



HAL
open science

Trapping measurements of volatile iodine by sand bed and metallic filters

Olivia Leroy, Celine Monsanglant Louvet

► **To cite this version:**

Olivia Leroy, Celine Monsanglant Louvet. Trapping measurements of volatile iodine by sand bed and metallic filters. *Journal of Radioanalytical and Nuclear Chemistry*, 2019, 322 (2), pp.1-10. 10.1007/s10967-019-06786-1 . hal-02454924

HAL Id: hal-02454924

<https://hal.science/hal-02454924>

Submitted on 24 Jan 2020

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.

Dear Author,

Here are the proofs of your article.

- You can submit your corrections **online**, via **e-mail** or by **fax**.
- For **online** submission please insert your corrections in the online correction form. Always indicate the line number to which the correction refers.
- You can also insert your corrections in the proof PDF and **email** the annotated PDF.
- For fax submission, please ensure that your corrections are clearly legible. Use a fine black pen and write the correction in the margin, not too close to the edge of the page.
- Remember to note the **journal title**, **article number**, and **your name** when sending your response via e-mail or fax.
- **Check** the metadata sheet to make sure that the header information, especially author names and the corresponding affiliations are correctly shown.
- **Check** the questions that may have arisen during copy editing and insert your answers/ corrections.
- **Check** that the text is complete and that all figures, tables and their legends are included. Also check the accuracy of special characters, equations, and electronic supplementary material if applicable. If necessary refer to the *Edited manuscript*.
- The publication of inaccurate data such as dosages and units can have serious consequences. Please take particular care that all such details are correct.
- Please **do not** make changes that involve only matters of style. We have generally introduced forms that follow the journal's style. Substantial changes in content, e.g., new results, corrected values, title and authorship are not allowed without the approval of the responsible editor. In such a case, please contact the Editorial Office and return his/her consent together with the proof.
- If we do not receive your corrections **within 48 hours**, we will send you a reminder.
- Your article will be published **Online First** approximately one week after receipt of your corrected proofs. This is the **official first publication** citable with the DOI. **Further changes are, therefore, not possible.**
- The **printed version** will follow in a forthcoming issue.

Please note

After online publication, subscribers (personal/institutional) to this journal will have access to the complete article via the DOI using the URL: [http://dx.doi.org/\[DOI\]](http://dx.doi.org/[DOI]).

If you would like to know when your article has been published online, take advantage of our free alert service. For registration and further information go to: <http://www.link.springer.com>.

Due to the electronic nature of the procedure, the manuscript and the original figures will only be returned to you on special request. When you return your corrections, please inform us if you would like to have these documents returned.

Metadata of the article that will be visualized in OnlineFirst

ArticleTitle	Trapping measurements of volatile iodine by sand bed and metallic filters	
Article Sub-Title		
Article CopyRight	Akadémiai Kiadó, Budapest, Hungary (This will be the copyright line in the final PDF)	
Journal Name	Journal of Radioanalytical and Nuclear Chemistry	
Corresponding Author	Family Name	Leroy
	Particle	
	Given Name	O.
	Suffix	
	Division	PSN-RES
	Organization	Institut de Radioprotection et de Sûreté Nucléaire (IRSN)
	Address	Saint Paul lez Durance, France
	Phone	
	Fax	
	Email	olivia.leroy@irsn.fr
	URL	
	ORCID	http://orcid.org/0000-0001-7379-1606
Author	Family Name	Monsanglant-Louvet
	Particle	
	Given Name	C.
	Suffix	
	Division	PSN-RES
	Organization	Institut de Radioprotection et de Sûreté Nucléaire (IRSN)
	Address	Saint Paul lez Durance, France
	Phone	
	Fax	
	Email	
	URL	
	ORCID	
Schedule	Received	1 July 2019
	Revised	
	Accepted	
Abstract	A series of experimental tests were performed to measure the efficiency of volatile iodine trapping on sand bed filters and metallic filters. These filtering media are used in French nuclear power plants to mitigate releases in case of severe accident. The results show that molecular iodine is more easily trapped than methyl iodide due to its high chemical affinity with stainless steel or with silver and cesium cations included in the filter medium. For methyl iodide, the trapping efficiency is low.	
Keywords (separated by '-')	Source term - Severe accident - Volatile iodine - Sand bed filter - Metallic filter	
Footnote Information		



1 Trapping measurements of volatile iodine by sand bed and metallic 2 filters

3 O. Leroy¹ · C. Monsanglant-Louvet¹

4 Received: 1 July 2019
5 © Akadémiai Kiadó, Budapest, Hungary 2019

6 Abstract

7 A series of experimental tests were performed to measure the efficiency of volatile iodine trapping on sand bed filters and
8 metallic filters. These filtering media are used in French nuclear power plants to mitigate releases in case of severe accident.
9 The results show that molecular iodine is more easily trapped than methyl iodide due to its high chemical affinity with stain-
10 less steel or with silver and cesium cations included in the filter medium. For methyl iodide, the trapping efficiency is low. **AQ1**

11 **Keywords** Source term · Severe accident · Volatile iodine · Sand bed filter · Metallic filter

12 Introduction

13 The main objective of a Containment Venting System (CVS)
14 is to preserve the integrity of the containment in limiting
15 the overpressure resulting from severe accident conditions
16 on a nuclear reactor. This venting procedure has a negative
17 effect which is a potential release of radioactive gases and
18 aerosols into the environment if it is not equipped with a
19 retention device.

20 Currently, some Nuclear Power Plants (NPP) are equipped
21 with Filtered Containment Venting Systems (FCVS). A
22 complete review of FCVS worldwide was undertaken in
23 2014 [1] and completed in 2018 [2], these reviews were
24 initiated after the Fukushima-Daiichi accident. In France,
25 the decision of implementing sand bed filters on all of the
26 58 PWRs (pressurized water reactors) was made in 1986
27 and since the mid-1990s all French NPPs are equipped with
28 a filtered containment venting system made of a metallic
29 prefilter located inside the containment in order to confine
30 most of the radioactivity ahead of the sand bed filter that is
31 located outside of the containment.

32 The R&D programs concerning FCVS began in France
33 in the eighties [3]. The PITEAS program (1982–1986) was
34 devoted to the sand-bed filtering process to retain particulate
35 radioactive products. The FUCHIA program (1989–1991)

validated the thermo-hydraulic and filtering behavior of the
36 filtered venting line (sand bed filter and associated piping,
37 without pre-filtration) in full scale. The effectiveness of a
38 filtration device is defined by the Decontamination Factor
39 (DF). The decontamination factor of a filter is obtained by
40 the measurement of the concentration upstream of the fil-
41 ter, divided by the concentration measured downstream of
42 the same filter. The overall retention efficiency with respect
43 to molecular iodine was measured but detailed analysis of
44 results has shown that I₂ is probably trapped by deposition
45 on the internal surfaces of the pipes (DF ~ 10). Complemen-
46 tary experiments performed in 1990–1991 aimed at assess-
47 ing the aerosol retention efficiency of the metallic pre-filter
48 located inside the containment [4]. Nevertheless, the filtra-
49 tion efficiency of this pre-filter for I₂ has not been established
50 by those experiments. Potential effects of radiations in the
51 FCVS on iodine deposits stability and especially the effect of
52 air radiolysis products had not been accounted for. However,
53 recent source term R&D programs have shown that iodine
54 oxide particles and gaseous organic iodides may contribute
55 significantly to the outside releases in case of venting [5].
56 The filtration efficiency of metallic filters and of sand bed
57 filters for these species was not investigated in the past.

58 Sand bed filters and metallic filters are efficient to trap
59 aerosols but are not initially designed to trap gaseous fission
60 products. Among these gaseous fission products iodine is
61 well known to have a high contribution to radiological con-
62 sequence at short term after the accident. The main volatile
63 iodine species are constituted of molecular iodine (I₂) and
64

A1 ✉ O. Leroy
A2 olivia.leroy@irsn.fr

A3 ¹ PSN-RES, Institut de Radioprotection et de Sûreté Nucléaire
A4 (IRSN), Saint Paul lez Durance, France

65 organic iodide [6] with a special attention to methyl iodide
66 which is the most volatile.

67 Thus, in the framework of the MiRE project [7] (Mitiga-
68 tion of outside releases in case of nuclear accident) dealing
69 with Fission Product (FP) behavior (especially iodine and
70 ruthenium), IRSN performed experiments to review and
71 evaluate the potential trapping of I_2 and CH_3I through sand
72 bed filter and metallic filter.

73 After a short description of the IRSN experimental facilities
74 used for these studies, this paper presents the series of
75 tests performed to characterize the trapping of iodine gase-
76 ous species by sand bed filter and metallic filter. In addi-
77 tion, complementary tests were carried out in presence of
78 some additives in the sand filter to evaluate the potential
79 trapping increase resulting from the presence of other
80 potential reactive elements released from the core. A test
81 was also performed to evaluate the stability of the trapping
82 in the medium term (about 1 month to get sufficient activ-
83 ity decrease of iodine isotopes), that is to say the potential
84 release of the molecular iodine trapped in the metallic filter
85 due to the accumulated irradiation conditions in the filter
86 itself along time.

87 Experimental

88 The metallic filter used in our tests is a small part of a car-
89 tridge similar to those installed on French PWRs [6]. It is a
90 PALL® Corporation product. On French PWRs, it consists
91 of 92 filtering elements (“cartridges”) of 800 mm length
92 and 60 mm diameter each, with a total filtration surface
93 of 33 m². These filtering elements are constituted from
94 the internal to the external parts by a perforated internal
95 grid; a metallic weaved supporting layer; a first filtering

96 metallic medium (PMF FH 200); a second filtering medium
97 (PFM 40); a metallic weaved protective layer. The metallic
98 filter (MF) used for tests is a cylindrical section (52 mm
99 length representing a geometrical surface of 96 cm²) of the
100 PALL® cartridge. The filter was equipped with two flanges
101 in order to setup the experimental facility (Fig. 1). For tests
102 performed in the PERSEE experimental line, some pieces
103 (40 mm diameter) of the filter was cut and used. Some steel
104 wood was also tested (simulant of MF) to see any difference.

105 The sand used for tests was mainly a SIBELCO® prod-
106 uct from Hostun in Isere Valley, (France). It was sieved
107 between 0.5 and 0.7 mm in order to be representative of
108 sand present on French NPP’s with no pre-treatment (SB).
109 To complete the tests, sifted sand is used (SS). Another sand,
110 Fontainebleau type (FS), whose characteristics are perfectly
111 known and reproducible (median diameter 0.25 mm), was
112 used in some tests for comparison. Different sizes of sample
113 were designed for the tests. In severe accident, the operat-
114 ing conditions correspond to a maximum gas velocity of
115 10 cm/s at the start of the venting procedure. Then the veloc-
116 ity decreases later on when the pressure in the containment
117 decreases. The gas composition, at around 1 bar, is mainly
118 a steam/air mixture with a steam fraction varying between
119 20 and 30%_w.

120 Experimental molecular iodine test bench

121 Filtration efficiency facility

122 The set-up used for measuring decontamination factors of
123 sand bed filters and metallic filters with respect to molecular
124 iodine is schematized in Fig. 2. A gas flow allows the trans-
125 fer of gaseous molecular iodine through the filter (sand bed

Fig. 1 Section of filter (left)—
filter equipped with flanges
ready for irradiation (right)



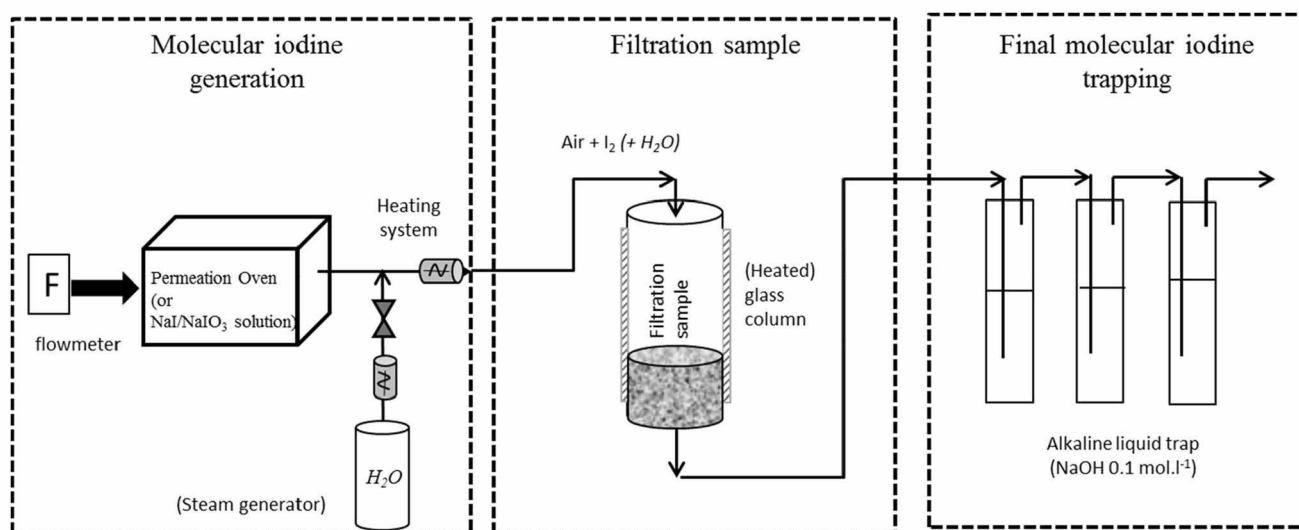


Fig. 2 Experimental facility used for the determination of decontamination factor with respect to molecular iodine

126 or metallic filter section) where it remains partly trapped.
 127 The molecular iodine not trapped by the filter is entrained
 128 towards alkaline liquid traps and is dissolved in liquid phase
 129 to form iodide and iodate anions.

130 It can be subdivided into three parts, corresponding
 131 respectively to the generation, the filtration sample and the
 132 trapping of molecular iodine:

133 • Two different molecular iodine generation systems are
 134 used. For sand bed filter tests, gaseous molecular iodine
 135 is produced from an acidic liquid phase based on Dush-
 136 man's reaction [8] using a sodium iodide and a sodium
 137 iodate solution. A glass reactor containing the NaI/NaIO₃
 138 solution is heated to 50 °C and it is covered to shelter its
 139 content from light. It is instrumented with a temperature
 140 sensor (Teflon[®]-coated PT 100) and a pH probe (Fisher
 141 Bioblock[®] brand, 6 mm gel microelectrode). It is also
 142 equipped with a gas inlet, regulated by a flowmeter, at
 143 the bottom of the reactor and an outlet for the gaseous
 144 reactants on the top plug. The sulfuric acid necessary
 145 for the reaction is introduced via a peristaltic pump in
 146 order to allow a regular production of molecular iodine.
 147 At the end of the test, the reaction is stopped by add-
 148 ing a solution of sodium hydroxide, thus the solution
 149 reaches a pH higher than 10. For tests performed without
 150 steam injection (dry air), a guard flask (not represented
 151 in Fig. 2) is added to condense the steam coming from
 152 molecular iodine generation. The gaseous I₂ concentra-
 153 tion lied between 32 and 426 ppm (as a function of the
 154 test), injected upstream of the sand sample.

155 For the metallic filter tests, gaseous molecular iodine
 156 of 470 ppb is generated using a permeation oven (VICI[®]
 157 150 °C) with three iodine permeation tubes (VICI[®], three

20 cm units) inside. Gaseous iodine is obtained by sublimation of solid molecular iodine pellets. The temperature of the permeation oven is fixed to 100 °C and the argon flow rate is 0.1 L TPN/min (1 atm, 0 °C). This device needs to be calibrated as a function of the operating temperature and pressure. When needed, a steam generator is used in order to fix the relative humidity (RH) in the gas flow.

- The filtration module consists of a glass column inside which the sample is placed. The glass makes it possible to limit the retention of iodine on the walls. For the sand bed test, two columns, filled with sand, can be used (Ø 10 cm or 4.6 cm) with a sintered glass type 3 (porosity 16–40 microns) on the bottom to maintain the sand. The metallic filter section is placed in the glass column (Ø 10 cm), heated to 100 °C by heating cords. Thanks to the flanges, the sweeping gas goes radially through the metallic filter from its outside to its inside surfaces.
- The final molecular iodine trapping module consists in three alkaline liquid traps (NaOH 0.1 mol/l). At regular time intervals, a sample of trap solution is taken. The liquid samples are then analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) to determine the amount of iodine not retained by the filter, the detection limit is about 8×10^{-9} mol/l.

EPICUR irradiation facility

184 The experimental set-up used to study the medium term irra-
 185 diation behavior of molecular iodine previously deposited in
 186 the metallic filter consists of an irradiator with ⁶⁰Co sources
 187 (totaling 893 TBq as of September 2012) and a polished
 188 stainless steel loop including an irradiation vessel connected

189 to a selective filter of gaseous iodine species called May-
 190 pack (Fig. 3), further details are available in Ref. [9]. The
 191 metallic filter previously loaded with iodine is installed in
 192 the irradiation vessel. Temperature, pressure and gaseous
 193 atmosphere composition are controlled in the irradiation ves-
 194 sel. The specific design allows a homogeneous face velocity
 195 of the sweeping gas, radially from the outside to the inside
 196 surfaces of the metallic filter. The effect of radiations deliv-
 197 ered by the fission products in the metallic pre-filter after
 198 an accident is represented by ^{60}Co sources that deliver an
 199 average dose rate of several kGy/h. Under the effect of radi-
 200 ation and thermal constraints, the iodine gaseous species
 201 released, from the iodine deposited on the metallic filter,
 202 are transported to the May-pack device. This system makes
 203 it possible to differentiate and measure the various species
 204 of iodine released: particulate iodine in a quartz fiber filter
 205 (particulate), molecular iodine in a silver clad copper filter
 206 called knit-mesh (I_2) and then penetrating species (probably
 207 organic iodide) in an impregnated charcoal filter. Thanks to
 208 the use of ^{131}I to label molecular iodine, continuous meas-
 209 urements are performed on the Maypack filter stages (NaI
 210 counters are placed above each filtration stage of the May-
 211 pack device) in order to quantify on-line the amount of the
 212 different species volatilized and trapped on the selective fil-
 213 ters. At the end of the irradiation phase, the iodine filtra-
 214 tion system is recovered and the major parts of the experimen-
 215 tal loop are dismantled and washed. The different filters, the
 216 loaded metallic pre-filter and the washing solutions of the
 217 irradiation vessel of the experimental loop are counted after

218 the test in order to compare these post-test measurements
 219 with the online measurements and to calculate the overall
 220 iodine mass balance at the end. Nevertheless, the online
 221 gamma measurements are not as accurate as post-test meas-
 222 urements provided with γ counting on each filter separately
 223 after dismantling. The corrective factor is the ratio between
 224 the sum of the activities measured on each filter of the stage
 225 during the post-test measurements and the activity measured
 226 online at the end of the test. So, all the on-line kinetics data
 227 are corrected by these ratios to establish the “true” kinetics
 228 data presented here.

229 Description of tests

230 A series of tests was performed to characterize the efficiency
 231 of sand bed filter with respect to molecular iodine. The main
 232 studied parameters are: the face velocity, the height of the
 233 sand bed and the sand composition (with and without addi-
 234 tives). A velocity of 10 cm/s corresponds to the maximum
 235 face velocity expected in the sand bed filter during depres-
 236 surization of the reactor containment following a severe
 237 accident. The test matrix is presented in Table 1. For the
 238 tests without humidity (SB1 and SB5), the initial moisture
 239 content of the sand is about 2% wt. For the tests with wet
 240 atmosphere, the humidity of the sand is about 10% wt. In
 241 addition to tests performed on sand alone, additional tests
 242 have been carried out with additives in order to check the
 243 possible iodine retention with these additives which are
 244 selected for their affinity for iodine species (like Cs or Ag).

Fig. 3 Process schema of the EPICUR facility

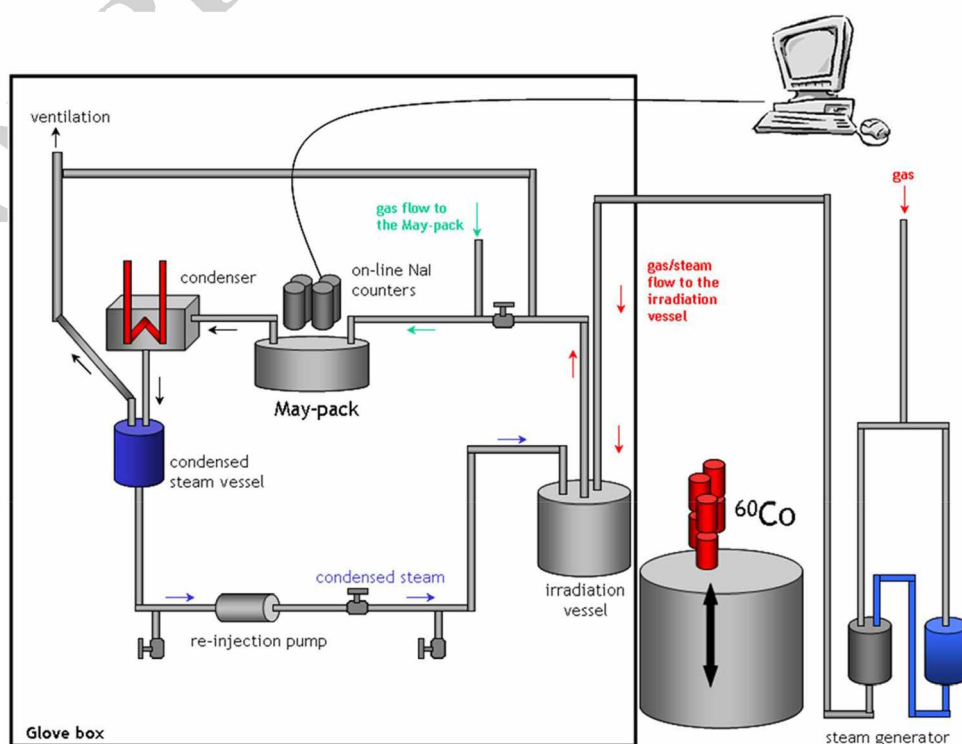


Table 1 Experimental matrix for molecular iodine with sand bed tests

Tests	Parameters tested	Sand—w/wo additive	Column diameter Ø, sand height (cm)	Flow velocity (cm/s)
SB1	Reference—low speed	Dry—w/o additives	Ø 10 cm, 15	0.3
SB2	Humidity	Wet—w/o additives	Ø 10 cm, 15	0.3
SB3	Effect of Cs deposits	Wet—with CsOH	Ø 10 cm, 15	0.3
SB4	Effect of Ag ⁰ deposits	Wet—with Ag particles	Ø 10 cm, 15	0.3
SB5	High speed	Dry— w/o additives	Ø 4.6 cm, 20	10
SB6	Effect of Ag ⁺ deposits	Wet—with AgNO ₃ (10% _w solution)	Ø 4.6 cm, 20	10
SB6bis		(10% _w powder)		

245 For SB3, a CsOH solution (concentration at 50%_w) is deposited at 2.5 cm from the upper part of sand, it corresponds to
 246 a target (Cs/I)_w ratio of 2.5 to have an excess of cesium with respect to iodine in proportion which could be encountered
 247 in SA conditions. For SB4, a metallic silver powder (2.6 g) is mixed with a fraction of the sand and deposited at the top
 248 of the column to reach a target (Ag/I)_w ratio of 8.9. These two additives (Cs and Ag) are present in nuclear accident
 249 because cesium is a fission products and silver comes from control rods degradation. The idea was to be assessing possible
 250 increase of iodine trapping in more relevant conditions. Another alternative was to check if the initial impregnation
 251 of sand by Ag⁺ would promote the trapping of iodine. For SB6 and SB6bis, 50 g of Ag (in AgNO₃ form) are mixed
 252 with 500 g of sand either directly in powder form or in silver nitrate solution and then dried at 60 °C. Tests duration is
 253 between 90 min and 180 min depending on the conditions.

254 The decontamination factor of our experimental metallic filter with respect to molecular iodine (MF-I₂) was investigated.
 255 For this test, the I₂ generation kinetics is measured during 1 h using a by-pass line to determine the injected iodine.
 256 Then, during 4 h, a flow of I₂ was injected at a face velocity of 1 cm/s through the metal filter maintained at
 257 (100 ± 3) °C with a RH of (40 ± 4)% (23%_w). Subsequently, the desorption of I₂ from the metal filter was tested under
 258 the same conditions but without I₂ flow. The device is heated without air flow up to 100 °C. The time 0 corresponds to
 259 the injection of air/steam mixture once the target temperature was reached. The first measurement was performed at
 260 50 min.

275 Another test, performed on the EPICUR facility (MF-I₂ stab.), was devoted to test the stability of molecular iodine
 276 trapped on a metallic filter and then submitted to irradiation. Before the irradiation phase, the metallic filter is loaded with
 277 labeled molecular iodine (I¹³¹). Molecular iodine was produced in an acidic liquid phase from the Dushman's reaction
 278 at 50 °C in presence of radioactive iodine used for labeling (¹³¹I, Perkin Elmer). After iodine loading and γ counting
 279 (13.8 mg of iodine on cylindrical section), the filter is inserted in the irradiation vessel. A specific design allows
 280 a homogeneous face velocity of the sweeping gas, radially from the outside surface to the inside surface of the metallic
 281 filter. The experimental conditions of the irradiation test, including two desorption phases at 100 °C and 120 °C, are
 282 presented in Table 2.

290 Experimental organic iodine test benches

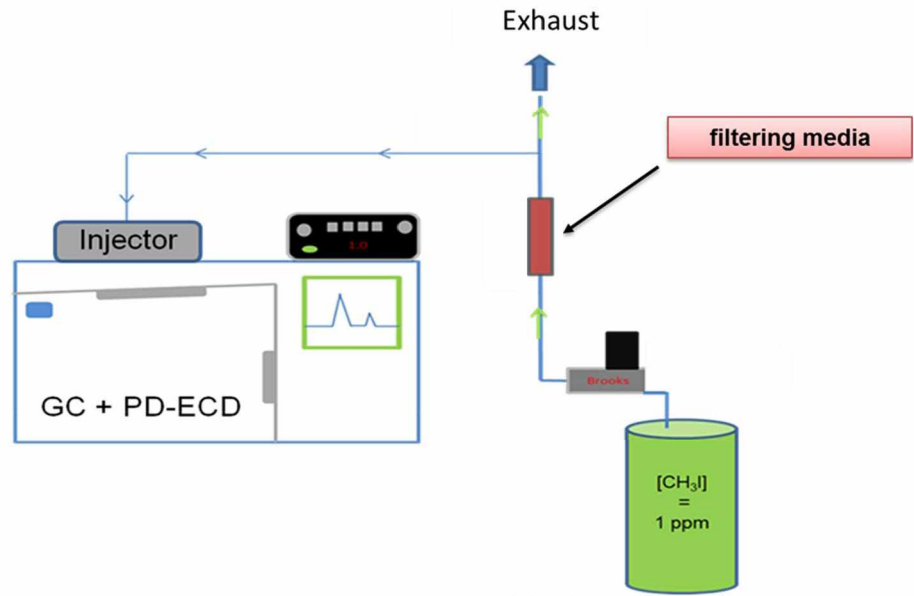
291 Filtration efficiency facilities

292 The test bench (Fig. 4) allows to measure, by gas chromatography (Perkin Elmer® GC), decontamination factors for
 293 CH₃I on different filtering media. The detector is a specific pulsed discharge—electron capture detector (PD-ECD) (¹),
 294 very sensitive to halocarbons and other electronegative compounds, and especially to methyl iodide. Organic iodine is
 295 obtained from a pressurized bottle at 100 bars and a standard concentration of 1 ppm. The CH₃I concentration of 500 ppb,
 296 injected upstream of the sand sample, is prepared by dilution

Table 2 Experimental conditions for the remobilisation test of molecular iodine trapped on metallic filter under irradiation

	Temperature (°C)	Pressure (bas abs)	Gas	Air gas flow rate (g/h)	Water flow rate (g/h)	Dose rate (kGy/h)	Duration (h)
Pre-irradiation phase	100	2.5	Air + steam (35% RH)	51.5	6.8	—	5
Irradiation (phase I)	100	2.5	Air + steam (35% RH)	51.5	6.8	2.0	16
Irradiation (phase II)	120	3.5	Air + steam (35% RH)	48	9.6	2.0	16
Post-irradiation (phase I)	120	3.5	Air + steam (35% RH)	48	9.6	—	5
Post-irradiation (phase II)	120	3.5	Dry air	60	0	—	1

Fig. 4 Experimental facility used for the determination of DF with respect to methyl iodide



301 with a filtered compressed air flowrate. The gas flowrate at
 302 the sand bed filter inlet is 7.7 L/min NTP (Normal Tem-
 303 perature and Pressure conditions: 1 atm, 0 °C), giving an
 304 average face velocity of 10 cm/s. The tests were carried out
 305 at ambient temperature and relative humidity close to 0%.
 306 The filter holder for the sand tests is a cylinder with 4 cm
 307 diameter and with 2.5 or 5.0 cm height of sand correspond-
 308 ing to ~ 500 mg for 5 cm.

309 Additional tests with radioactive iodine (^{131}I) were per-
 310 formed in the PERSEE facility (Fig. 5). It is designed to
 311 test filtering media inside sample holders. The test consists

in taking two layers of materials. The first layer is the
 312 tested filtering media (sand or part of metallic filter in
 313 this case). The second layer is a cartridge filled with ref-
 314 erence activated charcoal, well-known media with a high
 315 decontamination factor for methyl iodide. After condition-
 316 ing during several hours, both medias are challenged with
 317 a pulse of methyl iodine (150 ppb) tagged with radioac-
 318 tive methyl iodine. The measurement of the ^{131}I activity
 319 present inside the medias by gamma spectrometry allows
 320 determining the DF. The flowrate is controlled by flowme-
 321 ter at about 18 L/min at NTP.
 322

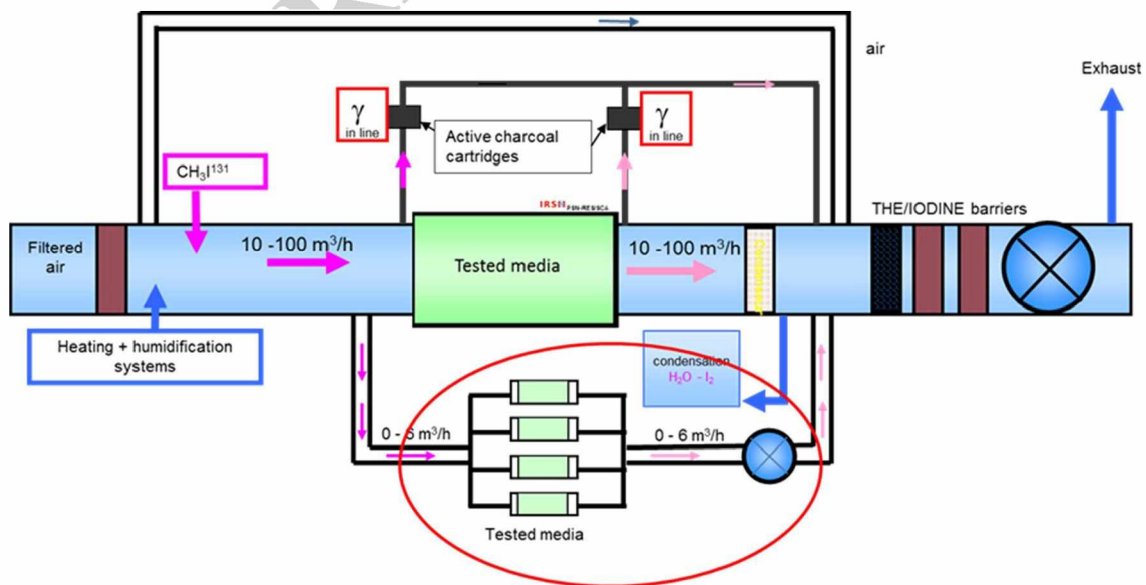


Fig. 5 Experimental facility used for the determination of DF with respect to radioactive methyl iodide

323 **IRMA irradiation facility**

324 In addition to the EPICUR facility, another irradiation facility was used. Indeed, the samples of media to be tested were irradiated in the IRMA cell, also fitted up with ^{60}Co sources (4 sources with a total activity of 896 TBq as of September 10, 2018). This facility allows studying dose or dose rate effects induced by photons on medias or more generally for characterizing the media evolution after irradiation. The number of sources to be used can be adapted according to the target dose rate. It was, as of September 10, 2018, 14 kGy/h at 10 cm of the 4 sources. The duration of the irradiation can vary from a few hours to several weeks depending on the target dose rate and the target integrated total dose. For the present studies, the objects were irradiated until 1 MGy at about 10 kGy/h.

338 **Description of tests**

339 SIBELCO[®] (SB) and Fontainebleau (SF) sands were tested before and after irradiation (1 MGy), the SF with a small grain size. To complete these tests, different quantities of

AgNO₃ crystals (between 10 and 30% weight in AgNO₃ form) or CsOH crystals (12% or 24% in CsOH weight) were added to the Sibelco[®] sand. This tagging is carried out either by washing the sand with salt solutions and then by evaporating water in the dark either by mechanical mixing of nitrate powders. Some of these sand samples were also irradiated to check the global chemical stability. All tests are performed at room temperature in air, except the five test performed with labeled iodine performed in temperature and 3%_w in steam as reported in Table 3.

In addition, two tests were carried out on part of a real metallic pre-filter (40 mm diameter) in the same conditions as the last five tests of the Table 3 (^{131}I , 80 °C, 6% R.H., 10 cm/s).

Results and discussion**Molecular iodine test bench**

In sand bed filter without additives, the results show (Table 4) that with a low face velocity (0.3 cm/s) or high

Table 3 Experimental matrix for organic iodine and sand bed tests

	Type of material SB: SIBELCO [®] sand SF: Fontainebleau sand SS: sifted sand	Impregnation	Irradiation
Reference tests	SB	Without impregnation	Irradiated
	SF	Without impregnation	Irradiated
Effect of CsOH	SB	12% CsOH	Non irradiated
	SB	23% CsOH	Non irradiated
	SF	12% CsOH	Non irradiated
	SF	24% CsOH	Non irradiated
Effect of CsOH + irradiation	SB	12% CsOH	Irradiated
	SB	24% CsOH	Irradiated
	SF	24% CsOH	Irradiated
	SF	11% CsOH	Irradiated
Effect of AgNO ₃	SB	23% AgNO ₃	Non irradiated
	SF	24% AgNO ₃	Non irradiated
Effect of AgNO ₃ + irradiation	SB	11% AgNO ₃	Irradiated
	SB	23% AgNO ₃	Irradiated
	SF	11% AgNO ₃	Irradiated
	SF	23% AgNO ₃	Irradiated
100% powder	AgNO ₃ powder	–	Non irradiated
	CsOH powder	–	Non irradiated
“FCVS conditions”	SB (^{131}I test, 80 °C, 6% R.H.)	10% _w AgNO ₃ in powder form	Non irradiated
	SB (^{131}I test, 80 °C, 6% R.H.)	20% _w AgNO ₃ in powder form	Non irradiated
	SB (^{131}I test, 80 °C, 6% R.H.)	30% _w AgNO ₃ in powder form	Non irradiated
	SB (^{131}I test, 80 °C, 6% R.H.)	10% _w AgNO ₃ in powder form (in layers: AgNO ₃ first, sand after)	Non irradiated
	SS (^{131}I test, 80 °C, 6% R.H.)	15% AgNO ₃ (impregnation in solution form)	Non irradiated

Table 4 Decontamination factor for sand bed filter tests with respect to molecular iodine

Tests	Parameters	DF
SB1	Reference—low speed	1.0
SB2	Humidity	1.14
SB3	Effect of Cs deposits	173
SB4	Effect of Ag ⁰ deposits	7
SB5	High speed	0.96
SB6	Effect of Ag ⁺ solution—high speed	7521
SB6bis	Effect of Ag ⁺ powder—high speed	14,080

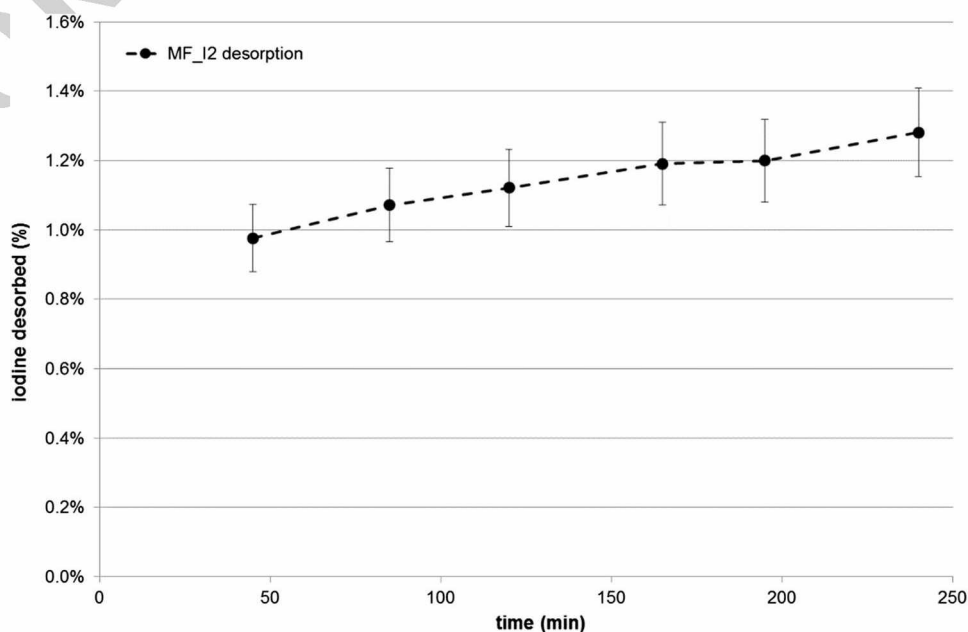
360 face velocity (10 cm/s) and with dry or wet sand, the DF is
 361 close to 1 (SB1, SB2 and SB5). Less than 1% of molecular
 362 iodine is trapped. The sand bed filter alone cannot trap
 363 I₂, as expected. The use of additives makes it possible to
 364 increase the decontamination factor, even with a high face
 365 velocity I₂ is converted into of less or no volatile species.
 366 The best results are obtained with the sand doped with
 367 10% of silver (SB6bis) with a DF increase up to 14,000.

368 Over 4 h, the DF of the metallic filter with respect to
 369 molecular iodine is 11. This value may be considered as a
 370 low value because nuclear aerosols, composed of fission
 371 products and structural materials, already trapped on the
 372 filter may react with molecular iodine and so increase the
 373 trapping efficiency by chemical interaction [10]. During
 374 the desorption phase, at 45 min, a significant desorption
 375 of about 1% is measured. It corresponds to the complete
 376 phase of heat-up (about 1 h) plus 50 min of tests condition.
 377 After the first 45 min, the release rate is relatively slow
 378 and constant (0.11%/h). After 4 h, a low but quantifiable

iodine quantity is measured in the liquid traps, about 1.3%
 (Fig. 6).

Iodine deposition on steel surface has been studied previ-
 ously [10] but not for filters. The literature is also quite poor
 at low temperature (~100 °C). Usually it is reported that
 the retention of elemental iodine (I₂) on iron yields metal
 iodide as FeI₂ [11]. Wren et al. [12] studied, under ambient
 temperature iodine adsorption and desorption on various
 stainless steel surfaces (100 h). The adsorbed iodine desor-
 bed partially only under air atmosphere. The major part
 of iodine didn't desorb indicating that some iodine was irre-
 versibly adsorbed. However, our test duration is too short
 (4 h) to highlight this stop of desorption which was observed
 on 100 h duration tests. Nevertheless, it is likely that the
 same conclusions may apply. So, extrapolating our measured
 released kinetics leads to a potential maximum release of
 about 6% at 48 h.

For “MF_I₂ stab” test involving I₂ previously deposited
 on the metallic filter, results of iodine release are presented
 in Fig. 7. During the pre-irradiation sweeping phase with
 moist air (35% RH) at 100 °C, iodine is quickly measurable
 on the impregnated charcoal. The release is continuing dur-
 ing the irradiation phase of the test. This “organic” release
 is regularly observed in previous test. It may be attributed
 to the presence of organic pollution in the loop, in the irradi-
 ation vessel or on the filter that may react with gaseous I₂.
 So this quantity can be re-attributed to “molecular iodine”
 fraction at the direct outlet of the filter and summed to the
 knit-mesh activity. A slight increase in kinetics is observed
 between 100 and 120 °C. We observe also an increase of
 iodine release after 30 h of irradiation but this increase is
 probably due to an experimental artefact linked to unwanted

Fig. 6 Evolution of the desorption kinetics (%) at 100 °C and 40% R.H during MF_I₂ test

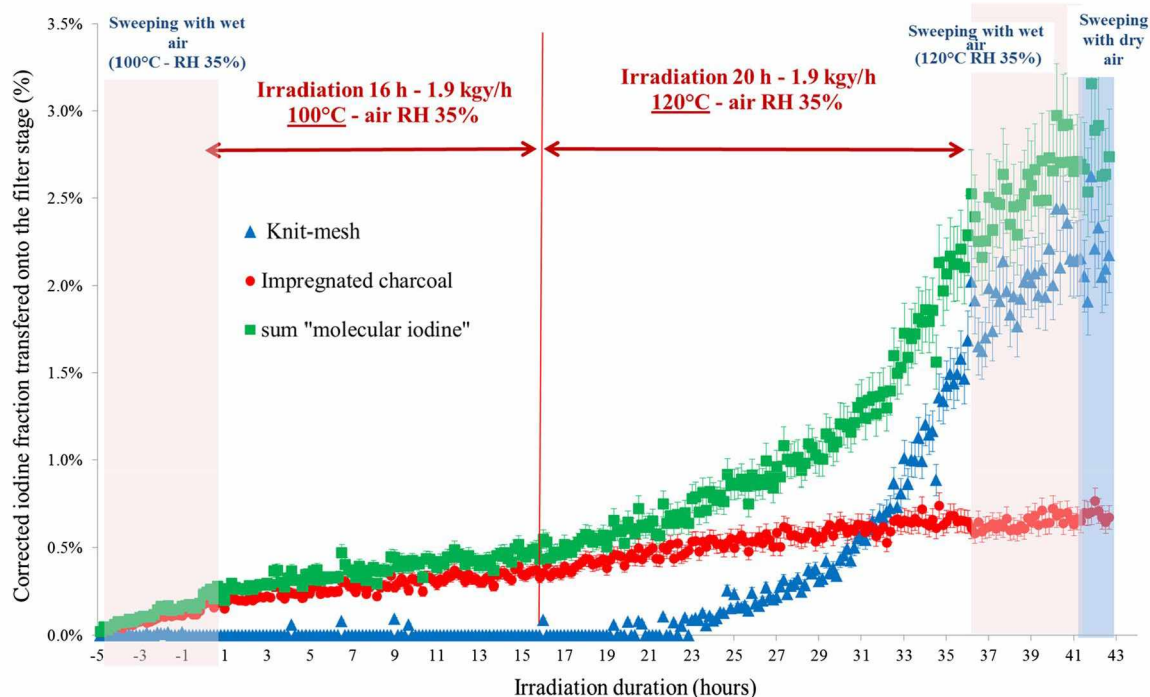


Fig. 7 Iodine fraction released recovered on impregnated charcoal filled circle and knit-mesh filled triangle and the two contribution summed into filled square from the metallic filter during the irradiation test

411 pressure fluctuations and cumulated temperature effect.
 412 The increase of temperature promote the iodine desorption
 413 trapped by physisorption process. At the end of the test, the
 414 release of iodine measured thanks to the May-pack filter is
 415 weak (~3% after 36 h of irradiation).

416 The global release corresponds to the difference between
 417 the activity of the metallic pre-filter before and after irradiation,
 418 it is expressed in percentage of the activity loaded in
 419 the filter before irradiation. The global release is 6.2% of
 420 molecular iodine. This result is quite similar to that extrapolated
 421 in the desorption test without irradiation. By comparison
 422 with pure thermal desorption results and this desorption
 423 test under irradiation, it can be stated that there is no significant
 424 effect of the irradiation on the desorption process.

425 Organic iodine test bench

426 In sand bed filter, as expected, there is no retention of
 427 CH_3I . The decontamination factors are close to 1 for all
 428 the sand configurations (and materials) tested. Indeed, the
 429 sand has a compact structure (no real porosity) in contrast
 430 to the materials conventionally used for the adsorption
 431 of iodine. Its specific surface area is small (of the order
 432 of $1 \text{ cm}^2/\text{g}$), to be compared with specific surfaces up to
 433 $1000 \text{ m}^2/\text{g}$ for usual porous materials. In addition, silica
 434 is known to be chemically inert. Finally, concerning the tests
 435 devoted to improve the filtering efficiency of the sand bed

436 filter with some chemical additives, the results obtained
 437 are not conclusive. The treatment of the sand with AgNO_3
 438 solution leads only to a slight DF increase (~1.4 vs. 1.0)
 439 contrary to I_2 (SB6, SB6bis in Table 4). So, the results
 440 confirmed that the silver-impregnated sands are not efficient
 441 to trap methyl iodide. It is probably due to a not
 442 sufficient dispersion of silver species inside the materials
 443 as well as the absence of porosity. Indeed, porosity may
 444 promote the physical adsorption in a first step of the trapping
 445 process before chemical reactions between methyl
 446 iodide and silver [13].

447 For the metallic filter, CH_3I is not trapped. This result is
 448 consistent with literature data. Rosenberg [14] investigated
 449 the vapor phase deposition of CH_3I on 304 stainless steel
 450 plate at $115 \text{ }^\circ\text{C}$, in air/steam mixture at 0.35 cm/s and he
 451 showed that the deposition velocity was four to five orders
 452 of magnitude lower than for I_2 . It is worth noticing that the
 453 tested conditions are ideal conditions where no aerosol is
 454 impacted on the surfaces as it can be in FCVS operating
 455 conditions of the metallic filter. Some silver or cesium aerosol
 456 deposits should promote the iodine trapping but for methyl
 457 iodide this effect should be quite small due to the structure
 458 of the molecule, which is a haloalkane. This molecule is
 459 not very reactive with respect to surfaces (the reactivity is
 460 done via substitutions or binding breaks under high radiation)
 461 because it is a saturated compound with a strong C–I
 462 binding energy, which is not the case of I_2 .

463 **Conclusions**

464 The main conclusion of these test series is that the part of
 465 molecular iodine and organic iodine, coming out of the pre-
 466 filter stage, is not trapped by the downstream sand bed filter,
 467 dry or wet. This is probably due to the absence of inter-
 468 nal porosity (like zeolite for instance) which would have
 469 promoted the physical adsorption. The addition of silver or
 470 cesium inside the sand, leads to a significant increase of
 471 the trapping for molecular iodine thanks to the formation of
 472 metallic iodide particle; however, it has practically no effect
 473 for methyl iodide. The best results for trapping gaseous I₂ are
 474 obtained with the sand doped with 10%_w in silver (AgNO₃
 475 powder) with a DF increase up to 14,000. Concerning the
 476 metallic filter, the trapping is significant (DF ~ 10) for I₂ and
 477 it is moreover almost irreversible: less than 5% of trapped I₂
 478 being released after 24 h whereas for methyl iodide, there is
 479 no trapping. Research is going to identify porous materials
 480 able to trap methyl iodide.

481 **Acknowledgements** This work was performed in the frame of the
 482 French research program ANR-11-RSNR-0013-01 called MiRE (Miti-
 483 gation of Iodine Releases in the Environment).

484 **References**

- 485 1. OECD/NEA/CSNI (2014) Staus report on filtered containment
 486 venting, NEA/CSNI/R.7
- 487 2. Yang J, Lee DY, Miwa S, Chen S-W (2018) Overview of filtered
 488 containment venting system in nuclear power plants in Asia.
 489 Ann Nucl Energy 119:87–97. <https://doi.org/10.1016/j.anuce>
 490 [ne.2018.03.047](https://doi.org/10.1016/j.anuce)
- 491 3. Guieu S (2014) French NPPs filtered containment venting design.
 492 Paper presented at the international society for nuclear air treat-
 493 ment technologies—33rd nuclear air cleaning conference, St.
 494 Louis, MO, 22–24 June 2014
- 495 4. Kaercher M (1992) Design of a pre-filter to improve radiation pro-
 496 tection and filtering efficiency of the containment venting system.
 497 In: 22nd DOE/NRC nuclear air cleaning and treatment conference,
 498 Denver, Colorado (USA), 24/27 Aug 1992

5. Raimond E, Clément B, Denis J, Guigueno Y, Vola D (2013) Use
 499 of Phébus FP and other FP programs for atmospheric radioac-
 500 tive release assessment in case of a severe accident in a PWR
 501 (deterministic and probabilistic approaches developed at IRSN).
 502 Ann Nucl Energy 61:190–198. <https://doi.org/10.1016/j.anuce>
 503 [ne.2013.05.035](https://doi.org/10.1016/j.anuce)
6. Jacquemain D, Guentay S, Basu S, Sonnenkalb M, Lebel L, Alle-
 504 lein HJ, Liebana B, Eckardt B, Ammirabile L (2014) OECD/NEA/
 505 CSNI Status report on filtered containment venting. Report NEA/
 506 CSNI/R 2014-7
7. Cantrel L, Albiol T, Bosland L, Colombani J, Cousin F, Gre-
 507 goire AC, Leroy O, Morin S (2018) Research works on iodine
 508 and ruthenium behavior in severe accident conditions. J Nucl Eng
 509 Radiat Sci. <https://doi.org/10.1115/1.4038223>
8. Dushman S (1904) The rate of the reaction between iodic and
 510 hydriodic acids. J Phys Chem 8(7):453–481
9. Bosland L, Colombani J (2017) Study of iodine releases from
 511 epoxy and polyurethane paints under irradiation and development
 512 of a new model of iodine-Epoxy paint interactions for PHEBUS
 513 and PWR severe accident applications. J Radioanal Nucl Chem
 514 314(2):1121–1140. <https://doi.org/10.1007/s10967-017-5458-9>
10. Funke F, Hellmann S (1994) Reaction of iodine with steel sur-
 515 faces: part I—literature study. Nuclear sciences and technology,
 516 EUR 15668/1 EN. European Commission
11. Evans GJ, Deir C, Ball JM (1994) The retention of iodine in
 517 stainless steel sample lines. Paper presented at the 23rd DOE/
 518 NRC nuclear air cleaning and treatment conference, Buffalo, NY
 519 (United States), 25–28 July 1994
12. Wren JC, Glowa GA, Merritt J (1999) Corrosion of stainless
 520 steel by gaseous I₂. J Nucl Mater 265(1–2):161–177. [https://doi.org/10.1016/s0022-3115\(98\)00504-2](https://doi.org/10.1016/s0022-3115(98)00504-2)
13. Bučko T, Chibani S, Paul JF, Cantrel L, Badawi M (2017) Dis-
 521 sociative iodomethane adsorption on Ag-MOR and the formation
 522 of AgI clusters: an ab initio molecular dynamics study. Phys Chem
 523 Chem Phys 19(40):27530–27543. [https://doi.org/10.1039/c7cp0](https://doi.org/10.1039/c7cp05562e)
 524 [5562e](https://doi.org/10.1039/c7cp05562e)
14. Rosenberg HS, Genco JM, Morrison DL (1969) Fission-product
 525 deposition and its enhancement under reactor accident condi-
 526 tion deposition on containment-system surfaces. BMI-1865. US
 527 Atomic Energy Commission

Publisher's Note Springer Nature remains neutral with regard to
 528 jurisdictional claims in published maps and institutional affiliations.

Journal:	10967
Article:	6786

Author Query Form

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your article, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query	Details Required	Author's Response
AQ1	Please confirm the inserted city name is correct for affiliation.	