

Study of the stability of iodine oxides (IxOy) aerosols in severe accident conditions

Olivia Leroy, Loic Bosland

▶ To cite this version:

Olivia Leroy, Loic Bosland. Study of the stability of iodine oxides (IxOy) aerosols in severe accident conditions. Annals of Nuclear Energy, 2023, 181, pp.109526. 10.1016/j.anucene.2022.109526 . hal-03969323

HAL Id: hal-03969323 https://hal.science/hal-03969323

Submitted on 6 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



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

1	Title page
2	Study of the stability of iodine oxides (IOx) aerosols in severe accident
3	conditions.
4	
5	Olivia Leroy, Loic Bosland
6	
7	Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES/SEREX/L2EC, PSN-
8	RES/SAM/LETR, F-13115 Saint-Paul-Lez-Durance, France
9	<u>olivia.leroy@irsn.fr</u>

Study of the stability of iodine oxides (IOx) aerosols in severe accident conditions.
 O. Leroy¹, L. Bosland¹

¹ Institut de Radioprotection et de Sûreté Nucléaire (IRSN), PSN-RES/SEREX/L2EC, PSN-RES/SAM/LETR, F-13115 Saint-Paul-Lez-Durance, France

14 Abstract

15

12

13

Iodine oxide aerosol are formed during a nuclear severe accident in the containment due to 16 17 oxidation of volatile iodine either molecular iodine or organic iodide. These oxides may exist under 18 different chemical forms and more or less stable, decomposition rate has to be experimentally 19 studied to better estimate the source term. Decomposition rates under irradiation have been 20 determined at 80°C and 120°C in presence of humidity. I_xO_y aerosols generated are not thermally 21 stable and the molecular iodine release is dominant. Iodine oxide aerosols decompose under 22 irradiation, whatever the surface deposition and lead to mainly gaseous molecular iodine. The 23 aerosols speciation seems to evolve in humid environment under irradiation towards less stable 24 species. The temperature has a significant effect on iodine oxides decomposition, as well as the 25 nature surface. It has been showed that the radiolytic decomposition of iodine oxide aerosols into 26 molecular iodine can significantly impact the source term evaluation.

27

28 Keywords

29 iodide oxide aerosol, severe accident, radiolytic processes, thermal processes

30

31 **1** Introduction

32 lodine chemistry is of interest in the field of nuclear safety but also in the atmospheric field. Indeed, the life 33 cycle of radioactive species potentially emitted to the atmosphere during a nuclear accident will be the 34 same as that of the same natural stable species under similar atmospheric conditions. In atmospheric field, 35 the oceans provide the main source of iodine to the atmosphere [1] and the annual iodine concentrations 36 are highly positively correlated with those of marine elements involving higher iodine concentrations under 37 oceanic climate than for transition, continental and mountainous ones [2]. In addition, recent literature in 38 atmospheric and nuclear iodine chemistry issues has demonstrated a strong reactivity of molecular iodine 39 and methyl iodide in atmospheric conditions with a rapid evolution of these gaseous forms depending on 40 the day/night phases and seasons [1]. The presence of fine particles in the coastal atmosphere has been 41 long established, they are therefore most likely iodine oxide polymers resulting from oxidation of gaseous 42 iodine [3]. Atmospheric iodine oxides are form by direct and indirect ozone-driven photo-oxidation 43 reactions of iodine species emitted from the sea or ice. Therefore, iodine can have several major impacts, 44 including the decomposition of ozone and influence the albedo of the Earth by acting as cloud 45 condensation nuclei. In atmospheric field, the aerosols speciation is well characterized [4-6] but the 46 mechanisms of formation remain less known and quite complex. Several laboratory studies have been 47 studied the kinetics of the photochemistry of organic [7-9] and inorganic iodine [10-12] and the processes 48 leading to the formation of IOx particles in the atmosphere. Saiz-Lopez et al. [1] summarized in a chemical 49 review the current understanding and uncertainties of the main gas- and condensed-phase iodine 50 photochemistry processes. Recently, an atmospheric iodine gas-phase mechanism containing reactions 51 combined to the air quality mechanism was implemented into a 0D box model in order to evaluate the 52 behaviour of iodine fission products released in the atmosphere [13, 14].

53 During, Chernobyl (1986) and Fukushima Daiichi (2011) accidents, significant quantities of radioactive 54 iodine have released into atmosphere [15, 16]. Molecular iodine and iodomethane are the main gaseous 55 species that are expected to be released in case of severe nuclear accident. The radiological impact of these 56 gaseous species is of concerns and requires knowledge about its behaviour [17-20]. From the 1980's, the 57 radiolytic oxidation of molecular iodine (I₂) to iodine oxides in an high irradiative atmosphere has been 58 demonstrated [12]. More recently, in severe accident research field, some analytical experimental 59 programs have shown the formation of iodine oxides [21-24]. The objective of Program on Air Radiolysis 60 and lodine adsorption on Surfaces (PARIS) was to study the reactivity of I_2 with the air radiolysis products 61 [25, 26]. The amount of iodine oxides formed in PARIS tests is the result of the competition between the 62 reactions consuming I_2 (adsorption on surface, transfer to the sump, reaction with organics ...) and depends 63 on the thermal hydraulics conditions and dose rate. Although a large number of tests were performed 64 during PARIS project, the objective of these tests was to study the formation kinetics of iodine oxides 65 particles. However, their speciation and decomposition kinetics could not be studied. In THAI program [27] 66 and at VTT, in Finland, in the EXCSI facility [28], tests were devoted to study the formation and behaviour of 67 iodine oxide aerosols produced by the reaction of gaseous I₂ with ozone. The iodine oxides particles 68 formation appears to be a fast process with a diameter of the particle ranged from dozens to a few 69 hundred of nanometres. This approximate size was also confirmed by more recent environmental studies 70 [29]. To be capable to predict potential releases in major nuclear accident, the stability of these oxides 71 remains an open issue as mentioned several experimental and modelling works [21, 30-33]. The formation 72 of iodine oxide aerosols by the reaction of methyl iodide (CH3I) with oxygen atoms (O) and hydroxyl 73 radicals (OH) has been investigated [21, 34]. These tests showed that both the presence of ozone and 74 photolysis were necessary for iodine oxide particle formation from CH₃I. The number and size of particles 75 was strongly dependent on humidity. The air steam atmosphere can lead the formation of such radical due 76 to radiation in severe accident conditions.

The thermal and radiation stability of these iodine oxides products requires further study to fully determine and model their behaviour and better predict in a more accurate manner their release and the radiological

79 consequences in the environment in case of severe accident as well as the efficiency of mitigation 80 measures to prevent iodine release.

81 Some particulate IOx decomposition experiments were performed in the Source Term Evaluation and

82 Mitigation (STEM) project [35] (hosted by OECD/NEA/CSNI and operated by IRSN) and are presented in this

article. They are part of a broader approach that consists in studying the stability and decomposition of
 metallic aerosols (CsI and CdI₂) [36] and non-metallic (like IOx) in the containment conditions [32]).

85

86 2 **PROPERTIES AND STABILITY OF IODINE OXIDE SPECIES**

The formation of iodine oxide aerosols particles from gaseous elemental iodine and ozone has been reported in the literature at the beginning of the 1980' [12]. By successive oxidation of I, IO and IO₂ primary products, the final product I_4O_9 is formed with ozone. Many studies [6, 12, 37-40] have reported the different decomposition and hydration reactions of different iodine oxides. The synthesis of these main reactions is reported in Table 1.

92

odine oxide particles.
odine oxide particle

Species	Thermal decomposi	Hydration		
	Reaction	Temperature (°C)		
I_2O_4	$5I_2O_4 \rightarrow 4I_2O_5 + I_2$	100 -200	$5I_2O_4 + 4H_2O \rightarrow I_2 + 8HIO_3$	
I_4O_9	$4I_4O_9 \rightarrow 6I_2O_5 + 2I_2 + 3O_2$	75-120	$5I_4O_9 + 9H_2O \rightarrow I_2 + 18HIO_3$	
	$5I_4O_9 \rightarrow 9I_2O_5 + I_2$	140-185		
I_2O_5	$2I_2O_5 \rightarrow 2I_2 + 5O_2$	280-350	$3I_2O_5 + H_2O \rightarrow HI_3O_8$	
			$HI_3O_8 + H_2O \rightarrow 3 HIO_3$	
шо	$6HIO_3 \rightarrow 2I_2O_5.HIO_3 + 2H_2O$	70-110	Very soluble in water:	
niO3	$2I_2O_5$.HIO ₃ \rightarrow $3I_2O_5$ + H ₂ O	200-250	$HIO_3 \rightarrow H^+ + IO_3^-$	

93

94 Under thermal conditions, the decomposition of I_2O_4 and I_4O_9 particles lead to the formation of I_2O_5 95 particles and molecular iodine gaseous (I_2), whereas under wet conditions, these species form HIO₃ aerosol

96 and gaseous I_2 (same observation for I_2O_5 particles). I_2O_5 is also known to be very soluble and quickly

decomposes into IO_3^- and H^+ in aqueous solution. In addition, it appears from the literature that hydration

98 rates are going to dependent on the size particle, shape, available surface area and relative humidity [40].

99 Smaller particles should have higher hydration rate and the higher surface area should have large hydration

100 rate as well.

- 101 These reaction pathways are known for iodine oxides, however there are still gaps in the knowledge on the
- 102 fate of the iodine oxides particle form even if some recent work provide information on morphologies on
- 103 iodine particles as a function of humidity [29].

104 3 **Description of experiments**

105 Hereafter are described the results obtained for six relevant experiments performed to study the 106 decomposition of iodine oxide aerosols. The studied experimental parameters were the dose rate, the 107 influence of the temperature, the aerosols concentration effect, and the nature of the surface. The 108 comparison of the results obtained for the tests allows estimating the potential effect of each parameter. 109 lodine oxides are generated and deposited on coupons made either of quartz or paints, paint being present 110 in nuclear containment building and is considered potentially reactive with iodine.

111

112 3.1 Preparation of the coupons

113 Four tests were performed using quartz coupons which are chemically inert in our test conditions. The 114 quartz coupon is first cleaned with ethanol to remove potential trace of grease then oven drying. No other 115 treatment is performed on the quartz coupon before loading phase with aerosols.

116 Two tests, devoted to study the nature of surface and the aerosols concentration, were performed using 117 epoxy painted coupons. The painted and quartz coupons were 56 mm in diameter and 3 mm thick. The 118 epoxy painted coupon were made of black steel, recovered with 2 layers of CENTREPOX[®] (40 μ m) and 1 119 layer of HYDROCENTRIFUGON® (50 µm). HYDROCENTRIFUGON® paint is an epoxy type paint, which is used 120 in the French nuclear plants. CENTREPOX® is also an epoxy type paint used to avoid the corrosion of the 121 surfaces and for decontamination purposes. The epoxy painted coupons were preheated at 130°C for 96 h 122 in a dry atmosphere prior to the loading phase and the irradiation phase to simulate ageing process. These 123 tests are representatives of the containment building conditions in severe accident conditions [41].

124

125 3.2 Aerosols loading phase

126 lodine oxide aerosols are produced by direct oxidation between ozone and gaseous molecular iodine. ¹³¹ is

127 used to label the molecular iodine produced in acidic solution from Dushman's reaction [42] (reaction 1) : 128 $5 I^{-} + IO_{3}^{-} + 6 H^{+} \rightarrow 3 I_{2} + 3 H_{2}O_{2}$

129 O3 is produced by an ozone generator COM-AD and analysed by ozone analyser Ozomat GM-OEM from 130 ANSEROS.

131 Reactants (I₂ and O₃), formed separately, are contacted in a glass reactor (3.9 I), called IOx reactor. An 132 aerosol fog, composed of fine white particles, is formed instantaneously. These labelled iodine oxide 133 aerosols are deposited by settling on a coupon positioned at the bottom of the IOx reactor during for few 134 minutes. After aerosols loading and γ counting, the coupon is inserted in the irradiation vessel.

135 The initial iodine concentration on the coupon, expressed in mol.m⁻², is calculated, using the activity

- 136 measured on the coupon (after gamma counting) and assuming that the ratio ¹²⁷I/¹³¹I on the coupon is the 137 same as the one in the solution.
- 138



Figure 1 – Schema of the iodine aerosols generation device

144

145 **3.3** Aerosols analyses

146 The aspect and the size of the particles deposited were quantified by Scanning Electron Microscopy 147 coupled by Energy Dispersive X-ray (SEM-EDX) (JEOL) with non-active iodine oxides particles that were 148 formed and deposited on surfaces with the same protocol than the one described above. The molecular 149 identification was determined by Raman spectrometry. Raman spectra were obtained from a JobinYvon[®] 150 (LABRAM HR) spectrometer used in a point-by-point automated scanning mode with 1 μm as a minimum 151 step. The Raman backscattering was excited at 532 nm. The elemental composition was analysed by X-ray 152 photoelectron spectroscopy (XPS) (NOVA-KRATOS).

153

154 **3.4** Irradiator facility

The experimental set-up, EPICUR, used to study the radiolytic instability of iodine oxide aerosols under radiation consists of a loop containing a panoramic irradiator, an electro-polished stainless steel irradiation vessel (4.8 l), connected through electro-polished stainless-steel tubes to an iodine filtration system (called Maypack). The panoramic gamma-ray irradiator (6 sources of ⁶⁰Co delivering an average irradiation dose rate of several kGy.h⁻¹) is used to simulate the effect of radiation associated with the presence of radioactive products in the containment vessel during an accident. The simplified view of the experimental EPICUR loop is presented in Figure 2.



Figure 2 - Simplified view of the experimental EPICUR loop.

164 During the test, the different volatile iodine species released from the IxOy aerosols decomposition in the 165 irradiation vessel are transferred to the May-pack device and trapped on the different species-selective 166 filters: the quartz filter traps the aerosols species, Knit-mesh filters trap molecular iodine (I_2) and charcoal 167 filters trap other species, particularly organic iodides (RI) in our experiments. Thanks to the use of ¹³¹I 168 labelled IxOy aerosols, gamma measurements are performed placing a gamma counter above each stage of 169 filter of the May-pack device, allowing on-line measurements and the evaluation of the release kinetics of 170 the different volatile species during the test. At the end of the tests, the irradiation vessel and the May-171 pack device are recovered. The different filters of the May-pack, the coupon and the rinsing solutions of the 172 irradiation vessel of the experimental loop are also gamma counted in order to calculate the iodine activity 173 balance.

174 175

188

3.5 Experimental conditions

176 Various parameters have been varied in order to understand the behaviour of iodine oxide aerosols under177 severe accident conditions:

- The specific objective of the IOx1 test consists in studying the purely thermal decomposition of
 iodine oxides aerosols on inert quartz coupon (without irradiation),
- 180 Under irradiation, the temperature is an important parameter in the containment. It was thus
 181 varied between 80°C (AER-7) and 120°C (AER-8), performed on a quartz coupon.
- The AER-10 test was devoted to evaluating the reproducibility of the experimental data of the reference test (AER-7).
- The nature of the coupon surface has also been investigated on epoxy painted coupon with AER9
 test.
- The influence of the initial concentration of iodine oxide aerosols on an epoxy painted surface was
 checked with AER-13 test.

189 Each test is divided into 3 phases:

190- A pre-irradiation phase from 1 to 9h to check the iodine release due to the thermal processes and191separate them from radiolytic processes. IOx-1 test is entirely devoted to check thermal stability for192a longer exposure time (43 h),

- the irradiation phase (30h) to check the iodine release due to the irradiation of the iodine aerosols
 deposit
- and the post-irradiation phase (~5h) to check whether volatile iodine is still released after the
 irradiation is stopped.

A mixture of air and humidity was used as the carrier gas in the EPICUR irradiation vessel with a fixed gas flow rate that allows a low residence time of the released iodine species in the vessel (~ 20 minutes). The experimental conditions of the iodine oxide aerosols decomposition tests are detailed in Table 2 and Table 3.

Table 2 – Experimental Parameters of AER tests.

Test	IOX-1	AER-7	AER-8	AER-9	AER-10	AER-13
Surface coupon	Quartz	Quartz	Quartz	Epoxy paint	Quartz	Epoxy paint
Concentration	(1.9 ± 0.1)x10 ⁻³	(2.4 ± 0.1)x10 ⁻³	(3.7 ± 0.2)x10 ⁻³	(3.2 ± 0.1)x10 ⁻³	$(1.8 \pm 0.1) \times 10^{-3}$	(4.5 ± 0.2)x10 ⁻⁵
(mol (I).m⁻²)						
т	120 then 80	80	120	80	80	80
(°C)						
Air with R.H. (%)	50	50	50	50	50	50
Dose rate (kGy.h ⁻¹)	No irradiation	3.7 ± 0.4	3.3 ± 0.3	3.4 ± 0.3	3.1 ± 0.3	1.4 ± 0.2
Irradiation duration	/	30	30	30	30	30
(h)						
Parameters studied	Thermal	Reference	Temperature	Surface	Reproducibility	Low I _x O _y
	decomposition					concentration

Table 3 – Duration of the three phase of AER tests.

Test	IOX-1	AER-7	AER-8	AER-9	AER-10	AER-13
Duration of pre-irradiation	23h – 120°C	1h (dry air)	1h (dry air)	1h (dry air)	1h (dry air)	1h (dry air)
sweeping phase (no	20h – 80°C		8.5h (50% R.H.)		9h (50% R.H.)	
irradiation) (hour)	1h (dry air) – 80°C					
Irradiation phase (hour)	0	30h	30h	30h	30h	45h
Dose (KGy)	0	111 ± 12	99 ± 9	102 ± 9	93 ± 9	63 ± 9
Duration of the post-	0	4h (50% R.H.)	4h (50% R.H.)	4h (50% R.H.)	4h (50% R.H.)	5h (50% R.H.)
irradiation sweeping		1h (dry air)	1h (dry air)	1h (dry air)	1h (dry air)	1h (dry air)
phase (no irradiation)						
(hour)						

215 4 **Results and discussion**

216 4.1 Aerosol's characterisation

217 The SEM observations showed the presence of particles whose sizes are under 10 µm with some dispersion 218 and size distribution whatever the nature of the coupon (Figure 3). There is also an intermediate range 219 between 2 and 5 µm, as well as the smallest below 1 µm. The largest particles represent 20% of the 220 population, the other two ranges represent 80%. EDX analyses on the whole observed area indicate the 221 presence of molecular iodine into the particles (7 to 10%) and the residual I_2 deposited on the support at 222 about 5% (Figure 4). The aerosols of our study seem larger than those observed in other studies [27, 28], 223 probably because of the hygroscopic nature of such particles. However, the physico-chemical parameters 224 (concentration, volume, temperature, relative humidity ...) are very different in three types of experiments 225 and which might contribute to explain the differences in aerosol sizes. In addition, aerosol in the 1 μ m 226 range would be expected to act as nucleation kernels for the emerging iodine oxides, and this would 227 significantly shift particles size distributions to larger sizes.











234 235

236

Figure 4 – EDX spectra performed on a particle (5 μ m).

237 Raman analyses (Figure 5) of iodine oxide aerosols deposited on quartz coupons showed bands at 772, 626, 238 456, 404, 326 and 190 cm⁻¹ on different particles. The comparison of the bands highlighted with the bands 239 of different iodine oxide aerosols found in the literature [37, 43, 44] allowed these bands to be assigned to 240 the corresponding species. From the RAMAN analyses performed, it was showed that the iodine oxides 241 deposited on the coupon at room temperature are mostly I_2O_4 and/or I_4O_9 amorphous species with 242 possibility adsorbed low fraction of I_2 and/or HIO₃. I_2O_4 is formed by the self-recombination of OIO. I_2O_4 is 243 not stable but complexes of I₂O₄ with IO and OIO are stable [45]. Galvez et al. reported some large 244 thermodynamic values for the I_2O_4 homodimer ($I_2O_4 + I2O_4 \rightarrow I_2O_4$... I_2O_4) which shows a very high stability 245 with a lifetime of 1.25×10^5 s based on thermo-computation performed at 298K.

246 The bands seen in the Raman spectrum of I_2O_5 (doublet at 840 and 830 cm⁻¹, strong band at about 723 cm⁻¹ 247 and medium intensity bands at 377 and 323 cm⁻¹) are absent from the spectrum of the crystalline product 248 deposited on quartz coupon. Thus, I_2O_5 species is not expected to have been significantly formed in our 249 experimental conditions of generation at room temperature.

250 Regarding the Raman analyses carried out on an epoxy coupon, the analysis of the iodine oxide aerosols 251 deposited on these supports does not make it possible to extract the characteristic vibration bands, due to 252 excessively intense fluorescence interference phenomena due to the presence of different functional 253 groups of the epoxy paint.



230

257 258

259

Figure 5 – The Raman spectrum of iodine species deposited on quartz coupon.

The XPS analyses showed that the main signature detected on the surface of the sample is silica (SiO₂), quartz and iodine oxides. The statistical analysis carried out at 9 points on the sample showed a homogeneity of the composition at the extreme surface, that the aerosols are present homogeneously on the surface of the quartz coupon. The results of elemental analyses showed a corrected O / I ratio of 1.8-1.9 (considering only oxygen bound to iodine) which is consistent with of the formation and deposition of I₂O₄ species on the coupon as observed with the RAMAN analysis.

266 The formation of iodine oxide particles from gaseous elemental iodine and ozone has been reported in the 267 literature [12, 37]. By successive oxidation of the I, IO and IO₂ primary products, the final product I_4O_9 is 268 formed with ozone. Previous studies [28, 46] have performed gamma irradiation of I₂ vapor in air and have 269 obtained results consistent with a number of potential products, such as I₂O₄, I₂O₅, I₄O₉ and HIO₃. More 270 recent studies [5, 6, 38, 47] have also shown that the formation of I_2O_4 specie appears to be the pivotal 271 species in the initial polymerization steps to form iodine oxides, in agreement with our results. The 272 chemical composition of products is never not clearly established and the particles may comprise several 273 different iodine oxides, including hydrated ones (like $H_2O-I_2O_4$ or HIO_3). So, iodine (IV) oxide (I_2O_4) is a 274 probable reaction product of ozone and gaseous molecular iodine which can be next oxidised for 275 temperature higher than 100°C (see table 1). I_xO_y species (I_2O_4 , I_4O_9 , I_2O_5) can also react with steam and 276 lead to the formation of hydrated species (ex-: $I_2O_5-H_2O$) and HIO₃. For the rest of the paper, the 277 deposited species will be named IxOy.

278 It worth noting that iodine can also be formed by radiolytic oxidation of CH_3I as shown in other studies [48, 279 49].

280

281 **4.2** Stability of iodine oxide aerosols

Table 4 gives the final measurements of the global volatilisation, the corrected fractions on each species trapped on the may-pack and the iodine activity balance. The global release corresponds to the difference between the activity on the coupon before and after the irradiation, it is expressed in percentage of the activity loaded in the coupon before irradiation. The I₂ volatilisation measured only in the knit-mesh filter is underestimated. Indeed, the iodine loss in the iodine activity balance is due to I₂ trapped irreversibly on the stainless-steel surface of the EPICUR device. In addition, the activities measured on the rinsing solutions of 288 the loop and the may-pack could be attributed to I_2 trapped on stainless surface. However, the activity

289 measured on the rinsing solution of irradiation vessel could be attributed to I_2 and/or deposited aerosols.

test	IOx-1	AER-7	AER-8	AER_9	AER_10	AER-13
Parameters studied	Thermal	Reference test	Temperature	Surface	Reproducibility	Low concentration
	decomposition					
Global volatilisation (%)	26.9 ± 0.3	14.3 ± 0.2	59.3 ± 1.6	58.4 ± 0.7	13.0 ± 0.9	12.9 ± 0.8
Final release on the quartz	2.6 ± 0.1	0.5 ± 0.03	0.1 ± 0.01	12.9 ± 0.8	0.06 ± 0.004	0.3 ± 0.03
fiber filter (aerosols) (%)						
Final release for I ₂ on the	9.6 ± 0.5	5.3 ± 0.2	54.4 ± 3.5	15.6 ± 1.5	0.8 ± 0.05	1.2 ± 0.1
knitmesh stage (%)						
Final release for RI on the	1.5 ± 0.03	1.2 ± 0.03	2.6 ± 0.3	2.3 ± 0.1	0.4 ± 0.01	0.4 ± 0.01
charcoal stage (%)						
Activity of the rinsing solution	3.3 ± 0.01	4.1 ± 0.01	1.4 ± 0.01	10.9 ± 0.05	3.5 ± 0.01	2.3 ± 0.2
of the irradiation vessel (%)						
Activity of the rinsing solution	4.5 ± 0.01	1.1 ± 0.01	1.9 ± 0.01	13.7 ± 0.03	6.1 ± 0.01	3.7 ± 0.2
of loop and MP (%)						
lodine activity balance (%)	94.5 ± 0.5	98.0 ± 1.0	101.3 ± 4.2	97.2 ± 1.5	97.8 ± 0.9	97.4 ± 3.3

294

296

298

- 299 The on-line gamma measurements are not as accurate as post-test measurements provided with
- γ -counting on each filter. So, a corrective factor is calculated by the ratio between the sum of the activities measured on each filter of the stage during the post-test measurements and the last on-line activity measured at the end of the test. All the on-line kinetics data are corrected by these ratios to establish the "corrected kinetics data" presented here.
- The influence of several parameters was checked and discussed in the following section. Except for AER-9 test (nature surface effect), activities trapped on the quartz fiber filter are very low compared to the global volatilization. In the same way, the organic iodide species release, trapped in charcoal filter, are attributed to the presence of organic pollution in the loop (possible carbonaceous layer absorbed on steel surface), in the irradiation vessel, on the coupon or in the carrier gas and also represent a very low amount of the global release.
- 310 Figure 6 shows the released percentage of corrected molecular iodine from the coupons for IOX-1, AER-7,
- 311 AER-8 and AER-9 tests. AER-10 and AER-13 are not represented because the one-line values are too close to
- 312 the detection limit. In the X-axis, the "zero" represents the beginning of the irradiation except for the AER-0
- 313 test performed without irradiation.
- 314



316 317

Figure 6 – Corrected on-line molecular iodine fraction trapped during the test for IOX-1 (120°C/80°Cwithout irradiation), AER-7 (80°C- reference test), AER-8 (120°C- temperature effect) and AER-9 (80°Csurface effect) (uncertainty 10%).

318319

320 4.2.1 Effect of the temperature on the thermal decomposition

321 The specific objective of the IOX-1 test consists in studying the purely thermal decomposition of iodine 322 oxide aerosols (without irradiation) (Figure 6). Contrarily to the decomposition of metallic iodine aerosols 323 [36], the purely thermal decomposition leads to a significant release, which reveals that the thermal 324 decomposition of iodine oxide aerosols is important above 100°C. The thermal instability is consistent with 325 the speciation of these species initially produced, i.e. I_2O_4 that might decompose into I_2 and I_2O_5 according 326 to Table 1. The release of molecular iodine is predominant; it becomes significant only after about 10h of 327 heating at 120°C in moist air for which the release is linear until the end of the 120°C phase (~0.65% per 328 hour) and it represents about 7.6% of the initial activity loaded on the coupon at the end of the heating 329 phase at 120°C. A possible explanation of this induction period of about 10 hours could be that the thermal 330 decomposition of the IxOy occurs in 2 kinetics; a first slow kinetics with a low production of molecular 331 iodine, then an increase in the kinetics after 10 hours. At that time, one possible explanation is that the

332 induction may be explained by the hydration process which promotes I_xO_Y decomposition (table 1). After

the heating temperature decrease from 120°C to 80°C, the kinetics of molecular iodine release decreases,

which can be because the thermal instability of I_2O_4 is more important at 120°C than at 80°C as indicated in Table 1. As soon as I_2 and I_2O_5 are formed at 120°C from I_2O_4 decomposition, the reduction of the temperature from 120°C to 80°C does not lead to I_2O_5 decomposition which is consistent with the I_2O_5 temperature range stability indicated in Table 1. The global release is significant (26.9%), which reveals the significant thermal instability of iodine oxides at temperatures above 100 °C.

No iodine oxides should be formed in non-irradiated conditions [25]. The low aerosols release on the quartz filter (2.6%) is certainly due to an experimental artefact. During the last minutes of the cooling down phase, the valve between the irradiation vessel and the may-pack was accidentally closed, which resulted a slight overpressure in the irradiation vessel and an increase of the activity trapped on the quartz filter upon reopening the valve. This caused a rapid transfer of the iodine oxide species present in the irradiation vessel to the may-pack. A purely physical transport of species cannot to be excluded. Another possibility is that some gaseous inorganic iodine could have been partly trapped by the aerosol filter.

346

347 4.2.2 Reference test and reproducibility

348 In AER-7 test, the results showed that I_xO_y were not stable under irradiation, however the global 349 volatilisation was quite low and their decomposition led mainly to the formation of molecular iodine. As 350 specified later, the iodine fraction trapped on the quartz filter and on the charcoal stage were low. It can be 351 seen that the release of molecular iodine seemed to be linear until the thirteenth hour of the irradiation 352 phase then the kinetics decreased. These results show that the radiolytic decomposition (below 100°C) of 353 I_xO_y is weaker than the thermal decomposition at 120°C. Furthermore, when the irradiation was stopped, 354 the molecular iodine fraction production was increase on during the sweeping phase. This phenomenon 355 could be explained by the ending of reactions of radiolytic oxidation of I_2 in aerosols oxides (reaction 356 between I_2 and ozone) causing the equilibrium to shift towards the production of molecular iodine coming 357 from the decomposition and / or hydration of I_xO_y . However, more activity should have been seen on the 358 aerosol stage of the may-pack. Another explanation is that, as the thermal decomposition observed at 80°C 359 in IOx1 test is very low and that the thermal post-irradiation of AER7 test is more important, an evolution of 360 the I_xO_y speciation could have occurred during the irradiation. The new IOx species formed during the 361 irradiation would be unstable as soon as the irradiation is stopped and would decompose in a faster 362 manner than the I_xO_y species existing before the irradiation starts. This kind of species could be iodine 363 nitroxides compounds ($I_xN_yO_z$) known to be reservoir of iodine compounds in the atmosphere [50-53] i.e. 364 unstable compounds. More especially, IONO₂ has been reported to have a lifetime of about 6 hours at 25°C 365 [54] and that the thermal dissociation of IONO₂ should be the main decomposition pathway of IONO₂ above 366 290 K.

367 Observations by optical microscopy and Raman analyses of coupon was performed after the activity decay 368 (i.e. 6 months after the test which could not allow to catch the presence of any of the suspected unstable 369 reservoir species like $I_xN_yO_z$). Larger particles were observed (up to 20 μ m) representing 10 to 15% of the 370 population. Particles of average size of 5 to 10 μ m represented 20% of the population and submicron 371 particles represented the rest. EDX analysis showed an increase in the amount of iodine in larges particles 372 containing up to 40% iodine. Iodine diffused inside larger particles. Observations have also brought to light 373 crystallization phenomena. The RAMAN spectrum of I_2O_4 was found with narrow bands in accordance with 374 more crystallized structures as well as bands possibly corresponding to I_2O_5 . Hydrated species were not 375 detected (like HIO₃ or $IO_x - H_2O$) but it could also be due to the storage conditions (ambient temperature) 376 during the decay time (6 months).

377 The comparison of the post-test measurements of the AER-7 (reference test) and AER-10 test allows 378 evaluating the reproducibility of the data obtained on the release of iodine volatile species at 80°C and 50% 379 of R.H. in air from a quartz coupon. The initial concentration of iodine oxide on the coupon and the dose 380 rate at the level of the coupon were similar for both tests (Table 2). Although the on-line measurements of 381 the AER-10 test were below the on-line detection limit, the post-test measurements of each filter are 382 higher than the post-test detection limit (100 Bq) and were therefore relevant. Table 4 shows that the 383 results were directly reproducible in terms of global volatilization (~14%) even taking into account the low 384 decrease of dose rate from 3.7 to 3.1 kGy/h between these two tests. In addition, correcting the molecular 385 iodine values with the rinsing solution of the loop and the may-pack, and the missing activity balance

values, the molecular iodine amounts (~9%) were reproductible. In both tests, the species mainly volatilized was I_2 , attributed to the decomposition of I_xO_y deposited on the quartz coupon.

388

389 4.2.3 Effect of the temperature under irradiation

390 In AER-8 test, the release of molecular iodine starts during the sweeping phase at 120°C but it represents 391 only 2.5% of the initial activity loaded on the coupon. The induction phase already observed in IOX-1 392 confirms the thermal decomposition of deposited I_xO_y into volatile iodine with a slow reaction kinetics 393 before the irradiation starts. As soon as the irradiation started, the release kinetics is increased. The 394 molecular iodine is the main species volatilized (56.4% of the initial activity loaded on the coupon). Half of 395 the release comes from the post irradiation phase. The speciation seems to be modified during the 396 irradiation as a higher release is observed as soon as the irradiation is stopped whereas almost no release is 397 observed before the irradiation. It suggests the formation of temporary I_xO_y aerosol species formed under 398 irradiation that would not be thermally stable in the range 80-120°C.

399 Observations by optical microscopy and Raman analyses of coupon was performed after the activity decay 400 (*i.e.* 6 months after the test). 3 populations are distinguished, from 4 to 10 μ m, from 1 to 2 μ m and less 401 than 1 μ m each representing one third of the population. The EDX analysis showed an average percentage 402 of 20% iodine on large particles and 8% for medium. RAMAN analysis showed the bands around 179.6, 338.4, 465.5, 637.8 and 775.9 $\rm cm^{-1}$ characteristic of the I_2O_4 compound. Iodine oxides compounds 403 404 decompose into crystalline I_2O_5 and gaseous I_2 [39]. Contrarily to what was expected, neither the 405 characteristic bands of the I_2O_5 species have been found nor its crystalline structure. But, in presence of 406 steam, both species can later on decompose into HIO_3 and I_2 .

407 The effect of the temperature under irradiation was studied with comparison of AER-7 and AER-8, with I_xO_y 408 aerosols deposited on a quartz coupon (Table 4 and Figure 6). The AER-7 test was carried out with a coupon 409 irradiated at 80°C and the AER-8 test was carried out with a coupon irradiated at 120°C during 30h each. 410 The initial concentration of iodine oxide on the coupon and the dose rate at the level of the coupon were 411 similar for both tests. In AER-7 test, the decomposition of I_xO_y in I_2 is mainly due to the radiation 412 composition because the test is performed at 80°C. In AER-8 (120°C), deposited I_xO_y aerosols decompose 413 around 100°C [4, 5] into I_2 and I_2O_5 and in HIO₃ in presence of humidity. The decomposition of the different 414 species (I_2O_4 and I_2O_5) into I_2 might be due to a synergic effect of radiation and thermal decomposition, 415 which would explain the increase of I_2 release when the temperature increases from 80 to 120°C during the 416 irradiation phase. Taking into account measurement uncertainties, the results show that when the 417 temperature is increase from 80°C to 120°C the global volatilisation, mostly in molecular iodine form, 418 increases drastically.

419

420 4.2.4 Effect of the nature surface

421 AER-9 test was devoted to evaluating the nature of the coupon surface (epoxy paint) in the decomposition 422 of iodine oxides at 80°C. The results presented in Table 4 and Figure 6 show an important global 423 volatilisation (~59%), similar than that of AER-8 (120°C), but with a significant part present on the quartz 424 fiber filter (13%). At the end of the test, the molecular iodine released reach 12.6%. In Table 4, the 425 molecular iodine fraction is corrected by adding the activity measured on rinsing solutions of loop and may-426 pack and the missing activity of iodine mass balance. Despite the presence of organic radical sources (paint) 427 that might be released in the atmosphere, the formation of organic iodide (RI) is not very significant and 428 remains of the same order of the measured values in test with quartz coupon.

429 These results could be compared to those of VTT/Chalmers [38] on the volatilisation studies from iodine 430 aerosols under the influence of surface materials. The iodine oxide particles deposited on surfaces were 431 originally most likely I_2O_4 or a mixture of I_2O_4 and I_2O_5 , like ours. For doses up to 392 KGy (14 kGy/h and 432 50°C), the release of iodine is more important from painted surfaces than from metallic surfaces.

433

434 The important production of species trapped on the quartz fiber filter could be due to aerosol species 435 and/or to I_2 by parasitic trapping. Observations by optical microscopy of this quartz fiber filter were 436 performed after the activity decay *(i.e.* 6 months after the test). The observations (Figure 7) showed 437 particles fixed on the constitutive fibers of the filter. The sizes of these particles were between 200 nm and 438 5 µm. Raman analyses of these species provided the evidence of the presence of aerosols trapped on the 439 quartz fiber filter. The spectra are consistent with the formation of I_2O_4 and I_2O_5 species. As for the IOX1

test, the presence of iodine oxide on the filter does not exclude that some gaseous inorganic iodine couldhave been partly trapped by the aerosol filter.

- 442
- 443
- 444
- 445



- 446
- 447

Figure 7 - Optical microscopy observation of the quartz fiber filter of the AER-9 test.

448

449 Nevertheless, the significant aerosols release with an epoxy coupon might be due to different phenomena:

450 - A physical transport, linked to the gas sweep, of the upper layer of aerosols deposited on the coupon.

However, the deposited concentration is similar to that of AER-8 and this phenomenon was not observed inthis test.

453 - deposited IOx aerosols are considered inert towards the paint surface. However, it is not excluded that

- 454 some of them might have reached the paint coupon before their final speciation had been reached. In that 455 case, these intermediate species (like IO, IOO, IIO, $I_2O_2...$) could have reacted with the paint and led to a 456 specific release under irradiation.
- 457 Some I2 might have been adsorbed on the paint coupon during the IOx loading phase and might have458 been released under irradiation.
- The RAMAN analyses being very difficult to conduct on a paint coupon, the speciation of the iodine oxide species deposited on painted coupons and the quantification of the amount of residual I₂ loaded on epoxy painted coupon by parasitic trapping could not be conducted.
- 462

463 4.2.5 Effect of the concentration

In AER-13 test (low IOx amount deposited on a painted coupon), the global release of iodine is weak (~13%) and the release of molecular iodine is low (7.5% corrected value) and close to the detection limit during online measurement. In post-test analyses, 95% of the remaining iodine on the coupon after irradiation remain adsorbed on the paint, even after a washing phase.

468 The effect of the concentration on painted coupon was studied with comparison of AER-9 and AER-13 tests.

469 Compared to the results of AER-9, the decrease of the dose rate (factor 2.4) and of the iodine concentration

470 leads to a decrease of the global volatilization (factor 4.5). AER-13 results are close to those LD3 test [18]

471 where molecular iodine are loaded in the painted coupon (concentration and dose rate are similar). It is 472 known that iodine creates strong chemical bonding onto paint that may be desorbed slowly under I_2 form

472 known that iodine creates strong chemical bonding onto paint that may be desorbed slowly under I_2 form 473 or release organic form in a smaller extent. So, given the low iodine concentration and availability of sites,

474 the produced I_2 would be absorbed back onto the paint as suggested by PARIS project [25].

476 **5 Conclusions**

477 Experimentally, it was clearly observed that iodine oxides can be formed by oxidation of molecular iodine 478 quite quickly at room temperature. In our experimental conditions, I_2O_4 and/or I_4O_9 amorphous species 479 (with the possibility of having absorbed low fraction of I_2 and/or HIO₃) are initially reaction products of 480 ozone and gaseous elemental iodine, deposited on quartz coupon.

481 The experimental tests aimed to quantify the thermal $(80^{\circ}C - 120^{\circ}C)$ and radiolytic decomposition of iodine 482 oxide aerosols deposited on dry surface in presence of 50% of relative humidity. The thermal 483 decomposition test (IOX-1) showed the thermal instability of IxOy (initially deposed in I₂O₄ form) is more 484 important at 120°C than at 80°C. In addition, an induction period before the beginning of the release of 485 about 10h is observed and could be explain by the hydration process (Table 1) that promotes IxOy 486 decomposition into HIO₃ because HIO₃ is the most stable iodine oxide in moist atmosphere. The 487 temperature increase from 80 to 120°C promotes a higher molecular iodine release. The decomposition of 488 deposited IxOy (probably I_2O_4) into I_2 might be due to the synergic effect of radiation and thermal 489 decomposition. The surface nature has been checked and it was found an increase of the global 490 volatilisation when iodine oxides aerosols are deposited on an epoxy painted coupon. Nevertheless, at a 491 lower initial concentration deposited, the release of I_2 is lower, probably in favour of chemical reaction with 492 the paint.

493 It was shown that iodine aerosols particles decompose under irradiation, whatever the surface deposition

494 and lead to mainly gaseous molecular iodine. As these experimental observations are a high interest due to

495 their impact source term evaluation, a more complete understanding of their radiolytic instability is

496 necessary. In particular in conditions close to a nuclear accident in the presence of other gases, such as CO 497 and/or H_2 , or different humidity conditions may modify the chemical reactivity of the iodine oxides.

498

499 Acknowledgments

Authors acknowledge the OECD hosting the STEM project, the STEM partners for their support (Electricité De France, the Atomic Energy of Canada Limited, the Teknologian tutkimuskeskus VTT (Finland), Ústav Jaderného výzkumu Řež a.s (Czech Republic), The Gesellschaft für Anlagen – und Reaktorsicherheit (Germany), The Korea Atomic Energy Research Institute, The Korea Institute for Nuclear Safety and The US Nuclear Regulatory Commission). We particularly thank C. Cunin, C. Duffieux, L. Martinet and J. Colombani

505 for their contribution to this study.

References

- 1. Saiz-Lopez, A., et al., *Atmospheric chemistry of iodine*. Chemical Reviews, 2012. **112**(3): p. 1773-1804. DOI: 10.1021/cr200029u.
- 2. Roulier, M., et al., *Atmospheric iodine, selenium and caesium depositions in France: I. Spatial and seasonal variations.* Chemosphere, 2021. **273**. DOI: 10.1016/j.chemosphere.2020.128971.
- 3. Sipilä, M., et al., *Molecular-scale evidence of aerosol particle formation via sequential addition of HIO3*. Nature, 2016. **537**(7621): p. 532-534. DOI: 10.1038/nature19314.
- 4. Plane, J.M.C., et al., *An experimental and theoretical study of the reactions OIO + NO and OIO + OH*. Journal of Physical Chemistry A, 2006. **110**(1): p. 93-100. DOI: 10.1021/jp055364y.
- 5. Gómez Martín, J.C., et al., *On the mechanism of iodine oxide particle formation*. Physical Chemistry Chemical Physics, 2013. **15**(37): p. 15612-15622. DOI: 10.1039/c3cp51217g.
- 6. Ristovski, Z.D., et al., *Characterization of iodine particles with Volatilization-humidification Tandem Differential Mobility Analyser (VH-TDMA), Raman and SEM techniques*. Atmospheric Chemistry and Physics Discussions, 2006. **6**(1): p. 1481-1508.
- 7. Zhang, S., et al., *Temperature-dependent kinetics study of the reactions of OH with C 2H5I, n -C3H7I, and iso-C 3H7I*. Journal of Physical Chemistry A, 2012. **116**(38): p. 9497-9506. DOI: 10.1021/jp300575f.
- 8. Zhang, S., et al., *Kinetic study of the reaction of OH with CH3I revisited*. International Journal of Chemical Kinetics, 2011. **43**(10): p. 547-556. DOI: 10.1002/kin.20583.
- 9. Zhang, S., et al., *Kinetic study of the reaction of OH with CH2I2*. Physical Chemistry Chemical Physics, 2011. **13**(24): p. 11671-11677. DOI: 10.1039/c1cp20885c.
- 10. Finkenzeller, H., et al., *lodic acid formation and yield from iodine photolysis at the CERN CLOUD chamber*, in *EGU General Assembly* 2021.
- 11. Martín, J.C.G., P. Spietz, and J.P. Burrows, *Kinetic and mechanistic studies of the i2/O3 photochemistry*. Journal of Physical Chemistry A, 2007. **111**(2): p. 306-320. DOI: 10.1021/jp061186c.
- 12. Vikis, A.C. and R. MacFarlane, *Reaction of iodine with ozone in the gas phase*. Journal of Physical Chemistry, 1985. **89**(5): p. 812-815. DOI: 10.1021/j100251a019.
- 13. Fortin, C., et al., *Box modelling of gas-phase atmospheric iodine chemical reactivity in case of a nuclear accident*. Atmospheric Environment, 2019. **214**. DOI: 10.1016/j.atmosenv.2019.116838.
- 14. Trincal, J., et al., *Impact of atmospheric species reactivity on radioactive gaseous iodine transport in severe accident conditions*. WIT Transactions on Ecology and the Environment, 2015. **198**: p. 77-86. DOI: 10.2495/air150071.
- 15. Imanaka, T., G. Hayashi, and S. Endo, *Comparison of the accident process, radioactivity release and ground contamination between Chernobyl and Fukushima-1*. Journal of Radiation Research, 2015. **56**: p. i56-i61. DOI: 10.1093/jrr/rrv074.
- 16. Steinhauser, G., A. Brandl, and T.E. Johnson, *Comparison of the Chernobyl and Fukushima nuclear accidents: A review of the environmental impacts*. Science of the Total Environment, 2014. **470-471**: p. 800-817. DOI: 10.1016/j.scitotenv.2013.10.029.
- 17. Sobanska, S., et al., *Infrared matrix-isolation and theoretical studies of interactions between CH3I and water*. Journal of Molecular Structure, 2021. **1236**. DOI: 10.1016/j.molstruc.2021.130342.
- 18. Bosland, L. and J. Colombani, *Study of iodine releases from epoxy and polyurethane paints under irradiation and development of a new model of iodine-Epoxy paint interactions for PHEBUS and PWR severe accident applications*. Journal of Radioanalytical and Nuclear Chemistry, 2017. **314**(2): p. 1121-1140. DOI: 10.1007/s10967-017-5458-9.
- 19. Leroy, O. and C. Monsanglant-Louvet, *Trapping measurements of volatile iodine by sand bed and metallic filters*. Journal of Radioanalytical and Nuclear Chemistry, 2019. **322**(2): p. 913-922. DOI: 10.1007/s10967-019-06786-1.
- 20. Guilbert, S. and L. Bosland. *Radiolytic oxidation of iodine in the containment at high temperature and dose rate.* in *International conference on Nuclear Energy for New Europe (NENE).* 2007. Portorose, Slovenia.
- 21. Dickinson, S., et al., *Experimental and modelling studies of iodine oxide formation and aerosol behaviour relevant to nuclear reactor accidents*. Annals of Nuclear Energy, 2014. **74**: p. 200-207. DOI: https://doi.org/10.1016/j.anucene.2014.05.012.

- 22. Herranz, L.E., T. Haste, and T. Kärkelä, *Recent advances in the source term area within the SARNET European severe accident research network.* Nuclear Engineering and Design, 2015. **288**: p. 56-74. DOI: 10.1016/j.nucengdes.2015.03.014.
- Dickinson, S., et al., *Recent advances on containment iodine chemistry*. Progress in Nuclear Energy, 2010.
 52(1): p. 128-135. DOI: 10.1016/j.pnucene.2009.09.009.
- 24. Cantrel, L., et al., *Research works on iodine and ruthenium behavior in severe accident conditions.* Journal of Nuclear Engineering and Radiation Science, 2018. **4**(2). DOI: 10.1115/1.4038223.
- Bosland, L., et al., PARIS project: Radiolytic oxidation of molecular iodine in containment during a nuclear reactor severe accident: Part 2. Formation and destruction of iodine oxides compounds under irradiation Experimental results modelling. Nuclear Engineering and Design, 2011. 241(9): p. 4026-4044. DOI: https://doi.org/10.1016/j.nucengdes.2011.06.015.
- Bosland, L., et al., PARIS project: Radiolytic oxidation of molecular iodine in containment during a nuclear reactor severe accident: Part 1. Formation and destruction of air radiolysis products—Experimental results and modelling. Nuclear Engineering and Design, 2008. 238(12): p. 3542-3550. DOI: https://doi.org/10.1016/j.nucengdes.2008.06.023.
- 27. Funke, F., et al., *Iodine oxides in large-scale THAI tests.* Nuclear Engineering and Design, 2012. **245**: p. 206-222. DOI: 10.1016/j.nucengdes.2012.01.005.
- 28. Kärkelä, T., et al., Experimental study on iodine chemistry (EXSI) Containment experiments with elemental iodine. 2009 NKS-204
- 29. R'Mili, B., et al., Important effects of relative humidity on the formation processes of iodine oxide particles from CH3I photo-oxidation. Journal of Hazardous Materials, 2022. **433**: p. 128729. DOI: https://doi.org/10.1016/j.jhazmat.2022.128729.
- 30. Bosland, L., et al., *Modeling and interpretation of iodine behavior in PHEBUS FPT-1 containment with ASTEC and COCOSYS codes.* Nuclear Technology, 2012. **177**(1): p. 36-62. DOI: 10.13182/nt12-a13326.
- 31. Bosland, L., et al., *Modeling of iodine radiochemistry in the ASTEC severe accident code: Description and application to FPT-2 PHEBUS test.* Nuclear Technology, 2010. **171**(1): p. 88-107. DOI: 10.13182/nt10-a10774.
- 32. Bosland, L., et al., *Study of the stability of CsI and iodine oxides (IOx) aerosols and trapping efficiency of small aerosols on sand bed and metallic filters under irradiation.* Progress in Nuclear Energy, 2021. **142**. DOI: 10.1016/j.pnucene.2021.104013.
- 33. Haste, T., et al., *lodine benchmarks in the SARNET network of excellence*. Journal of Nuclear Engineering and Radiation Science, 2016. **2**(2). DOI: 10.1115/1.4031652.
- 34. Zhang, S., Etudes cinétiques de l'oxydation radicalaire en phase gazeuse d'iodures organiques et de la formation de particules d'oxydes d'iode sous conditions simulées de l'enceinte d'un réacteur nucléaire en situation d'accident grave, 2012, Université Aix-Marseille, France.
- 35. Source Term Evaluation and Mitigation (STEM) Project. 2011-2015; Available from: https://www.oecdnea.org/jcms/pl_25255/source-term-evaluation-and-mitigation-stem-project.
- 36. Bosland, L. and J. Colombani, *Study of the radiolytic decomposition of CsI and CdI2 aerosols deposited on stainless steel, quartz and Epoxy painted surfaces.* Annals of Nuclear Energy, 2020. **141**. DOI: 10.1016/j.anucene.2019.107241.
- 37. Sunder, S., J.C. Wren, and A.C. Vikis, *Raman spectra of 1409 formed by the reaction of iodine with ozone.* Journal of Raman Spectroscopy, 1985. **16**(6): p. 424-426. DOI: 10.1002/jrs.1250160611.
- 38. Tietze, S., et al., Adsorption and revaporisation studies on iodine oxide aerosols deposited on containment surface materials in LWR. 2012 NKS-272 ISBN 978-87-7893-345-4 NKS
- 39. Chase, M.W., *NIST-JANAF thermochemical tables for the iodine oxides.* Journal of Physical and Chemical Reference Data, 1996. **25**(5): p. 1229-1339.
- 40. Little, B.K., et al., *Physiochemical characterization of iodine(V) oxide, part 1: Hydration rates*. Propellants, Explosives, Pyrotechnics, 2015. **40**(4): p. 595-603. DOI: 10.1002/prep.201400225.
- 41. Zoulalian, A. and E. Belval-Haltier, *Interaction between molecular iodine in a gas phase and paints aged in a nuclear power plant*. Nuclear Technology, 2000. **130**(3): p. 362-371. DOI: 10.13182/nt00-a3099.
- 42. Dushman, S., *The rate of the reaction between iodic and hydriodic acids*. Journal of Physical Chemistry, 1904. **8**(7): p. 453-481.
- 43. Ellestad, O.H., et al., *Infrared and Raman studies of cristalline* I_2O_5 , (IO)₂SO₄, (IO)SeO₄ and I_2O_4 . Acta Chemica Scandinavica, 1981. **35**: p. 155-164. DOI: 10.3891/ACTA.CHEM.SCAND.35A-0155.
- 44. Durig, J.R., O.D. Bonner, and W.H. Breazeale, *Raman studies of iodic acid and sodium iodate*. Journal of Physical Chemistry, 1965. **69**(11): p. 3886-3892. DOI: 10.1021/j100895a041.

- 45. Gálvez, O., et al., *A theoretical study on the formation of iodine oxide aggregates and monohydrates*. Physical Chemistry Chemical Physics, 2013. **15**(37): p. 15572-15583. DOI: 10.1039/c3cp51219c.
- 46. Glowa, G. and J. Ball, *Gas phase radiolysis of iodine*. 2012 report N° 153-126530-440-017 Atomic Energy of Canada Limited
- 47. Saunders, R.W., et al., *Studies of the formation and growth of aerosol from molecular iodine precursor*. Zeitschrift fur Physikalische Chemie, 2010. **224**(7-8): p. 1095-1117. DOI: 10.1524/zpch.2010.6143.
- 48. Tang, I.N. and A.W. Castleman Jr, *Kinetics of γ-induced decomposition of methyl iodide in air*. The Journal of Physical Chemistry, 1970. **74**(22): p. 3933-3939. DOI: 10.1021/j100716a014.