

ToF-SIMS and XPS characterizations of model fission products (I, Cs) deposits after thermal treatment simulating late phase conditions of a nuclear power plant severe accident.

LE FESSANT Elouan¹, GREGOIRE Anne-Cécile¹, NUNS Nicolas³, SIMON Pardis², MAMEDE Anne-Sophie², PAUL Jean-François², CANTREL Laurent¹

¹ Institut de Radioprotection et de Sûreté Nucléaire, PSN-RES,
BP 3, 13115 Saint-Paul-lez-Durance.

² Univ. Lille, CNRS, Centrale Lille, Univ. Artois, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

³ Univ. Lille, CNRS, INRAE, Centrale Lille, Univ. Artois, FR 2638 - IMEC - Institut
Michel-Eugène Chevreul, F-59000 Lille, France

Abstract. During a Severe Accident (SA) occurring in a nuclear power plant, many Fission Products (FP) are released from the degraded fuel and are transported in the Reactor Coolant System (RCS). Depending on their volatility, FP can be either deposited on the surface of the Reactor Coolant System (RCS) or transported into the containment building from where they may be released into the environment in case of early containment failure. This was the case for the Fukushima Daiichi (FD) accident with important FP releases which were observed following the containment vessel failure which lasted up to several weeks after the accident. If early phase releases were well predicted by SA simulation codes, delayed releases were not correctly predicted [1]. Such discrepancies can be attributed to the revaporization of deposits inside the RCS which were not yet modeled in the SA simulation tools. Previous experiments over the past 20 years evidenced the possible formation and revaporization of CsI [2]. However, up to now, no clear CsI revaporization mechanism has been determined. In order to propose a mechanism, this study (scheduled within the OECD/NEA/ESTER project) aims at determining the speciation of each species remaining on the substrate after revaporization tests under different conditions using XPS and ToF-SIMS (X-ray Photoelectron Spectroscopy and Time of Flight Secondary Ion Mass Spectrometry). These two combined techniques allow the identification of the main species of the residue leading to the proposition of two revaporization reactions.

Keywords: XPS, ToF-SIMS, Revaporization, CsI

1. Introduction

During a Severe Accident (SA) occurring in a nuclear power plant, many Fission Products (FP) released from the reactor core region under gaseous or aerosols forms can be either deposited on the surface of the Reactor Coolant System (RCS) or transported into the containment building. During the Fukushima Daiichi (FD) accident, important FP releases involving iodine and cesium were observed following the containment vessel failure and lasted for several weeks after the start of the accident. While early releases are correctly predicted by SA simulation tools, simulations of delayed releases should be improved [1]. The delayed releases observed in the case of FD can be attributed to the revaporization of deposits inside the RCS. To improve simulations, especially in the case of iodine and cesium, the revaporization behavior of CsI – which is one of the main expected deposited forms in the RCS - has been studied for several decades.

Previous experiments over the past 20 years evidenced the conditions that favor the revaporization of CsI deposits [2-3]. CsI powder revaporization is thus reported to start below 500°C and to be completed around 750°C in a steam atmosphere – the main revaporized species is CsI as vapor which can be transported by the steam flow in colder zones where it condenses as submicrometric aerosols. More recent work focused on the revaporization of CsI aerosol deposits

in a temperature ramp (250-750°C)[4]. Under pure air, iodine (I) was released mainly (up to 90% of the initial amount of I) as molecular iodine (I₂) whereas, under pure steam, only CsI was vaporized. For a mixed air/steam atmosphere, revaporization results partly in the formation of gaseous I₂ and CsI, regardless of the air/steam ratio.

Up to now, no clear mechanism for CsI revaporization has been determined – especially in oxidizing conditions. In order to address this issue, our study (in the frame of the OECD/NEA/ESTER project) aims to determine the speciation of each species remaining on oxidized 304L stainless steel samples (called the substrate). After CsI revaporization under different conditions surface characterization techniques are used such as XPS (X-ray Photoelectron Spectroscopy) and ToF-SIMS (Time of Flight - Secondary Ion Mass Spectrometry). Indeed, XPS provides the chemical environment of each element present in the 10 nm surface layer and ToF-SIMS allows the identification of elemental and molecular fragments emitted from the outermost surface. These two complementary techniques allow the identification of the main species remaining at the substrate surface.

Experimentations performed in this study focused on isothermal treatments (between 200 °C and 600 °C) under an oxygen partial pressure over 10⁻² atm. The first results highlight an increase in gaseous iodine release with

temperature. The main objective of this paper is to investigate the nature of the residue, allowing then a better understanding of the mechanisms resulting in the release of gaseous species.

2. Experimental protocol

To be as representative as possible of a SA situation in the RCS, our experimental protocol consists in 4 successive steps:

- 1) Substrate preparation: during a SA, RCS Stainless Steel (SS) is oxidized by the temperature rise combined with steam. Hence, coupons (1.2 cm²) of SS representative of RCS (304L) are oxidized to simulate the RCS oxidation. These pieces of oxidized SS will be used as a substrate for aerosol deposits;
- 2) CsI deposition: a previous study [4] showed that deposits obtained by aerosol impaction at room temperature behave as deposits obtained at higher temperatures. Thus, we retained the technique of aerosol deposition at room temperature. Aerosols are generated by nebulization-drying a CsI concentrated aqueous solution and next deposited by impaction on the SS oxidized sample;
- 3) CsI revaporization: deposits are vaporized in the ATMIRE experimental revaporization setup to simulate FP revaporization (an open flow reactor placed in a high-temperature furnace allowing the atmosphere control above the studied sample);
- 4) Characterization: Both elementary analyses (ICP-MS) and surface analyses (XPS and ToF-SIMS) are performed to determine the mass of residue and to identify its nature with possible interaction with the substrate. XPS analyses are done on a Kratos Analytical AXIS Ultra^{DLD} with a monochromatic Al K α source at 1486.6 eV. The adventitious C 1s (285.0 eV) binding energy (BE) was used as an internal reference. ToF-SIMS analyses are performed on a ToF-SIMS V instrument (ION-TOF GmbH) with a Bi⁺ beam (25 keV, 1,15 nA).

3. Experimental results

Different isotherms were investigated to highlight the temperature influence on CsI reactivity. Two levels of temperature were retained: 410 °C and 520 °C. Tests were performed under 0.8 atm steam partial pressure and 0.2 atm in air (4.10⁻² oxygen partial pressure).

3.1 Cs speciation after revaporization at 410 °C

Remaining elements on the SS coupon were analyzed by XPS after thermal treatment at 410°C of CsI deposit.

Atomic surface composition is detailed in Table I. Cs and O dominates the surface composition whereas the SS elements are detected in low or trace amounts (Mn, Ni, Fe and Cr). Chemical states of these elements are attributed to Cr³⁺ (peak at 275.5 eV, [5]), Fe³⁺ (710.5 eV, [5]), Mn³⁺ (639.4 eV [5]), and Ni²⁺ (855.7 eV [5]). However, the surface is mainly composed of residual Cs compounds. No iodine is detected on the surface, thus iodine is completely revaporized from the coupon.

Table I: XPS surface composition after revaporization at 410°C

Elements	O	Cs	C	Mn	Cr	Ni	Fe
Atomic composition (%)	59.7	24.4	9.0	3.7	0.7	1.3	1.2

Cs 3d_{5/2} XPS spectrum presents a single component at 724.0 eV which is attributed to Cs⁺ [5]. All I is revaporized during the thermal treatment. Thus, Cs remaining in the residue is not under the CsI form. The focus is then placed on oxygen, the main surface element.

O 1s XPS spectrum features a broad peak (Figure 1) which can be decomposed into two components at 531.4 eV (40%) and 529.4 eV (60%). The higher BE component could be mainly attributed to hydroxide while the lower BE component at oxide [5]. Given the atomic OH/Cs ratio close to 1, the presence of CsOH can be assumed. Cs as oxide (Cs₂O, Cs 3d_{5/2} BE = 725.2 eV [5]) is not considered due to its instability under air atmosphere [6].

Complementary surface analysis by ToF-SIMS (Bi⁺ beam) revealed the significant presence of CsO⁺, CsOH⁺ and CsOH₂⁺ fragments confirming the nature of CsOH residue on the sample. No fragment of Cs-C-O or Cs-M-O has been found (M corresponding to metal as Mn, Cr, Ni, or Fe).

Thus, according to these complementary surface results, the residue after revaporisation at 410°C is composed of CsOH.

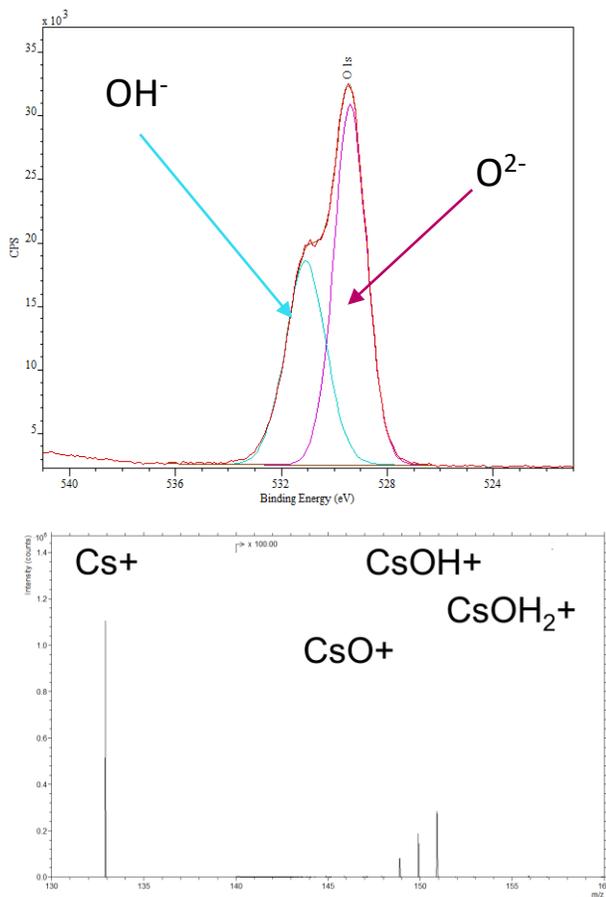


Figure 1: O 1s XPS and ToF SIMS spectra of CsI deposited on SS coupon after revaporization at 410°C in air/steam atmosphere

3.2 Cs speciation after revaporization at 520 °C

Remaining elements on the SS coupon were analyzed by XPS after thermal treatment of CsI at 520°C. Atomic surface composition is detailed in Table II. Cs and O dominate the surface composition. Except for Cr which is detected in low amounts (4.7%), the other substrate elements (Fe, Ni, Mn) are below the detection limit as well as iodine.

Table II: XPS surface composition after revaporization at 520 °C

Elements	O	C	Cs	Cr (+VI)	Cr (+III)
Atomic composition (%)	53.6	30.0	11.7	2.1	2.6

No iodine is detected on the surface, thus iodine is completely revaporized from the coupon.

After revaporisation at a higher temperature (520 °C), Cs is detected in lower amount (11.7%) compared to the revaporisation at 410 °C (24.4%). The Cs 3d_{5/2} peak shows one component at 724.0 eV corresponding to Cs⁺. As

hydroxide is also detected at the surface, Cs can be present as CsOH as previously at 410 °C. Moreover, chromium is significantly detected at the surface. Figure 2 shows that Cr 2p_{3/2} can be decomposed into two components: one at lower BE at 575.5 eV, attributed to Cr+III [5] and the second at 580.0 eV, attributed to Cr+VI [5]. It was shown in a previous study [7] that the appearance of Cr +VI after CsI revaporisation is due to the formation of caesium chromates as Cs₂CrO₄, as evidenced by Raman spectroscopy.

Thus, species based on Cs-Cr mixed oxide forms (featuring Cr(+VI)) can also be assumed. ToF-SIMS analysis of the sample confirmed this assumption with the detection of CsCrO⁺ (Figure 2) and Cs₂CrO₂⁺ fragments. Based on these data, we can deduce that Cs in the residue is mainly CsOH (90% of total residual Cs) and also Cs-Cr mixed oxide form (10%) identified as Cs₂CrO₄. This oxide is indeed the main mixed Cs-Cr oxide form reported in the literature in the same conditions [4], [8], [9]).

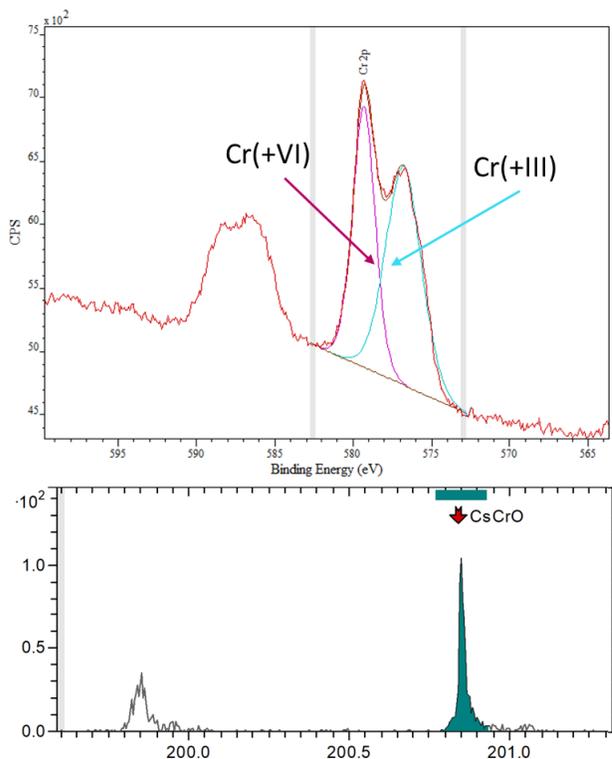


Figure 2: Cr 2p XPS and ToF SIMS spectra of CsI deposited on SS coupon after revaporization at 520°C.

3.3 Iodine Speciation

After revaporisation at 410 and 520°C, no (or trace below detection limit) iodine is detected on the surface by XPS analysis. However, ToF-SIMS is more surface sensitive than XPS, allowing the detection of iodine fragments. The presence of IO⁻, IOH⁻, CsIO⁻ and CsIOH⁻ is highlighted in

Figure 3. Cs_2I^+ is also detected. Thus, the remaining iodine is partly oxidized, partly as CsI . In these experimental conditions, ToF-SIMS allows only a qualitative analysis of detected iodine compounds, the distribution of iodine between these different forms cannot be established.

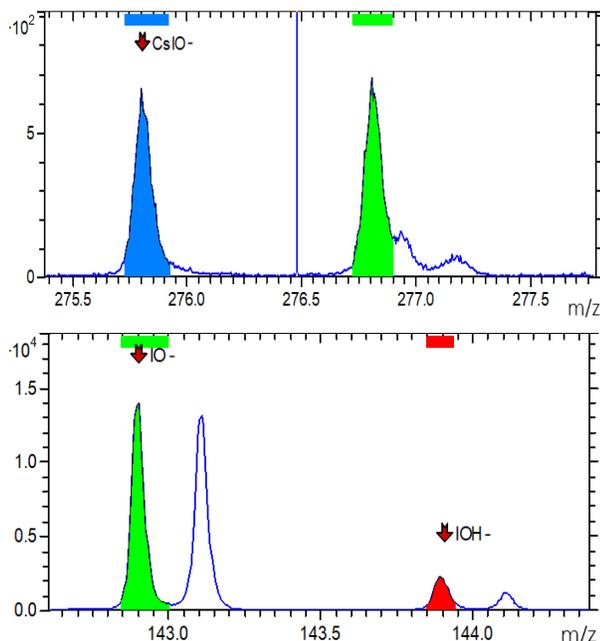


Figure 3: ToF SIMS spectrum of CsI deposit on SS coupon after revaporization at 410°C (with a Bi^+ ion beam and a negative polarity).

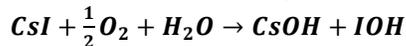
4. Conclusion

Analytical experimental work within the ESTER program focuses on the revaporization of synthetic FP deposits, CsI can be considered as a main source of volatile iodine in case of late-phase releases in oxidative conditions. The purpose is to understand revaporization phenomena to depict/characterize a mechanism that took place during the FD severe accident and led to late releases. The revaporization of CsI deposits under different isotherms was studied leading to an increase of the gaseous iodine release (compared to CsI gas) with temperature.

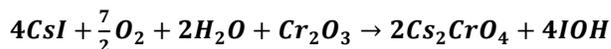
This study focuses on surface analyses of Cs and I residues after revaporization in order to have a better understanding of the revaporization mechanisms. The complementarity of XPS and ToF-SIMS allows the determination of CsOH as the main species in the residue. For the higher temperature, a small part of Cs is under Cs_2CrO_4 form (around 10% of Cs). At the same time, iodine is almost completely revaporized. Traces remaining are under CsI form but also under oxidized form as CsIO and HOI .

These results combined with the increase of gaseous iodine fraction release with temperature may be explained by the two global reactions:

- 1) The main reaction leading to the formation of CsOH :



- 2) In a smaller proportion leading to Cs_2CrO_4 :



Acknowledgments

This work was carried out on the surface analysis facility of the Advanced Characterization Platform of the Chevreul Institute, which is thanked for its help in the development of this work through the ARCHI-CM project supported by the “Ministère de l’Enseignement Supérieur de la Recherche et de l’Innovation”, the region “Hauts-de-France”, the ERDF program of the European Union and the “Métropole Européenne de Lille”. This work was supported by the partners (NRC, GRS, SSM, NRA, EDF, VTT, and KINS) of the OECD/ESTER program

References

- [1] F. Cousin, *et al.*, *Analysis of fission products behavior and environmental releases during the Fukushima-Daiichi accident by direct and inverse approach at IRSN* in Proceedings, NURETH, 18-23 August 2019, Portland, USA.
- [2] N. Girault, *et al.*, *Nucl. Technol.*, **169**, 218–238, (2010). doi: 10.13182/NT10-A9375
- [3] J. Kalilainen, *et al.*, *Nucl. Eng. Des.*, **267**, 140–147, (2014) doi: 10.1016/j.nucengdes.2013.11.078
- [4] D. Obada *et al.*, *J. Hazard. Mater.*, **409**, 124519, (2020), doi: 10.1016/j.jhazmat.2020.124519.
- [5] A. Naumkin, *et al.*, NIST Standard Reference Database 20. National Institute of Standards and Technology, (2012) doi: 10.18434/T4T88K.
- [6] A. Albu-Yaron *et al.*, *Adv. Mater.*, **18**, 2993-2996, (2006), doi : 10.1002/adma.200600983
- [7] A.S. Mamede *et al.*, *Appl. Surf. Sci.*, **369**, 510-519, (2016) doi : 10.1016/j.apsusc.2016.01.185
- [8] H. Shibasaki *et al.*, *Nucl. Technol.*, **134**, 62–70, (2001) doi: 10.13182/NT01-A3186.
- [9] K. Sasaki, *et al.*, *Microstructure analysis for chemical interaction between cesium and SUS 316 steel in fast breeder reactor application* in Proceedings, ICAPP, 24-28 June 2012, Chicago, USA