the charcoal trap was drastically reduced, near zero. Furthermore a second deposit area, at about 400 K, occurred. The authors interpreted the deposit phenomena with the same reactions as Holdoway (Eq. 5-1, and Eq. 4-1). RuO_2(s) is then in equilibrium either with RuO_3 or with RuO_4, according to temperature and oxygen partial pressure, as Schäfer *et al.* [30], as well as Bell *et al.* [21], have already assumed. Finally, Eichler [29] attributed the low temperature deposit area, at about 400 K, to the formation of RuO_3(s) in non-equilibrium conditions, even if its existence has not been established. RuO_3(g) would no longer be in equilibrium with RuO_2(s), as expected at high temperatures, but gaseous ruthenium trioxide would condense directly.

Another possible adsorption reaction at quite a low temperature can be:

RuO_4 (g) $\rightarrow$ RuO_3(ads) + 1/2 O_2 whose enthalpy of dissociation reaction has been calculated: -19.3 $\pm$ 11 kJ.mol^{-1}.

The existence of ruthenium trioxide in solid form was also mentioned by Kim *et al.* [71] who provides its XPS spectrum with binding energy values for Ru 3d5/2 and O1s. They found a surface layer corresponding to RuO_3 on anhydrous RuO_2(s).

As mentionned previously, Zimmerman *et al.* [35] focused their studies on RuO_4 photochemical decomposition and the resulting products formed. A thin brown layer of RuO_3(s), for irradiating photons with a wavelength of 438.5 nm, was observed. According to the authors, the only energetically possible elementary process would be:

$$2\ RuO_4(g) \rightarrow 2\ RuO_3 + O_2(g) \qquad\qquad\qquad \text{Eq. 5-2}$$

in which RuO_3 could either be gaseous ($\Delta G°_{298}$ = +197 kJ.mol^{-1} and $\Delta H°_{298}$ = +264 kJ.mol^{-1}) or solid.

Sakurai *et al.* [72] studied RuO_4(g) interactions with various surfaces, including stainless steels, at room temperature and low pressure. Contrary to the already quoted hypothesis concerning RuO_4 decomposition into (RuO_2 + O_2), they were not able to obtain any experimental evidence about dioxide formation, even if the black colour of the deposit is consistent with RuO_2. First, no oxygen release was experimentally measured. Secondly, the spectrum from X-ray diffraction did not correspond to that of RuO_2, and was different from the well characterized spectra of the oxides of the different metals concerned, and thirdly they even observed ruthenium deposits on gold, *a priori* well known to be non oxidable. These facts meant they could refute the assumption of metal oxidation by ruthenium tetroxide, reduced into RuO_2, which lead to form metal oxides. To support this assumption, no presence of ruthenium mixed oxides with atoms of the various substratum involved was detected by XRD and XPS analysis. No atom of the metal substratum on the deposit surface was also observed, not even in the sub-surface down to a depth of approximately 20 Å. Moreover, temperatures of about 1273 K are generally necessary to form mixed oxides [73], but these tests were carried out at room temperature.

Hydrolysis of this deposit turned out to be efficient and led to hydrogen peroxide release, measured with spectrophotometric and iodometric methods. Some of the hydrolysed compounds were able to cover the initial ruthenium black deposit and protect it from any later hydrolysis. The oxidation state of the ruthenium deposit was determined to +IV by performing XPS and IR analysis. According to all these elements, it was concluded that the deposit was not RuO_2, but a ruthenium tetroxide form modified being in contact with the metal. In fact a RuO_4 molecule is supposed to be linked to another one via peroxide Ru-O-O-Ru bonds. In that case, the black deposit observed would consist of $(RuO_4)_n$ polymerised with peroxide bonds.

The hydrolysis reaction may correspond to ruthenium hydroxide formation:

$$2 \ RuO_{4 \ (deposit)} + 8 \ H_2O \rightarrow 2 \ Ru(OH)_3 + 5 \ H_2O_2 \hspace{3cm} \text{Eq. 5-3}$$

Cains and Barnes [74] have also, using XRD spectral analysis, characterized ruthenium deposits formed from $RuO_4(g)$, at temperatures of about 423 K and above. Ruthenium dioxide in crystal form was determined without any bonds with ferrous metal. XPS analysis of Ru 3p and 3d levels confirmed it.

Supposing ruthenium tetroxide can be adsorbed easily on iron substrates, the information published in literature is not consistent concerning the adsorption mechanism involved and the deposited products resulting from the ruthenium-iron oxide interaction. If a pseudo-consensus about the ruthenium dioxide presence in the deposits exist, others species might be expected.

5.2 REACTIVITY OF DISSOLVED SPECIES WITH IMMERSED SURFACES

Immersed surfaces in sump contain substrates which are potentially reactive towards ruthenium species dissolved in this aqueous phase. Nevertheless, the total surface is quite small compared with total surface in the atmosphere. Most of the immersed steel or concrete surfaces are painted while a small section of steel surface is not painted. No data was found in the literature on paint/dissolved ruthenium interactions; but reactivity towards stainless steel has already been broached.

Carlson [75] studied the deposit of dissolved ruthenium onto stainless steel etched plates during 6 hours, in buffer solutions, at pH 4, 7 and 9, at 333 K. pH increases ruthenium adsorption on stainless steel. Whatever the buffer employed, the fraction deposited after 24 h (or 168 h) is always low, the maximum is reached at pH 9, with approximately 10 %, while it is only respectively 1% and 0.5% at pH 7 and 4. At pH 9, equilibrium is not reached after 24 hours, the kinetic of adsorption is slow. The temperature effect is significant, indeed deposited ruthenium fraction rises with temperature gradually, over the 6-hour test. Ru deposit did not appear homogeneous on sample plates, it depends strongly on the nature of the metal surface and on the presence, or not, of available adsorption sites. Finally, tests for re-dissolution were not conclusive, the desorbed fraction is very weak, ruthenium is probably chemisorbed.

Belloni *et al.* [76] carried out experiments on the adsorption of ruthenium on different surfaces, as platinum, glass, silver, etc. Unlike some other FPs, Ru adsorption does not follow a Langmuir isotherm, but the kinetic obeys Henry's law (linear isotherm). Moreover, ruthenium adsorption increases with temperature [75] [76], and is barely reversible.

Finally, we would like to point out the existence of an American patent [77] which reveals inhibition of stainless steel corrosion when there is ruthenium in acid solution in contact with steel surfaces. This may be due to surface covering with RuO_2, the latter would then have a covering property and such adsorption on steel would prevent any corrosion phenomenon. This mechanism is very probable, if a parallel is drawn between ruthenium and technetium. Indeed, chemical properties of RuO_2 are close to those of TcO_2, but pertechnetate ions, TcO_4^-, even in very low concentration, are well known [33] to have electrolytic iron and mild steel corrosion inhibitive properties, due to the formation of an insoluble TcO_2 film on their surface.

To sum up, ruthenium species are expected to be reactive on immersed surfaces, with steel or with paint, and the trapping seems to be almost irreversible.

6   CONCLUSION

Basically, the ruthenium chemistry is very complex and all the more so in severe accident conditions, where radiolytic phenomena are involved.

Ruthenium tetroxide is the most volatile ruthenium oxide at the conditions prevailing in the containment, with potential large consequence on source term, so understanding its behaviour is important because, for accidents involving highly oxidizing conditions such as air ingress, its presence in the containment reactor is suspected.

From a thermodynamic point of view, ruthenium tetroxide is not stable at around 373 K but kinetic effect seems to occur and could allow its existence for a while, promoted by the presence of air radiolysis products in the atmosphere resulting in rather oxidizing conditions. Experimental data tend to prove that RuO_4 remains stable at room temperature for a certain lapse of time.

Even if there are some discrepancies in literature concerning the adsorption mechanisms involved and the deposited products resulting from the ruthenium-stainless steel surfaces interaction, it is obvious that tetroxide is very reactive towards steel and paints also. This is true for immersed surfaces too.

In the sump, the oxidizing agents formed by water radiolysis could oxidise ruthenate and perruthenate ions in ruthenium tetroxide.

Concerning ruthenium dioxide which is the main compound of ruthenium expected to reach the containment under aerosol form, it is not soluble generally and it will be distributed in the sump, after settling, or will be deposited onto walls in the atmosphere. Nevertheless, considering redox potential, it can be expected that a fraction of the ruthenium dioxide deposits could be oxidised by ozone which is a product of air radiolysis. Unfortunately, no data was found in literature concerning this potential reaction which could greatly impact the ruthenium source term.

For all the reasons described above, it is of primary importance to obtain experimental data on ruthenium behaviour in severe accident containment conditions, and more precisely on ruthenium tetroxide stability in gaseous phase, and on possible formation of this oxide from ruthenium deposits, or from ruthenate and perruthenate anions.

In the near future, experiments will be carried out to explore this field in order to better quantify the ruthenium source term and get data on kinetics concerning all these potentially relevant reactions.

Acknowledgments

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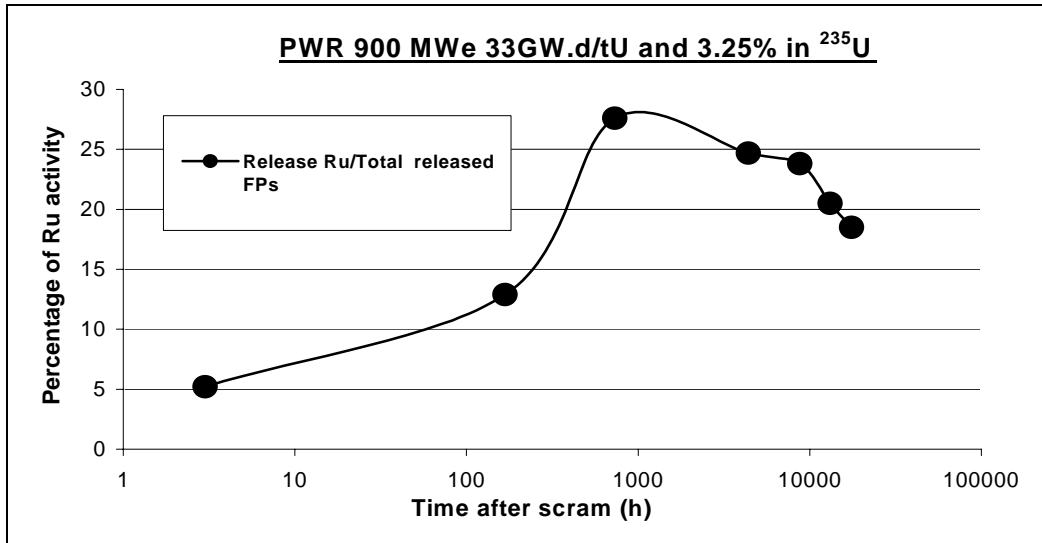
Figure 1: Percentage of Ru activity compared to the total activity of all other FPs.

Xenon and Ruthenium release percentages as functions of time
for HCE3 test H02 (sheathed Darlington fuel, air, 1890°C).

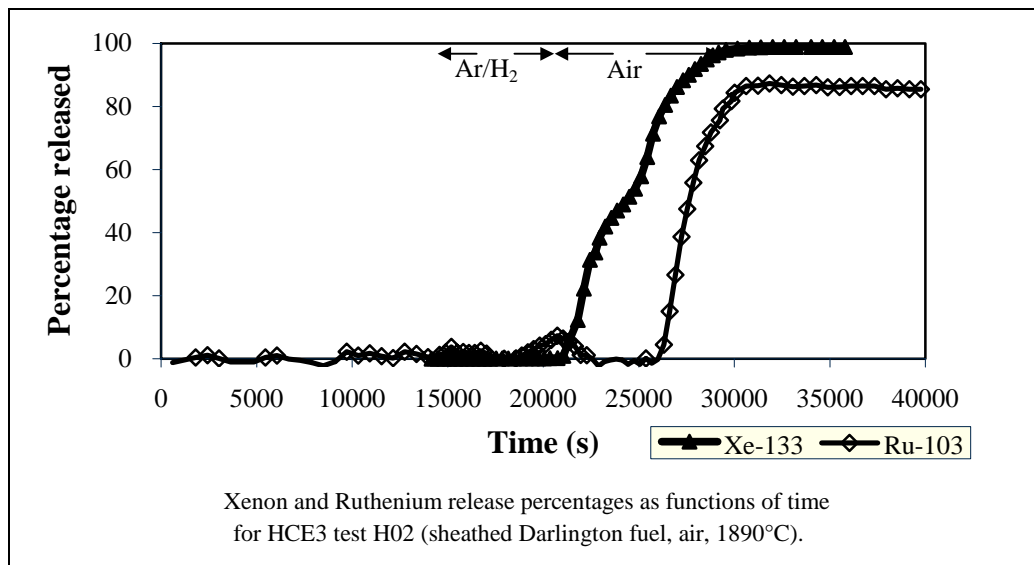Figure 2: Variation of Ru and Xe releases according to the nature of gas flow [12].
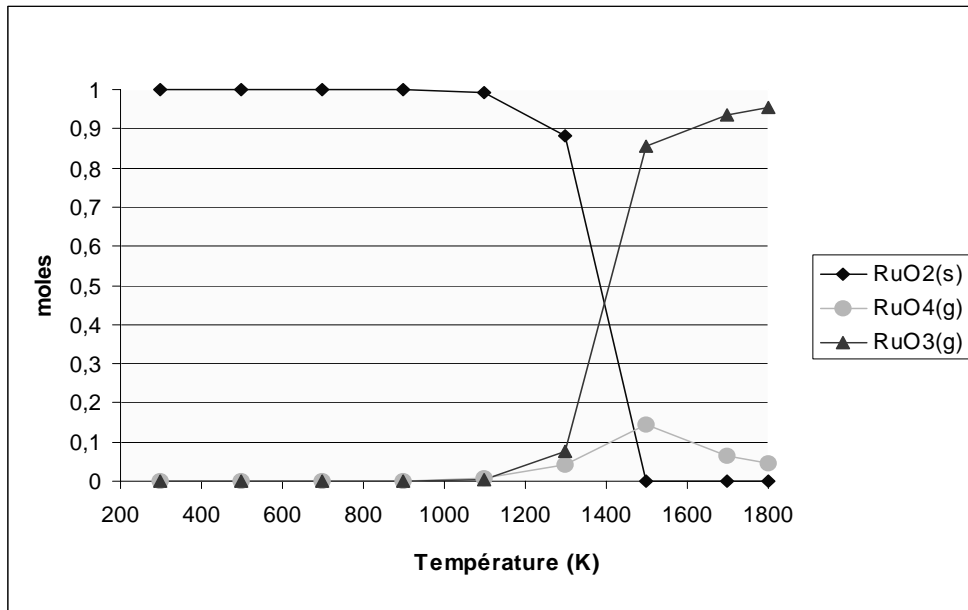
Figure 3: Thermodynamic stability of RuO_4 (g), RuO_3 (g) and RuO_2 (s) as a function of temperature for respectively 1 mole of Ru, 100 moles of H_2O, and 200 moles of O_2 (15% molar).
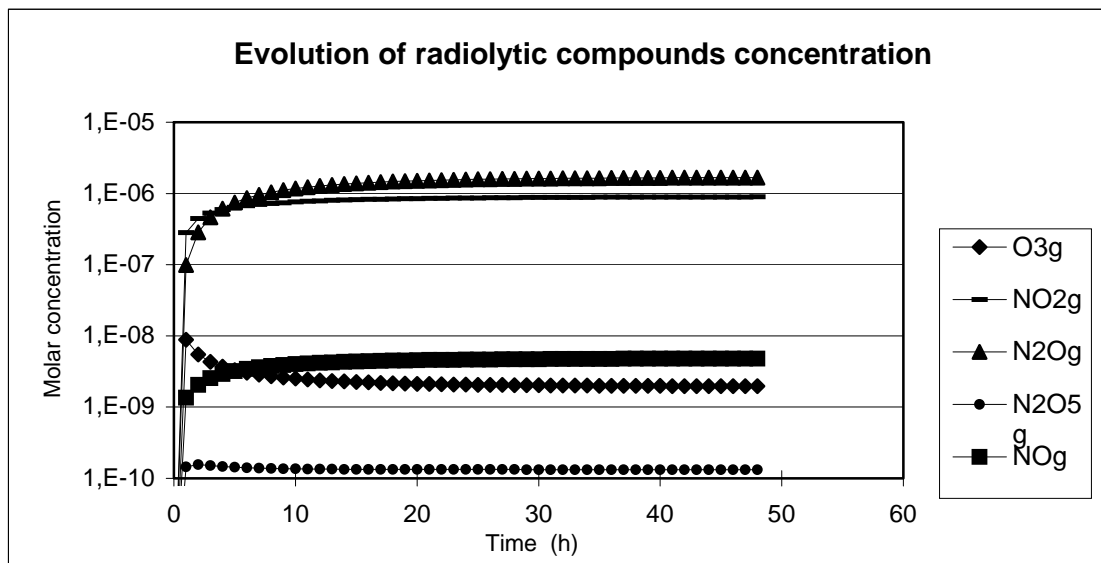

Figure 4: Air radiolysis compounds concentration profiles as a function of time (DR=10kGy.h^{-1}, at 373 K, steam mass fraction = 30%).

Oxidation state	Type of compound	Name	Physical state
+8	RuO_4 (associated with $H_2RuO_5/HRuO_5^-$)	Ruthenium tetroxide	(c), (aq), (g)
+7	RuO_4^-	Perruthenate ion	(aq)
+6	RuO_4^{2-}	Ruthenate ion	(aq)
	RuO_3	Ruthenium trioxide	(g)
+5	$Ru_2O_5, 2H_2O$	Hydrated pentavalent ruthenium oxide	(c)
+4	RuO_2	Ruthenium dioxide	(c)
	$RuO_2, 2H_2O$	Hydrated ruthenium dioxide	(c) and (aq)
	$Ru(OH)_2^{2+}/Ru_4(OH)_{12}^{4+}$	Ru monomer/tetramer	(aq)
	$Ru(OH)_4$	Ruthenium hydroxide	(aq)
+3	$Ru^{3+}/Ru(OH)_3$	Trivalent cation and its hydroxyde	(aq)
+2	Ru^{2+}	Divalent cation	(aq)
0	Ru	Metal ruthenium	(c)

Table I: Possible Ru oxidation states mentioned in this paper.

Temperature	k (min^{-1})	Calculated half-life (h)
293 K	1.3×10^{-8}	8.9×10^5
323 K	1.6×10^{-6}	7220
373 K	9.6×10^{-4}	12
423 K	1.2×10^{-1}	9.6×10^{-2}

Table II: Ruthenium tetroxide decomposition kinetic constant between 293 K and 423 K supplied by Ortner [41].

Temperature (K)	273	283	288	293	298	303	313	323	343	348
Solubility (g.L^{-1})	17.12	18.53	19.63	20.33	21.62	21.13	20.81	20.88	21.41	22.49

Table III: RuO$_4$ solubility in water as a function of temperature [25].

Oxidizing /Reducing Agent	E° (V)	E° (V) – k pH (4)	E° (V) – k pH (10)
RuO$_4$(aq)/RuO$_4^{2-}$	1.59	1.59	1.59
RuO$_4$(aq)/RuO$_4^-$	1.00	1.00	1.00
RuO$_4^{2-}$/RuO$_2$	2.01	1.24	0.53
RuO$_4^-$/RuO$_2$	1.53	1.02	0.55
RuO$_4$(aq)/RuO$_2$	1.40	1.02	0.65
RuO$_2$/Ru^{2+}	1.12	0.94	0.23
RuO$_2$/Ru	0.79	0.55	0.19
O$_2$/H$_2$O	1.23	0.99	0.64

Table IV: Redox potential in acid and alkaline medium, calculated with a 10^{-10} mol.L^{-1} reference concentration in ruthenium [33].

pH	4	7	10
Stable species	RuO$_2$(c)	RuO$_2$(c) RuO$_4^-$	RuO$_4^-$ RuO$_4^{2-}$

Table V: Stability domain of Ru oxides in aqueous solution, as a function of pH.

Oxidizing /Reducing agent	E° (V)	E° (V) – k pH (4)	E° (V) – k pH (10)
$RuO_4(aq)/RuO_4^{2-}$	1.59	1.59	1.59
$RuO_4(aq)/RuO_4^{-}$	1.00	1.00	1.00
RuO_4^{2-}/RuO_2	2.01	1.24	0.53
RuO_4^{-}/RuO_2	1.53	1.02	0.55
$RuO_4(aq)/RuO_2$	1.40	1.02	0.65
O_2/H_2O	1.23	0.99	0.64
$OH^{\bullet}/H_2O$	2.74	2.50	2.15
H_2O_2/H_2O	1.78	1.54	1.18

Table VI: Redox potential as a function of pH, calculated with a reference concentration of 10^{-10} mol.L^{-1} in ruthenium [33].

pH	4	7	10
Stable species	$RuO_2(c)$ RuO_4	$RuO_2(c)$ RuO_4^{2-}/ RuO_4^{-} RuO_4	RuO_4^{2-} RuO_4^{-}

Table VII: Stability range of Ru oxides, as a function of pH, containing oxidizing agents formed by water radiolysis.

Subtrates	Oxidation Products
primary alcohols	aldehydes, carboxylic acids
secondary alcohols	ketones
aldehydes	carboxylic acids
alkenes	aldehydes, carboxylic acids
alkynes	α-diketones, carboxylic acids
amides	imides
ethers	esters
sulphides	sulphones

Table VIII: Organic compounds able to be oxidised by RuO_4.

Sample	Temperature (K)	$^{103}RuO_2$ deposited (γ-counting/min)
1	323	1139
2	324	1474
3	328	1625
4	332	2063
5	339	2695
6	353	2936
7	277	4843
8	413	16092
9	465	23068

Table IX: Test results concerning $^{103}RuO_2$ deposit on stainless steel surfaces [69].