

# XPS investigations of ruthenium deposited onto representative inner surfaces of nuclear reactor containment buildings

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## Abstract

In the case of a hypothetical severe accident in a nuclear power plant, interactions of gaseous RuO<sub>4</sub> with reactor containment building surfaces (stainless steel and epoxy paint) could possibly lead to a black Ru-containing deposit on these surfaces. Some scenarios include the possibility of formation of highly radiotoxic RuO<sub>4</sub>(g) by the interactions of these deposits with the oxidizing medium induced by air radiolysis, in the reactor containment building, and consequently dispersion of this species. Therefore, the accurate determination of the chemical nature of ruthenium in the deposits is of the high importance for safety studies. An experiment was designed to model the interactions of RuO<sub>4</sub>(g) with samples of stainless steel and of steel covered with epoxy paint. Then, these deposits have been carefully characterised by scanning electron microscopy (SEM/EDS), electron probe microanalysis (EPMA) and X-ray photoelectron spectroscopy (XPS). The analysis by XPS of Ru deposits formed by interaction of RuO<sub>4</sub>(g), revealed that the ruthenium is likely to be in the IV oxidation state, as the shapes of the Ru 3d core levels are very similar with those observed on the RuO<sub>2</sub>·xH<sub>2</sub>O reference powder sample. The analysis of O 1s peaks indicates a large component attributed to the hydroxyl functional groups. From these results, it was concluded that Ru was present on the surface of the deposits as an oxyhydroxide of Ru(IV). It has also to be pointed out that the presence of “pure” RuO<sub>2</sub>, or of a thin layer of RuO<sub>3</sub> or Ru<sub>2</sub>O<sub>5</sub>, coming from the decomposition of RuO<sub>4</sub> on the surface of samples of stainless steel and epoxy paint, could be ruled out. These findings will be used for further investigations of the possible revolatilisation phenomena induced by ozone.

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## 1. Introduction

The study of ruthenium behaviour by the French “Institut de Radioprotection et de Sûreté Nucléaire” in cooperation with the CNRS, is motivated by several factors. Firstly, during nuclear reactor operation, the fission-product ruthenium will accumulate in the fuel. The quantity of ruthenium formed increases with fuel burn-up; moreover, its content is more important in mixed oxides (MOX) fuel than in classical UO<sub>2</sub> fuel. As a consequence, the

ruthenium amount formed in fuel life will continuously rise as utilities continuously optimize fuel performance. Secondly, Ru is a high specific activity fission-product. Finally, besides its ability to form oxide compounds which are very volatile, this fission-product has, in addition to its chemical toxicity [1–3], a high radio-toxicity, essentially through its isotopes <sup>106</sup>Ru ( $T_{1/2} = 369$  days) and <sup>103</sup>Ru ( $T_{1/2} = 39.3$  days). During a hypothetical nuclear reactor severe accident (SA), significant release of volatile ruthenium species from fuel matrix may occur if the fuel is oxidized, for instance in the case of air ingress in the reactor vessel. Ruthenium can then flow through the reactor coolant system, and finally reach the reactor containment building. Under the containment building thermal-hydraulic conditions, the most stable gaseous species is the ruthenium tetroxide: RuO<sub>4</sub>(g).

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$\text{RuO}_4(\text{g})$  has been reported to have a certain affinity for iron oxides [4,5] and for organic compounds [6,7]. Therefore, the significant part of surfaces present inside the French pressurised water reactor (PWR) containment buildings may act as an efficient trap for  $\text{RuO}_4(\text{g})$  and so has to be considered in terms of reactivity, as ruthenium is able of contaminating these inner surfaces (epoxy paints) and all stainless steel materials (316 L/304 L). As Ru could be trapped by the surface of these materials, it is believed that it would be present in a chemical form with an oxidation state below 8.

During a SA, the high dose rate in the containment building, linked to the presence of other fission-products than ruthenium, would induce air radiolysis products, notably ozone which is a strong oxidizing agent. Thus, ruthenium deposited onto inner containment surfaces, may be reoxidized up to  $\text{RuO}_4$ . In order to quantify, and next to understand the mechanism involved in this possible oxidation process, information concerning the Ru deposit are required. This paper presents the results of such an analysis and it constitutes a preliminary step of the study devoted to the Ru revolatilisation phenomena.

Over the past decade, it has been demonstrated that XPS technique could provide powerful information regarding oxidation state and stoichiometry for ruthenium oxides [8–11]. Nevertheless, the characterisation by this technique is a very complex subject because Ru 3d peaks are overlaid by C 1s peaks which come from carbon surface contamination. Argon sputtering treatments could be applied to clean up the surface of the samples, but potential secondary effects such as possible reduction of the oxides have to be considered very carefully.

Concerning interactions between gaseous ruthenium tetroxide and stainless steel substrates, some discrepancies exist between the different studies in the literature. Many authors [12–14] agree that ruthenium deposits from  $\text{RuO}_4(\text{g})$  consist of  $\text{RuO}_2$ , according to the reaction  $\text{RuO}_4(\text{g}) \rightarrow \text{RuO}_2(\text{s}) + \text{O}_2$ . Nevertheless, others have questioned this conclusion. For example Eichler et al. [15] attributed the low temperature deposit domain, at about 400 K, to the formation of  $\text{RuO}_3(\text{s})$  in non-equilibrium conditions, even if its existence has not been established. This assumption was also supported by Zimmerman et al. [16] who focused their studies on  $\text{RuO}_4$  photochemical decomposition onto steel substrates. The existence of ruthenium trioxide in solid form was also mentioned by Kim and Winograd [17] who provides well-characterised XPS spectra. They found a surface layer corresponding to  $\text{RuO}_3$  on anhydrous  $\text{RuO}_2(\text{s})$ . Sakurai et al. [18] studied  $\text{RuO}_4(\text{g})$  interactions with various surfaces, including stainless steels, at room temperature and low pressure. Contrary to the already quoted hypothesis concerning  $\text{RuO}_4$  decomposition into  $(\text{RuO}_2 + \text{O}_2)$ , they were not able to obtain any experimental evidence about dioxide formation, even if the black colour of the deposit is consistent with  $\text{RuO}_2$ . According to them, the deposit was not  $\text{RuO}_2$ , but a ruthenium tetroxide form modified by the interaction with the metal. In fact a  $\text{RuO}_4$  molecule is supposed to be linked to another one via peroxide  $\text{Ru-O-O-Ru}$  bonds. In that case, the black deposit observed would consist of  $(\text{RuO}_4)_n$  polymerised with peroxide bonds. It must be noticed that no experimental study of the

interaction between gaseous ruthenium tetroxide and paints has been carried out yet.

Therefore, the actual nature of this deposit is not well characterised up to now and this study is devoted to a better understanding of the properties of this over layer. For that purpose coatings of Ru compounds formed by the interaction of  $\text{RuO}_4(\text{g})$  with samples of stainless steel and also of painted steel, have been prepared and characterised.

In this paper, the experimental set-up dedicated to the generation of crystallised ruthenium tetroxide, and the preparation of the ruthenium coatings, by interaction of  $\text{RuO}_4(\text{g})$  onto the specific substrates previously cited, are briefly described. Then, an overview of the surface observations by SEM/EDS, and the results obtained by EPMA are presented. The XPS results of the ruthenium deposit samples surface analysis are presented and discussed.

## 2. Experimental

### 2.1. Preparation of samples coated with ruthenium deposit

Since  $\text{RuO}_4$  is not commercially available due to its instability, the first step consisted in generating this species as pure as possible, under a crystallised form. The principle of this process is based on the oxidation of Ru(III) to Ru(VIII), and then, thanks to its volatility, ruthenium tetroxide is transported as a gas and finally condensed in a liquid nitrogen cold trap. More details can be found in Ref. [19].

The deposition of ruthenium coatings onto surfaces of stainless steel and painted steel followed the procedure described hereafter. The  $\text{RuO}_4$  crystals were sublimated from the condenser reactor. The sublimation of  $\text{RuO}_4$  usually begins at temperature higher than 7 °C [7,20]. Then, a dry airflow transported ruthenium tetroxide vapours through a glass line to a temperature-controlled reactor, simulating the containment building (called “containment reactor” or CR). Previously, a surface sample was placed inside the CR.

The dimensions of the steel samples were 8.5 mm × 8 mm × 5 mm (thickness), and 13.3 mm × 10 mm × 5 mm (thickness) for the painted samples, in order to be close to the containment surface–volume ratio (0.35). The duration of each adsorption experiment was fixed at 24 h.

The temperature of the CR was set to 90 °C that is representative of the containment temperature during a SA. The pictures of a stainless steel sample, before and after ruthenium interaction, are presented in Fig. 1. The characteristic black colour deposit is clearly seen on these pictures.

### 2.2. Surface analysis experimental procedure

#### 2.2.1. SEM/EDS and EPMA

Concerning the analysis by SEM/EDS, the ruthenium deposits were examined by a Jeol 6330F scanning electron microscope equipped with an Oxford Si/Li LED. An X-ray analyzer coupled to the SEM allows us to perform a semi-quantitative analysis of the sample surfaces. Spectra were analysed using the IMIX/PGT software. We worked without

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