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# **Influence of SIC control rod material on the iodine release in case of nuclear severe accident – Chemical reactivity with fission products in thermal conditions of RCS**

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1 **Influence of SIC control rod material on the iodine release in case of nuclear**  
2 **severe accident – Chemical reactivity with fission products in thermal**  
3 **conditions of RCS**

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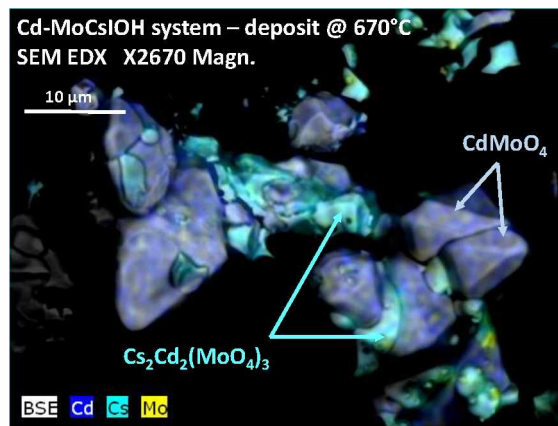
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14 **Graphical abstract**



15

16

17 **Abstract**

18 The effect of Silver-Indium-Cadmium (SIC) control rod on the transport of volatile fission products (I,  
19 Cs, Mo) in conditions of a Reactor Coolant System under NPP severe accident was investigated within  
20 three semi-integral tests in a thermal gradient tube. The experiments addressed separately the effect  
21 of each SIC element. Nature of transported and deposited species was investigated by ICP MS, ESEM-  
22 EDX, Raman Microspectrometry, XRD and XPS techniques.

23 For the first time, numerous metallic molybdates involving SIC components were evidenced. The  
24 formation of such metallic molybdates competes with the formation of Cs-molybdate and may in  
25 certain conditions strongly reduce the scavenging effect of Mo towards Cs. As a result the nature of  
26 transported iodine can be strongly modified, compared to chemical systems involving only Mo, Cs and  
27 I. The data obtained are useful to guide what species have to be added in the thermodynamic database  
28 used in the SA simulation software.

29

30 **Keywords:**

31 Severe accident, Reactor Coolant System, Metallic molybdates, Chemical reactivity, Iodine transport

32

33 **Highlights:**

34 The SIC components reacts with Mo oxide to form metallic molybdates

35 With respect to Mo oxide, SIC components can be ordered by increasing reactivity: In < Ag ~ Cd

36 The formation of SIC metallic molybdates competes with Cs-scavenging effect of Mo oxide

37 The presence of SIC elements has a strong influence on the nature of iodine released from the RCS

38

## 39 1. Introduction

40 During a severe accident (SA) occurring on a nuclear power plant (NPP), strong releases of volatile  
41 fission products (FPs) such as iodine, caesium or even molybdenum are expected. These FPs can  
42 contribute to high radiological consequences in case of releases into the environment following early  
43 containment venting procedure or containment failure - as was the case during the Fukushima Daichi  
44 NPP accident (Masson *et al.*, 2011; Chino *et al.*, 2011; Huh *et al.*, 2012; Stohl *et al.*, 2012; Lebel *et al.*,  
45 2016). In such situation, the accident management is strongly linked to the physico-chemical forms of  
46 the released radioisotopes, especially for iodine as gaseous or particulates species do not contribute  
47 to the same extent to radiological consequences (Hoeve and Jacobson, 2012; Geng *et al.*, 2017; Masson  
48 *et al.*, 2019).

49 In early accidental phase, the nature of the radioisotope released from the Reactor Coolant System  
50 (RCS) and accumulated in the nuclear containment building is directly linked to the physico-chemical  
51 phenomena prevailing in the RCS. Little information is available in the literature concerning the  
52 chemical speciation inside the RCS (Clément *et al.*, 2007). The phenomena occurring in the RCS during  
53 a SA are indeed very complex involving strong thermal gradients, rapid atmosphere changes from  
54 reducing to oxidizing conditions, complex chemical systems involving some more or less volatile FPs  
55 (Cs, I, Mo, Te), control rod (CR material such as Ag, In, Cd and B) and structure materials with release  
56 kinetics and thus element ratio depending on the extent of fuel degradation.

57 The chemical form of iodine and its behaviour after entering containment from the RCS break were  
58 previously documented in NUREG/CR-5732 (Beahm *et al.*, 1992). On the basis of thermodynamic  
59 computation it was considered that iodine entering the containment was at least 95 % under CsI form  
60 with the remaining 5% as I and HI under gaseous form. For caesium, the main prevailing assumption is  
61 that the CsOH is in large excess (Williams, 1994). After extensive experimental research and modelling  
62 on fission product release and transport in severe accident conditions over the past thirty years, the  
63 situation appears much more complex.

64 Indeed the large scale Phébus FP test series showed that in addition to CsI, other condensable iodide  
65 forms may exist in the RCS (Girault and Payot, 2013). Indeed, the deposits collected on the thermal  
66 gradient tubes (700 -150°C temperature range) of the Phébus experimental circuit and determined by  
67  $\gamma$ -spectrometric measurements presented several iodine condensation peaks not systematically  
68 correlated to caesium deposit. Moreover, the fractions of aerosol/gaseous iodine transported into the  
69 Phébus containment vessel (150°C) were variable and strongly dependent on the test scenario (Girault  
70 *et al.*, 2010, Girault *et al.*, 2012, Haste *et al.*, 2013), suggesting a complex chemistry during the transit  
71 though the experimental circuits. In addition, the small-scale Falcon ISP1/2 tests performed with  
72 simulatant fuel pellets (Williams, 1994) and VERCORS HT2/3 tests performed with actual spent fuel  
73 pellets (Pontillon and Ducros 2010) supported also the assumption of iodine being transported in  
74 others forms than CsI;  $CdI_2$  is suggested as a possible alternative. Deposition profile of the other main  
75 released FPs (Mo, Cs, Te ...) and CR elements (Ag, In, Cd) in the thermal gradient was also determined  
76 for these tests either by  $\gamma$ -spectrometry (VERCORS HT test) or after chemical leaching and elemental  
77 analysis (ICP OES – Falcon tests) . Based on the elements condensation peaks, the formation of various  
78 metallic molybdates were put forward (McFarlane *et al.*, 2002) as well as the formation of CsTe species  
79 (McFarlane and Leblanc, 1996; De Boer and Cordfunke, 1995) supporting the fact that caesium  
80 chemistry is also more complex than initially expected. The formation of caesium borates was also  
81 assumed based on separate effect tests (Bowsher and Nichols, 1985; Bowsher and Diskinson, 1986;  
82 Elrick *et al.*, 1987) but boron deposition profile could not be determined (no  $\gamma$ -emitter). The use of  
83 actual spent fuel for such experiments allows to be as close as possible of a reactor case but induces  
84 experimental issues due to the handling of highly reactive samples. As a consequence, the  
85 characterization of the deposited/transported material was limited mainly to  $\gamma$ -spectrometry which  
86 cannot provide any chemical speciation. Interpretation of such experiments relies thus mostly on  
87 computer simulations which in turn needs reliable thermodynamic and thermokinetic data for



88 chemistry of FPs and CR material at high temperature, even if recent works were performed to improve  
89 these data (Grégoire *et al.*, 2017; Miyahara *et al.*, 2019) works are still ongoing on this.

90 In order to improve the understanding of the main chemical formation, decomposition, deposition  
91 processes in which released FPs and control rod elements are involved in the RCS during a SA and also  
92 to build an experimental database allowing the validation process for models, the ISTP-CHIP (2005-  
93 2012) and the follow-up CHIP+ (2012-2018) experimental programs were launched at IRSN (Clement  
94 and Zeyen, 2005). The CHIP (Chemistry Iodine Primary circuit) experimental set-up and its small scale  
95 GAEC (Generation of AErosols in the reactor Coolant system) analog were designed as open flow  
96 reactors in which reagents are continuously mixed at high temperature (1600°C) and transported into  
97 a controlled thermal profile using carrier gas (steam/H<sub>2</sub>) reproducing as much as possible conditions  
98 of the RCS of a Light Water Reactor (LWR) during a SA. Chemical systems involving iodine, main  
99 released FPs which can interfere with iodine (Cs and Mo) and control rod material (B, Cd, Ag and In)  
100 were considered. Tellurium was not retained as this FP is about 5 times less abundant than Cs in the  
101 spent fuel (Jacquemain *et al.*, 2000; Grégoire *et al.*, 2008) and is not expected to have a significant  
102 influence on Cs reactivity. Only the natural stable isotopes of these elements were handled for safety  
103 consideration. One of the main issues was to achieve element concentrations and relative ratio as  
104 relevant as possible of conditions of interest. Deposited species, transported aerosols and gases were  
105 collected for off-line characterization with a focus on gaseous iodine quantification. Working with  
106 stable elements allowed involving various surface analytical techniques capable to unravel the nature  
107 of deposited and transported species that could not be applied for experiments with highly radioactive  
108 material. The studied chemical systems involved firstly only iodine with carrier gas (the I-O-H system)  
109 and were then extended to other main FPs (Cs, Mo) and Cr materials involving up to 7 elements  
110 (Grégoire *et al.*, 2018).

111 The experiments performed on the I-O-H system evidenced kinetic limitations for gas phase iodine  
112 reactivity (Grégoire *et al.*, 2017). The addition of caesium, in quite large excess relative to iodine to be  
113 relevant of severe accident scenarios, resulted in quantitative formation of caesium iodide, preventing  
114 thus any gaseous iodine transport whatever the gas atmosphere (steam or steam/hydrogen). No  
115 relevant kinetic limitations were evidenced (Grégoire *et al.*, 2015), so the main caesium species (CsI,  
116 CsOH) can be simulated with the thermodynamic equilibrium assumption. Mo is expected to act as a  
117 Cs sink by the formation in the gas phase of stables caesium molybdates as expected by  
118 thermochemical data (Tangri *et al.* 1989; Cordfunke and Konings, 1990) which then condenses on the  
119 colder parts of the RCS. The formation of caesium molybdates of various composition could be clearly  
120 identified in the deposits collected in the test lines (Lacoue-Nègre, 2010; Gouello *et al.*, 2013; Grégoire  
121 *et al.*, 2015) when both Mo and Cs were considered. The reactivity of the Mo-Cs-I-O-H system is quite  
122 well reproduced by simulation tools and its consequence on iodine transport well predicted both in  
123 reductive or oxidative atmosphere. First results obtained from the B-Cs-I-O-H systems tends to show  
124 that the formation of caesium borates is less favourable (Gouello, 2012; Grégoire and Mutelle, 2012).

125 As a follow up to the test performed only with the main FPs, the study of the extended systems  
126 addressed separately the influence of each element of the Silver-Indium-Cadmium control rod  
127 compared to tests performed with the Mo-Cs-I-O-H system in steam condition. In steam condition, we  
128 have demonstrated that the formation of stable caesium molybdates prevents CsI recombination and  
129 thus enhance the release of gaseous iodine (Grégoire *et al.*, 2015). On the contrary, silver, indium and  
130 cadmium (SIC) are expected to react with iodine to form metallic iodide (AgI, CdI<sub>2</sub> and possibly InI<sub>x</sub>  
131 species). Nevertheless, the formation of metal-molybdates is not excluded that would compete either  
132 with metal iodide or caesium molybdate generation.

133 Within that context this work aims at evaluating the chemical reactivity between FPs (I, Cs and Mo)  
134 and SIC control rod material (either Ag, or In or Cd) in thermal conditions of a RCS in order to highlight  
135 the role of SIC in the release of gaseous iodine during a SA. The main objective was to assess the  
136 influence of each additional element (Ag, In, Cd) on the nature of deposited and transported species  
137 compared to the Mo-Cs-I-O-H chemical system alone. A special attention was brought on the

138 formation of metallic iodide and metallic molybdates which may play a key role on gaseous iodine  
 139 persistence at 150 °C. Three tests were performed; each based on the Mo-Cs-I-O-H system in steam  
 140 conditions plus one element of the SIC control rod: the [In+MoCsI] test, the [Cd+MoCsI] test and finally  
 141 the [Ag+MoCsI] test. We are thus presenting the main results obtained from the extended system test  
 142 series with a special attention on the determination of the deposited and transported species.

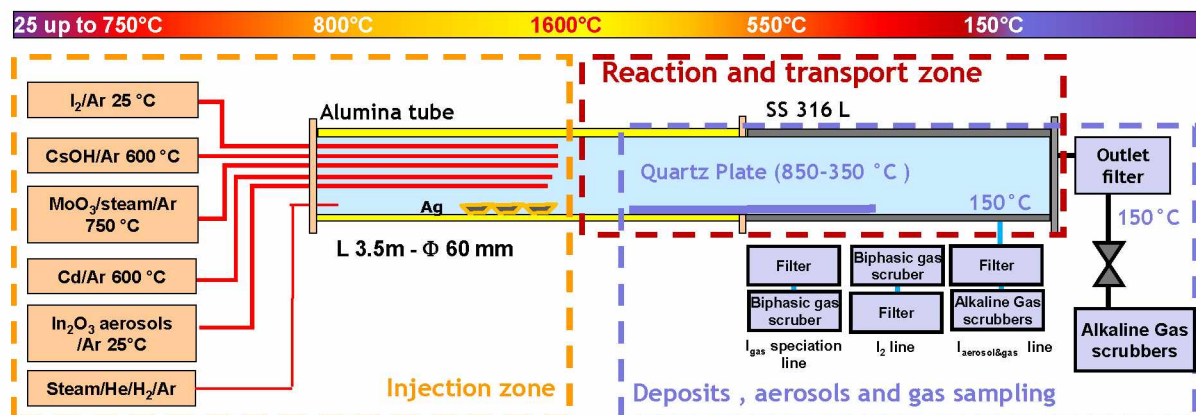
143 Hereafter, the CHIP experimental set-up, the test conditions and post-test operations including the  
 144 analytical techniques dedicated to species identification will be detailed. Experimental results will be  
 145 focused on element transport in the CHIP line with a special attention on iodine behaviour and the  
 146 identification of the condensed species. Discussion will be held in comparison with literature data.

## 147 2. Material and methods

### 148 2.1 CHIP Line description

149 The CHIP line has been described previously (Grégoire *et al.*, 2012; 2015; 2018) so that only features  
 150 concerning injection of I, Cs, Mo plus Cd, In and Ag will be detailed here.

151 The test line (3.5 m long and 60 mm in internal diameter) is composed of two tubes assembled by  
 152 a specific junction (Figure 1): an alumina tube (2 m) located in the high temperature zone and a  
 153 stainless steel tube (1.5 m) in the transport zone - simulating RCS piping. The thermal profile is obtained  
 154 by mean of several furnaces (High temperature tri zone CARBOLITE furnace completed by a series of  
 155 WATTLOW ceramic heaters) and is composed of three zones (injection zone, reaction zone and  
 156 aerosol/deposit and gas collection zone). Thermal profile is obtained after ~20-24 h of slow heating.  
 157 Residence time (10-11 s) from the high temperature zone to the outlet is representative of an accident  
 158 scenario featuring a break in the cold leg of the RCS.



159  
 160 *Figure 1: CHIP line configuration for injection of Ag, In and Cd*

161 In order to allow working with various chemical systems featuring a wide range of concentrations and  
 162 elemental ratio, elements are injected either in their metal, oxide or hydroxide form, depending on  
 163 their stability and volatility. One major issue to be addressed was the achievement of a controlled  
 164 injection of cadmium (as Cd metal), indium (as In<sub>2</sub>O<sub>3</sub> powder) and silver (as Ag metal) so as to achieve  
 165 concentrations and ratios relative to iodine relevant of an accidental scenario as observed during the  
 166 Phébus FP tests (Grégoire et Haste, 2013, Haste *et al.*, 2013, Girault and Payot, 2013). Several years of  
 167 development were necessary to succeed injecting those refractive and poorly soluble elements in a  
 168 controlled way.

169 Except for silver, vapours or aerosols are produced by the mean of external generators connected  
 170 to the inlet flange. The carrier gas (steam/Ar or He) is directly injected at the main line inlet (800°C)  
 171 whereas other reagents are transported directly into the high temperature zone via separate alumina  
 172 nozzles. At 1600°C, all the injected species are under vapour form at thermodynamic equilibrium.  
 173 Gaseous iodine is obtained by sublimation of molecular iodine pellets. Caesium, molybdenum and  
 174 cadmium vapours are produced by vaporization of respectively caesium hydroxide, molybdenum

175 trioxide and metallic cadmium. Indium oxide vapours are obtained by the injection of dry indium oxide  
176 aerosols produced at room temperature (RBG 1000 aerosol generator, PALAS) and then gradually  
177 vaporised in the pre-heating zone. Being more refractive than the other elements, silver is directly  
178 vaporised in the main line (at temperatures above 1200°C) from silver powder deposited in crucibles.  
179 At steady state, these generators produce a stable mass flow rate of each reagent for several hours –  
180 allowing thus the different sampling operations.

181 Apart from the carrier gas, at the outlet of the transport zone and in the sampling lines (150°C), only  
182 iodine can be possibly found in gaseous form, the other elements (FPs simulant and CR material) being  
183 transported as particulate material at this temperature level. In order to quantify the fraction of  
184 gaseous iodine released at the outlet, the CHIP line is terminated by an integral aerosol filter followed  
185 by gas scrubbers filled with an alkaline solution dedicated to trap gaseous iodine species and  
186 condensed steam. The integral aerosol filter is composed of quartz fibre cartridge with 0.9 µm porosity  
187 resulting in aerosol retention superior to 99.9%, for aerosol diameter ranging between 0.3 and 0.7 µm  
188 (see Table S1 in SD). The line outlet collects transported species over the entire test. Several sampling  
189 lines which can be sequentially operated, are also implemented on the CHIP experimental set-up.  
190 These lines are connected to the main CHIP line just before the outlet filter (Figure 1) and dedicated  
191 to sample a fraction (2 up to 8%) of the main flow at 150°C (temperature corresponding to a cold leg  
192 break of a RCS). These lines can be operated for short period and are able to catch changes in the  
193 transported flow depending on the test conditions. Different design have been developed to address  
194 different sampling objectives:

- 195 • collection of the transported aerosols and quantification of the total released gaseous iodine  
196 fraction. Such line is implemented with an inlet quartz fibre membrane filter (0.7 µm porosity  
197 resulting in aerosol retention >99%, see Table S1) allowing to trap the transported aerosols and  
198 downstream gas scrubbers filled with alkaline media (NaOH 0.1 M) in which all expected gaseous  
199 iodine species are readily soluble allowing the quantification of the total iodine gaseous fraction.  
200 Such line is labelled “I<sub>aerosol&gas</sub> line”;
- 201 • determination of the gaseous iodine speciation (Gouello *et al.*, 2013, Grégoire *et al.*, 2015). The line  
202 is still composed of an inlet filter but in this case, the gas scrubbers located downstream are filled  
203 with a biphasic mix of toluene dedicated for I<sub>2</sub> trapping and diluted nitric acid (0.015 M) dedicated  
204 for the other inorganic gaseous iodine species (e.g. HI, HOI) allowing to determine the composition  
205 of the gaseous iodine fraction (molecular iodine vs other inorganic forms). Such line configuration  
206 is labelled “I<sub>gas</sub> speciation line”;
- 207 • quantification of molecular iodine in presence of reactive species. As mentioned by Gouello *et*  
208 *al.* (2013), the drawback of the “I<sub>aerosol&gas</sub> line” and “I<sub>gas</sub> speciation line” is the possible loss of gaseous  
209 iodine due to interactions between gaseous iodine and reactive aerosols trapped on the filter (e.g.  
210 CsOH for instance). In order to address this difficulty, a third line configuration was developed in  
211 which the flow composed of gaseous species and aerosols is directed in gas scrubbers filled with a  
212 mix of toluene/diluted nitric acid. Molecular iodine is collected in the organic phase whereas  
213 inorganic iodine species and other aerosols are trapped in the aqueous phase. The line is  
214 terminated by a filter to trap the aerosols reminder. In such configuration, only the fraction of  
215 molecular iodine can be determined. Such line design is labelled “I<sub>2</sub> line”.

216 The redundancy of information which can be gained from the different sampling lines allows to  
217 characterize the iodine release at 150°C (gas/aerosol distribution, nature of gaseous iodine forms) with  
218 a good reliability.

219 In addition to the sampling of material transported at 150°C, a quartz plate is inserted in the main line  
220 for collecting condensed material in 850-350°C temperature range. Thus, two types of samples were  
221 collected: (i) condensed phases deposited on quartz substrate (1 x 5 cm) between 850 and 350°C and  
222 (ii) particles sampled at 150°C using a glass fibre filter.

223 Specification on line structure and chemical reagents are displayed in the supplementary information  
224 data files (Table S1 and Table S2) as well as the thermal profile in the transport zone (Figure S1).

## 225 **2.2 Test conditions**

226 Three tests were performed consisting in injecting the Mo-Cs-I-O-H chemical system in steam as  
227 previously described in Grégoire *et al.* (2015) (the [PL\_MoCsI\_3] test) plus one element representative  
228 of the SIC control rod: the [In+MoCsI] test, the [Cd+MoCsI] test and finally the [Ag+MoCsI] test.

229 The [PL\_MoCsI\_3] test will serve as reference test; it featured steam atmosphere with a chemical  
230 system involving an excess of Cs relative to I (Cs/I molar ratio of ~4) and Mo itself in excess relative to  
231 Cs (Mo/Cs ~3) in the range of ratios observed during Phébus FP test sequences (Haste *et al.*, 2013). The  
232 steam atmosphere is relevant of the Phébus test main release phase during which the transport of Cs,  
233 I, Mo in the experimental circuit was observed (Grégoire and Haste, 2013). The thermal hydraulic  
234 conditions simulate as close as possible a large RCS cold leg with high thermal gradient and short  
235 residence time in the transport zone (Jacquemain *et al.*, 2015). Inert gas (Ar or He) was added to adjust  
236 the residence time of elements in the CHIP line. In such conditions, formation of caesium molybdates  
237 partially prevents CsI to be formed in the gas phase and contributes to the transport of high gaseous  
238 iodine fraction (up to 90% of injected iodine mass, Grégoire *et al.*, 2015).

239 [In+MoCsI], [Cd+MoCsI] and [Ag+MoCsI] tests with extended chemical systems were performed with  
240 similar element injection for Mo, Cs and I. The SIC CR elements were injected in large excess relative  
241 to iodine. A similar thermal gradient and residence time was applied. As for the carrier gas  
242 composition, a mix of steam/inert gas was injected for the [In+MoCsI] and [Cd+MoCsI] tests as it was  
243 observed that those CR elements were also released during the Phébus tests main release phase (in  
244 steam atmosphere). A low amount of hydrogen (1.8% of the total atmosphere) was added for the test  
245 featuring silver, as this element was released later during the so-called “second oxidation phase”  
246 where low amounts of H<sub>2</sub> were measured in the Phébus circuit (Grégoire and Haste, 2013).

247

248 The thermal hydraulic conditions and element generation are reported in Table 1. Conditions of the  
249 reference [PL\_MoCsI\_3] test are recalled too. The element mean mass flow rates were determined  
250 from the total injected element masses (based on the final element mass distribution in the line) and  
251 the injection duration assuming a steady injection rate. Given uncertainty on ICP-MS analyses of each  
252 leaching solution, an average uncertainty of +/-7 % could be estimated for the element mean mass  
253 flow rate. As silver crucibles were placed directly in the main line, significant vaporization occurred as  
254 soon as the temperature in the crucible reached ~ 1100 °C. As a consequence, injection of low silver  
255 level in the line could not be avoided during the pre-heating phase, before injection of the other  
256 elements. Given the relative short duration of this pre-heating phase and low carrier gas flow applied  
257 during this phase, it is assumed that the main part of silver was injected during the main phase of the  
258 test as the other elements. The silver mass flow rate (displayed in Table 1) was determined from the  
259 overall silver mass collected in the CHIP line, including the deposits formed during the pre-heating  
260 phase and should be thus considered as a maximal value.



261 *Table 1: Conditions of [In+MoCsl], [Cd+MoCsl] and [Ag+MoCsl] tests and [PL\_MoCsl\_3] reference test*

Test Name	[In+MoCsl]	[Cd+MoCsl]	[Ag+MoCsl]	[PL_MoCsl_3] (Grégoire et al., 2015).
Test Loop	CHIP PL			
Main test tube material	Alumina (HT zone – 600°C) / stainless steel (600°C-150°C)			
<b><i>Thermal hydraulic conditions :</i></b>				
Pressure (Mpa)	0.2 MPa			
Carrier gas flow (l/min – NPT)	38.2 l/min	35.3 l/min	35.1 l/min	34.3 l/min
Max. temperature in the HT zone (°C)	1600°C			
Temperature profile in the transport zone	Strong $\nabla$ to outlet (150°C)			
Residence time in the transport zone (s)	~12 s			
Test duration (min)	357	337	338	421
<b><i>Carrier gas composition (v/v %)</i></b>				
	H <sub>2</sub> O/Ar	H <sub>2</sub> O/He/Ar	H <sub>2</sub> O/Ar/H <sub>2</sub>	H <sub>2</sub> O/He/Ar
	45.7/54.3	49.4/42.8/7.8	49.6/48.6/1.8	50.8/44.1/5.1
<b><i>Element injection</i></b> mean mass flow rate (mol/s) in the HT zone <sup>‡</sup>				
Iodine (as I <sub>2</sub> )	1.8 10 <sup>-7</sup> mol/s	1.7 10 <sup>-7</sup> mol/s	1.5 10 <sup>-7</sup> mol/s	1.5 10 <sup>-7</sup> mol/s
Caesium (as CsOH)	4.4 10 <sup>-7</sup> mol/s	5.5 10 <sup>-7</sup> mol/s	5.6 10 <sup>-7</sup> mol/s	6.0 10 <sup>-7</sup> mol/s
Molybdenum (as MoO <sub>3</sub> )	2.2 10 <sup>-6</sup> mol/s	2.0 10 <sup>-6</sup> mol/s	2.1 10 <sup>-6</sup> mol/s	1.9 10 <sup>-6</sup> mol/s
Indium (as In <sub>2</sub> O <sub>3</sub> )	8.1 10 <sup>-7</sup> mol/s	-	-	-
Cadmium (as Cd metal)	-	2.1 10 <sup>-5</sup> mol/s	-	-
Silver (as Ag metal)	-	-	7.4 10 <sup>-6</sup> mol/s <sup>‡</sup>	-

262 NPT conditions: 0°C, 0.101325 MPa ; <sup>‡</sup> Element flow rate based on the final mass distribution in the line and assuming a steady injection  
 263 rate (relative uncertainties below  $\pm 5\%$  except for iodine in the [Ag+MoCsl] test :  $\pm 50\%$ ); <sup>‡</sup> maximum flow rate as silver vaporization may  
 264 also occur during the pre-heating phase.

265

### 266 2.3 Element mass concentration and distribution along the thermal profile of CHIP line

267 In order to determine the element distribution in the CHIP line, several successive washing operations  
 268 were performed post-test to solubilize the deposited material. For the test series with injection of SIC  
 269 control rod material, the following solutions were used:

- 270 • alkaline media (NaOH 0.1 M) for easily soluble species such as I<sub>2</sub>, HI, HOI, Csl or Cdl<sub>2</sub> and partly  
 271 caesium molybdates;
- 272 • nitric acid (2 M) for an overall recovery of molybdates (MoO<sub>3</sub>, molybdic acid, metallic molybdates)  
 273 and cadmium species (Cd metal, oxide and possibly hydroxide);
- 274 • nitric acid (5 M) for metallic silver;
- 275 • boiling concentrated nitric acid (8 M) for indium oxides.

276 A last treatment was necessary for AgI recovery as this species is still insoluble in concentrated acidic  
 277 media. This treatment (Spies, 1936; Wang *et al.*, 1989) is based on the decomposition of AgI by hot  
 278 aqua regia (1/3 nitric acid; 2/3 hydrochloric acid). In presence of a large excess of chlorides, the  
 279 insoluble form of AgCl is favoured and I solubilized as iodine monochloride (ICl). The solution is then  
 280 filtered and the filtrate treated with sodium hydroxide (final pH above 13) allowing to hydrolyse the  
 281 iodine monochloride and form iodates and iodides. Analyses of solubilised iodine allows then to  
 282 quantify the amount of silver iodide. No similar approach could be developed for Cdl<sub>2</sub>/Csl separation  
 283 and quantification due to their strong solubility in aqueous media. Formation of such species will be  
 284 then deduced by default of other species.

285 The solutions were then analysed by multi-elemental analysis techniques: Inductively Coupled Plasma  
 286 Mass-Spectrometry (ICP-MS) for I, Cs, Mo, Cd and In (Varian 810 MS) or Inductively Coupled Plasma  
 287 Atomic Emission Spectroscopy (ICP-AES) for Ag (Perkin Elmer, 8100) with a relative uncertainty of +/-  
 288 8% at 95% confidence level. UV-visible quantification of I<sub>2</sub> in toluene was performed with an Agilent  
 289 8453 spectrometer at 309 nm and 498 nm with an uncertainty of +/- 6% (at 95 % confidence level).

### 290 2.4 Characterization of collected material

291 Material deposited in the thermal gradient onto quartz plate samples and aerosols collected on quartz  
292 filters, were post-test analysed. Size and morphology have been determined by Environmental  
293 Scanning Electron Microscopy (ESEM Quanta 200 FEI®) used in low vacuum mode (50-130 Pa), allowing  
294 to examine sample without metallisation. Measurements were carried out at an accelerating voltage  
295 of 10-25 kV to perform either Secondary electron or Back Scattering Electron (BSE) imaging with a  
296 lateral resolution of several hundred of nm. Semi-quantitative elemental composition was obtained by  
297 an energy-dispersive X-ray detector (EDX, Quantax-Roentec®) coupled to the ESEM microscope. ZAF  
298 (Atomic Number Z, Absorption and Fluorescence) corrections were applied. Elemental composition of  
299 single particles and cartography of larger zones (~20\*20 up to 100\*100 µm<sup>2</sup>) could be determined with  
300 a resolution of ~1µm<sup>3</sup>. Raman microspectrometry (RMS) was performed on the same sample zones to  
301 identify both elemental and molecular composition of condensed species. The Raman spectra and  
302 optical images were recorded by Labspec6 using a confocal Raman microspectrometer (Labram HR  
303 evolution, Horiba Jobin Yvon) equipped with a 100× 0.85 numerical aperture objective (Olympus). An  
304 excitation Nd:YAG laser with a wavelength of 532 nm and 6 mW power was used, and the scattered  
305 Raman signals were detected using an air-cooled multichannel charge-coupled device (CCD) detector.  
306 The data acquisition time for each measurement was 30 s with 2 accumulations. The spectral  
307 resolution was 1.8 cm<sup>-1</sup> using 1800 gr/mm grazing. A spatial resolution of 1 µm<sup>3</sup> is estimated.  
308 Measurements were carried out in both single point or automated imaging modes. Surfaces of 10\*10  
309 µm<sup>2</sup> up to 50\*50 µm<sup>2</sup> with ~2 µm as a minimum step (representing 2000-5000 spectra per zone) were  
310 scanned. After spectral treatment (LABSPEC6 software), the components were identified by  
311 comparison with reference spectra from Raman libraries and literature data or by acquiring spectra  
312 from reference materials. Complementary identification of samples was obtained from X-ray  
313 diffraction (XRD) analyses. Diffractograms were obtained using a AXS D8 or D2 PHASER diffractometers  
314 (Bruker) operating with Cu Kα radiation (λ = 1.54 Å). Samples were analysed at room temperature in  
315 the 2θ range of 10–70°, with a step size of 0.02°.  
316 Complementary, speciation of Cd, Mo, Cs and I in samples was provided by X-ray Photoelectron  
317 Spectroscopy (XPS). Measurements were carried out on a Kratos Analytical AXIS Ultra<sup>DLD</sup> spectrometer  
318 using monochromatic Al Kα source (1486.6 eV). Calibration was performed by taking the adventitious  
319 C1s peak (binding energy, BE = 285.0 eV). The uncertainties on the binding energy and on quantitative  
320 elemental analysis are +/-0.1 eV and +/- 10-20%, respectively. Assignment of photoelectron peaks was  
321 performed by comparison with photoelectron peaks acquired on reference compounds.  
322

### 323 3. Results

#### 324 3.1 Element distribution along the CHIP line and transported iodine forms

325 Element distributions are reported in Table 2 in terms of high/low temperature deposition, aerosol/gas  
326 transport at 150°C (conditions of a cold leg break). Distributions are expressed in % relative to the total  
327 mass injected in the high temperature (HT) zone for each element.

##### 328 3.1.1 Nature of iodine released at 150°C

329 The sampling lines allowed to evaluate the level and nature of iodine release at 150°C for each test.  
330 Results are presented in the Table 2 as gaseous form “I(gas)” and aerosol form “I(aerosol)”. The nature  
331 of each form is detailed in “Iodine gas identification”, and “Iodine aerosol identification” respectively,  
332 whenever it could be determined.

333 For the [In+MoCsI] test, indium was injected in excess relative to iodine (In/I~4.4), this weak excess is  
334 within the range of In/I ratios observed during the Phébus FP Tests (Jacquemain *et al.*, 2000; Grégoire  
335 *et al.*, 2008). Almost only gaseous iodine was released at 150 °C (“I<sub>aerosol&gas</sub> line” data), with average  
336 fraction close to 90% at 150°C (relative to the initial iodine mass injected in the HT zone). The molecular  
337 iodine fraction can be determined from the “I<sub>2</sub> line” data. For this test, the sampling in the “I<sub>gas</sub>  
338 speciation line” failed, so that the fraction of other inorganic gaseous iodine species is determined by  
339 difference between the “I<sub>aerosol&gas</sub> line” and “I<sub>2</sub> line” data. Roughly one half of the gaseous iodine is

340 identified as molecular iodine, the rest being attributed to an inorganic form, assumed to be mostly HI  
341 because the formation of HOI is less probable in such conditions (Grégoire *et al.*, 2017). Results are  
342 comparable to the reference [PL\_MoCsl\_3] test, indicating that the presence of indium does not  
343 significantly alter the chemical Mo-Cs-I-O-H system in steam atmosphere. As a consequence, it is  
344 confirmed that aerosols composed of  $InI_x$  species are not formed in these experimental conditions.

345 For the [Cd+MoCsl] test, cadmium vapours were generated in a very large excess relative to iodine  
346 ( $Cd/I \sim 125$ , much higher than observed in Phébus tests). For both " $I_{aerosol\&gas}$  line" and " $I_{gas}$  speciation  
347 line", the gaseous iodine fraction detected downstream of the aerosol filter is very low ( $< \sim 1\%$ ). On the  
348 contrary, a significant amount of gaseous molecular iodine is observed in the " $I_2$  line" (without inlet  
349 filter), representing 28% of initially injected gaseous iodine. The fact that a measurable gaseous iodine  
350 fraction could be detected only in the " $I_2$  line" can be accounted for by a significant retention of  
351 gaseous iodine species on aerosols collected on the inlet filter of the other sampling lines. Such  
352 retention was not observed during the reference [In+MoCsl] and [PL\_MoCsl\_3] tests, and may be due  
353 to presence of cadmium species in the case of the [Cd+MoCsl] test. We thus retain the value gained  
354 from the " $I_2$  line" (28% of initially injected iodine) for the gaseous iodine fraction. This value is  
355 considered as a minimum as only  $I_2$  fraction could be quantified in this line. The gaseous iodine fraction  
356 is nevertheless almost three times lower than that observed during the [PL\_MoCsl\_3] reference test  
357 (88.3%), indicating that cadmium species contribute to reduce the transport of gaseous iodine  
358 compared to the Mo-Cs-I-O-H system in steam. Nevertheless, such cadmium effect is observed for a  
359 very large Cd/I ratio.

360 The [Ag+MoCsl] test was performed with a large excess of silver relative to iodine ( $Ag/I \sim 55$ ), thermo-  
361 hydraulic conditions close to the reference test and a low level of hydrogen ( $H_2/H_2O \sim 0.04$ ) to limit  
362 possible silver oxidation. Contrarily to the tests performed with In and Cd, the " $I_2$  line" turned out to  
363 be inefficient to trap molecular iodine (if any) in presence of metallic silver particles. Indeed, we  
364 experimentally checked that silver particles react readily and quantitatively with molecular iodine  
365 dissolved in toluene to form silver iodide. As a result, we retain only the data gained from the " $I_{aerosol\&gas}$   
366 line" which shows a very low gaseous iodine fraction ( $< 2\%$ ). One should keep in mind that this gaseous  
367 iodine fraction may be underestimated owing to possible gaseous iodine retention on the particles  
368 trapped on the inlet filter of the sampling line (similarly to the [Cd+MoCsl] test). Iodine-containing  
369 particles (expected to be AgI or CsI) turned out to be mainly soluble in aqueous media suggesting that  
370 formation of insoluble AgI is not the main reaction pathway leading to the release of iodine as aerosols.  
371 Indeed, only 10%-25% of iodine collected in the sampling lines could be identified as AgI, that is not  
372 consistent with thermochemical simulations predicting more than 75% of AgI. As a consequence, the  
373 most probable iodine form to be released at 150°C is CsI.

374 Although the iodine nature at 150°C (cold leg break conditions) cannot be fully described in presence  
375 of cadmium or silver, these control rod materials tend to lower the gaseous iodine fraction formed  
376 along the thermal gradient.

### 377 **3.1.2 Element line distribution – comparison with reference test [PL MoCsl 3]**

378 Distribution of elements in the CHIP line is too coarse to allow for the identification of species  
379 condensation peak. CHIP line was divided into two parts labelled as "main line": the alumina tube for  
380 a temperature range of 1600-600°C and the stainless steel tube for 600-150°C (see Table 2). Except for  
381 iodine, the other element found at the line outlet (at 150°C) are attributed to transport in aerosol form  
382 owing to their low volatility. The following statements can be put forward based on the experimental  
383 results and compared with the [PL\_MoCsl\_3] reference test:

384 For iodine, no deposition is observed above 600°C for all tests. Deposition below 600°C is very low  
385 when iodine is mainly transported at the line outlet in gaseous form as for the [In+MoCsl] test (0.1%  
386 of total injection iodine found in the 600-150°C temperature range) or the [PL\_MoCsl\_3] reference  
387 test. When iodine is found mainly transported in aerosol form at 150°C, a significant iodine deposition  
388 is observed but only below 600°C : 13% for the [Cd+MoCsl] test and 15% for the [Ag+MoCsl] test. Such

389 iodine deposition in the CHIP line results from vapour condensation or aerosol deposition of iodine  
390 containing species as already observed in a previous CHIP test (Grégoire *et al.*, 2015).

391 Mo distribution in the CHIP line for the [In+MoCsl] test shows 7% deposited above 600°C, 21%  
392 deposited in the 600-150°C temperature range and 72% transported as aerosols. These values are  
393 comparable to that obtained for the reference test. On the contrary, in presence of Cd or Ag, Mo high  
394 temperature deposition is enhanced up to 31% ([Cd+MoCsl] test) and 47% ([Ag+MoCsl] test)  
395 simultaneously to a strong decrease of the deposition in the stainless steel tube (10% of Mo deposited  
396 below 600°C for both tests) and to a decrease of Mo found transported at 150°C (59% for the  
397 [Cd+MoCsl] test and 43% for the [Ag+MoCsl] test). This distribution is comparable to that observed for  
398 the MoCsl test in steam/hydrogen (Grégoire *et al.*, 2015), in which a significant reduction of Mo(VI) to  
399 the less volatile Mo(IV) and Mo(V) compounds was evidenced. Indeed reduction of Mo is not excluded  
400 as oxidation of Cd or Ag in the steam flow at high temperature results in the production of low amounts  
401 of hydrogen capable of reducing (even partly) the injected MoO<sub>3</sub> (in addition to the injected low  
402 hydrogen flow for the [Ag+MoCsl] test). As consequence Mo may be less reactive to form metallic  
403 molybdates and thus may contribute to the increased formation of metallic iodides (Csl, Cdl<sub>2</sub> and to a  
404 less extent AgI).

405 Indium and silver are mainly found deposited in the high temperature zone above 600°C (alumina tube)  
406 consistently with their strong refractive properties. For the [In+MoCsl] test, 42% of In is found in this  
407 zone, whereas deposition below 600°C represents only 10% of initially injected In. For the [Ag+MoCsl]  
408 test, 57% of silver is found deposited above 600°C and 6% below. On the contrary, cadmium which is  
409 more volatile is mainly found in the 600-150°C temperature zone (41% for the [Cd+MoCsl] test and  
410 less at high temperature (3% above 600°C).

411 Only caesium deposition pattern does not show significant changes in this test series: high  
412 temperature deposition (above 600°C) represents 6-13% of initially injected caesium, deposition in the  
413 600-150°C temperature range 13-16% so that for all test, Cs is mainly transported to the line outlet in  
414 aerosol form (73-80%).

415



416  
417

Table 2: [In+MoCsI], [Cd+MoCsI], [Ag+MoCsI] tests and [PL\_MoCsI\_3] reference test – Element distribution and iodine Gas/aerosol partition

Test Name	[In –MoCsI]	[Cd+MoCsI]	[Ag+MoCsI]	[PL_MoCsI_3] (Grégoire et al., 2015).
<u>Carrier Gas composition</u>	Ar/H <sub>2</sub> O 54.3/45.7	H <sub>2</sub> O/He/Ar 49.4/42.8/7.8	H <sub>2</sub> O/Ar/H <sub>2</sub> 49.6/48.6/1.8	H <sub>2</sub> O/He/Ar 50.8/44.1/5.1
<b><u>Element molar Ratio in the HT zone</u></b>				
Cs/I	2.5 ±0.2	3.1 ±0.2	3.6 ±1.8	4.0 ±0.4
Mo/Cs	5.0 ±0.4	3.7 ±0.2	3.7 ±0.3	3.2 ±0.3
X/I (X= Cd or In or Ag)	4.5 ±0.3	126 ±9	48 ±24 <sup>a</sup>	
Mo/X	2.7 ±0.2	0.1 ± 0.01	0.3 ±0.02	
<b><u>Element molar ratio in the sampling lines</u></b>				
<u>At 150°C</u>				
Cs/I	2.2 ±0.5	3.1 ±0.6	~3-12	2.7 ±0.6
Mo/Cs	5.3 ±0.3	2.3 ±0.5	1.9 ±0.1	3.4 ±0.5
X/I (X= Cd or In or Ag)	2.7 ±1	48 ±23	~20-65	
<b><u>Deposition in the main line</u></b>				
	1600 -600 °C (alumina tube) and 600-150 °C (stainless steel tube)			
	0%	0%	0%	0 %
I	<u>(0.1 ±0.01)%</u>	<u>(13 ±1.3)%</u>	<u>(15 ±7)%</u>	<u>(0.2 ±0.02)%</u>
Cs	(13 ±1.2)% <u>(13 ±1.2)%</u>	(10 ±0.9)% <u>(16 ±1.5)%</u>	(6 ±0.6)% <u>(14 ±0.1)%</u>	(11 ±0.9)% <u>(16 ±1.3)%</u>
Mo	(7.0 ±0.6)% <u>(21 ±2)%</u>	(31 ±2.8)% <u>(10 ±0.9)%</u>	(47 ±4.4)% <u>(10 ±0.9)%</u>	(4.0 ±0.3)% <u>(21 ±1.7)%</u>
X (X= Cd or In or Ag)	(42 ±3.8)% <u>(10 ±0.9)%</u>	(3.0 ±0.3)% <u>(41 ±3.8)%</u>	(57 ±5.4)% <u>(6.0 ±0.6)%</u>	
<b><u>Sampling line data: iodine transport at 150°C :</u></b>				
<b>I (gas)</b>	<b>(89.9 ±6.5)%<sup>b</sup></b>	<b>(28 ±6.3)%<sup>d</sup></b> <b>Other lines &lt; 1%</b>	<b>&lt; (2 ±1)%<sup>b</sup></b>	<b>(88.3 ±6.4)%<sup>b, c</sup></b>
Iodine gas identification				
I as I <sub>2</sub>	~ 1/2 <sup>d</sup>	1	nd	~ 2/3 <sup>c, d</sup>
I as HI	~ 1/2 <sup>b, d</sup>	-	nd	~ 1/3 <sup>c, d</sup>
<b>I (aerosol)</b>	<b>(10 ±6.5)%<sup>b</sup></b>	<b>(59 ±6.3)%<sup>d</sup></b> <b>Other lines &gt; 86%</b>	<b>&gt; (83 ±8)%<sup>b</sup></b>	<b>(11.5 ±6.4)%<sup>b, c</sup></b>
Iodine aerosol identification				
	nd	Traces of CdI <sub>2</sub> <sup>e</sup>	AgI ~1/10 to 1/4 <sup>b</sup>	nd
<b><u>Sampling line data: transport of other element 150°C :</u></b>				
Cs (aerosol)	(74 ±2.0)%	(74 ±2.0)%	(80 ±1.5)%	(73 ±1.6)%
Mo (aerosol)	(72 ±2.0)%	(59 ±3.0)%	(43 ±4.4)%	(75 ±1.7)%
X (aerosol) (X= Cd or In or Ag)	(48 ±4.0)%	(56 ±4.0)%	(37 ±5.4)%	

418 Data rounded to two significant figures; **a**: maximum ratio as silver vaporization may also occur during the heating phase; **b** :  
419 'I<sub>aerosol&gas</sub> line' data; **c**: 'I<sub>g</sub> speciation line' data; **d**: 'I<sub>2</sub> line' data; max. value for I<sub>g</sub> (resp. min value for I<sub>aer</sub>); **e**: Cd and I detected  
420 on few particles (main line deposit -EDX examination).

421

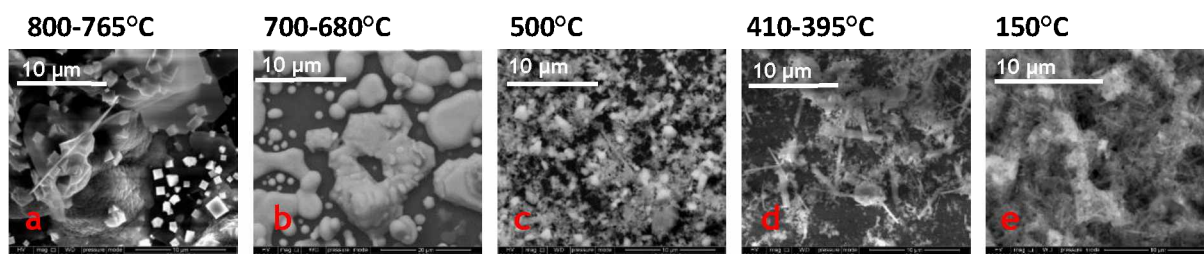
### 422 3.2 Characterization of condensed phase and aerosols in the 850-150 °C temperature 423 range

424 A full understanding of iodine behaviour cannot be obtained alone from sampling line data and the  
425 element distribution in the line even if some first important information could be gained. In order to  
426 complement these data, a detailed characterization of aerosols and/or condensed material was  
427 undertaken. Both condensed deposits collected in the main line (in a temperature range from ~850°C  
428 down to 350°C) and aerosols collected at 150°C were considered. Coupled analyses by SEM-EDX, RMS,  
429 XPS and XRD allowed to describe morphology, element composition and to identify the main species

430 in collected condensed matter. In the following sections, analysis of deposits are detailed with  
431 decreasing deposit collection temperature.

### 432 **3.2.1 Results for the [In+MoCs] test**

433 Deposit morphology evolution with decreasing temperature are observed by SEM in Back Scattering  
434 Electron imaging (BSE) as displayed on Figure 2.



435  
436 *Figure 2: [In+MoCs] test – SEM – BSE images of deposits collected in the 800-150°C temperature range*  
437 *(magnification  $\times 5000$  -  $\times 12200$ ).*

438 At high temperature (800-765°C), both cubic like particles (2-3  $\mu\text{m}$ ) and large amorphous structures  
439 can be identified (Figure 2.a). In dominates in cubic like structure whereas Si and O are found in  
440 amorphous structures. Mo and Cs are found in trace amount only. RMS allows to identify the cubic like  
441 particles (see Figure S2) as  $\text{In}_2\text{O}_3$  by comparison with literature data (Kranert *et al.*, 2014). The large  
442 amorphous structures observed in this temperature range are identified as melted silica with  
443 characteristics Raman bands at 230 and 416  $\text{cm}^{-1}$  (see Figure S3). Traces of mixed Cs-In polymolybdates  
444 have been identified at 765°C by their Raman characteristic bands at 786 and 935  $\text{cm}^{-1}$  (Maczka, 1997).

445 Around 700-680°C, large agglomerates of spherical or hexagonal like particles with diameter up to 10-  
446 30  $\mu\text{m}$  are observed together with some isolated needle-like particles (5-20  $\mu\text{m}$ , not shown here)  
447 (Figure 2.b). In addition to In, Cs and Mo are found as main components of the deposit with Mo/Cs  
448 elemental ratio close to 3; Mo/In ratio is close to 2. For the needle like particles, the higher Mo/In  
449 ratios (up to 5) indicates the possible presence of caesium molybdate species. Regarding elemental  
450 ratio and RMS identification (Figure S4),  $\text{CsIn}(\text{MoO}_4)_2$  is the main species identified in this temperature  
451 range and appears as the large hexagonal and spherical particles 10-30  $\mu\text{m}$ . Literature data predict the  
452 condensation of  $\text{CsIn}(\text{MoO}_4)_2$  below 650°C (Maczka, 1997) rather consistent with our experimental  
453 observations. The isolated needle like particles are identified by RMS as caesium molybdates  
454 ( $\text{Cs}_2\text{Mo}_4\text{O}_{13}$  and  $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ ) (see Figure S5) in agreement with Hoekstra (1973) and the binary diagram  
455 of  $\text{CsMoO}_4$ - $\text{MoO}_3$  recently reported by Smith *et al.*, (2021).

456 Around 600°C, mixed Cs-In molybdates are still observed (not shown). In addition, indium molybdate  
457 as  $\text{In}_2(\text{MoO}_4)_3$  is identified (Figure S6) by comparison with spectra reported by Maczka *et al.* (2005).  
458 This new species dominates deposit composition at this temperature. Given data of the  $\text{MoO}_3$ - $\text{In}_2\text{O}_3$   
459 binary diagram (Filipek *et al.*, 2012), indium molybdates should have been observed at higher  
460 temperature (eutectic point at 780°C) indicating possible competition with the formation of the mixed  
461 Cs-In molybdates (which are observed as of 765°C).

462 Below 500°C, micronic parallelepipedic particles and very fine needles (< 1 $\mu\text{m}$ ) are observed together  
463 with larger stick like crystallites (~5-20  $\mu\text{m}$ ). The stick-like particle size increases as the temperature  
464 decreases (Figure 2c and 2d). EDX analyses indicates a strong Mo enrichment in all particle types,  
465 suggesting that Mo compounds dominates deposition. Indeed, the large sticks are mainly identified by  
466 RMS as  $\alpha$ - $\text{MoO}_3$  (Figure S7) (McEvoy and Stevenson, 2005; Ding *et al.*, 2006) and more sparsely  
467  $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ . The aggregates of fine particles are tentatively attributed to molybdate species as their  
468 Raman spectra feature characteristic bands in the 900-1000  $\text{cm}^{-1}$  range typical of Mo-O vibration  
469 modes. Around 500°C,  $\text{In}_2(\text{MoO}_4)_3$  is found in fine crystallised needles together with two other likely  
470 In/Cs molybdates but not fully attributed. At 400°C, the fine particle agglomerates are mainly  
471 composed of a mixture of  $\alpha$ - $\text{MoO}_3$  and  $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ .

472 The submicronic aerosols transported at 150°C are mainly composed of  $\text{CsIn}(\text{MoO}_4)_2$  according to the  
 473 Raman and XRD data (see Figure S8) but the presence of  $\text{Cs}_2\text{Mo}_5\text{O}_{16}$  cannot be excluded.

474 Under the oxidative atmosphere of this test (injection of steam only and indium as indium oxide),  
 475 mainly Mo(VI) species were transported in the line that is confirmed by XPS (Figure S9). At 150°C, traces  
 476 of reduced Mo species were observed in the aerosols (Figure S9). Similarly to the [PL\_MoCsl\_3] test,  
 477 Mo-rich deposits are found below 600°C. Iodine was not detected in the solid samples consistently  
 478 with a transport almost only under gaseous form evidenced in the previous part. A summary of the  
 479 main identified species is displayed in Table 3.

480 Table 3: [In+MoCsl] test - Summary of the main identified species in the deposits and aerosols collected in the  
 481 800-150°C temperature range. Dominant species are in bold characters

Analyses	800-765°C	700-680°C	600-580°C	500°C	~410-395°C	150°C
SEM-EDX						
Morphology	Cubic particles In rich $\text{In}_2\text{O}_3$	Large hexagonal and flattened drop like particles (10- 30 $\mu\text{m}$ ); Cs and In rich		Micronic parallelepipedic particles Mo rich	Fine needles Mo and In-rich	Submicronic particles: mix
Elemental atomic composition and ratio	amorphous structure Si rich (fused silica) $\text{SiO}_2$	Mo/In ~2 Mo/Cs ~2	Not analysed	Fine needles: In and Mo rich	Numerous large stick like crystallites Mo-rich : $\alpha\text{-MoO}_3$ and possibly $(\text{Cs/In})_x\text{Mo}_y\text{O}_z$	Mo dominates Mo/In ~3 Mo/Cs ~4-5
Species		$\text{CsIn}(\text{MoO}_4)_2$		Some large stick like crystallites : $\alpha\text{-MoO}_3$ and possibly $(\text{Cs/In})_x\text{Mo}_y\text{O}_z$		
RMS	$\text{In}_2\text{O}_3$  $\text{CsIn}(\text{MoO}_4)_2$ (Cs and/or $\text{In})_x\text{Mo}_y\text{O}_z$  Fused silica	$\text{In}_2\text{O}_3$  <b><math>\text{CsIn}(\text{MoO}_4)_2</math></b> trigonal  $\text{Cs}_2\text{MoO}_4$ $\text{Cs}_2\text{Mo}_4\text{O}_{13}$ (p) $\text{Cs}_2\text{Mo}_7\text{O}_{22}$	<b><math>\text{In}_2(\text{MoO}_4)_3</math></b>  <b><math>\text{CsIn}(\text{MoO}_4)_2</math></b> trigonal  $\text{Cs}_2\text{Mo}_2\text{O}_7$	$\text{In}_2(\text{MoO}_4)_3$  Two distinct species of the type: <b><math>(\text{Cs/In})_x\text{Mo}_y\text{O}_z</math></b> $(\text{Cs/In})_x\text{Mo}_y\text{O}_z$  $\text{Cs}_2\text{Mo}_2\text{O}_7$ $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ (trace)  <b><math>\alpha\text{-MoO}_3</math></b>	$\text{In}_x\text{Mo}_y\text{O}_z$  $\text{Cs}_2\text{Mo}_2\text{O}_7$ $\text{Cs}_2\text{Mo}_7\text{O}_{22}$ (trace)  <b><math>\alpha\text{-MoO}_3</math></b>	<b><math>\text{CsIn}(\text{MoO}_4)_2</math></b> trigonal/ $\text{CsIn}(\text{MoO}_4)_2$ orthorhombic  $\text{Cs}_2\text{Mo}_5\text{O}_{16}$  (consistent with XRD)

482

### 483 3.2.2 Results for the [Cd+MoCsl] test

484 Condensed species were analysed in the 670°C -150°C temperature range. For temperature  
 485 higher than 670°C (alumina tube), very low amount of Cd-rich deposit are found (~3%, as reported in  
 486 Table 3). Sizes of condensed material decrease with decreasing temperature. Large octahedrons - and  
 487 rods-shaped particles are observed above 500°C when submicronic needles and ball-shaped particles  
 488 are found at lower temperatures (see Figure 3a to 3e).

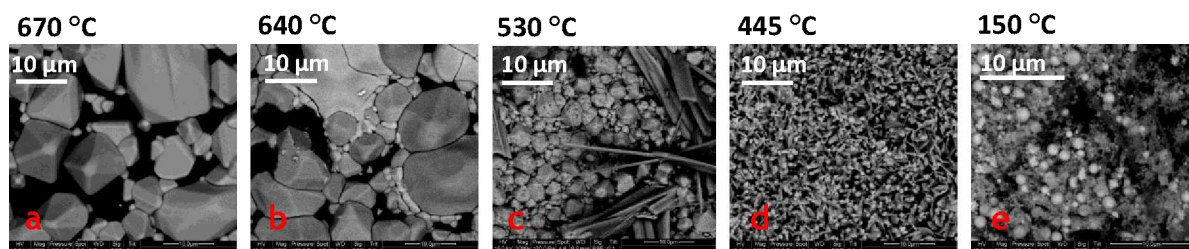


Figure 3: [Cd+MoCsI] test – SEM BSE images of deposits collected in the 670-150°C temperature range (magnification at  $\times 3000$ ).

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490  
491

492 By comparison with Raman spectra referenced in the literature or in data bases (Ozkan *et al.*, 1990;  
493 Phuruangrat *et al.*, 2011; Xing *et al.*, 2011; Tsyrenova and Pavlova, 2011), Raman spectra recorded  
494 from particles is assigned to several cadmium-rich species.

495 Cadmium molybdates (mainly  $\text{CdMoO}_4$ ), and mixed Cs-Cd molybdates ( $\text{Cs}_2\text{Cd}_2(\text{MoO}_4)_3$ ) are identified  
496 by RMS and XRD as main deposited species over all the 670-430°C temperature range (Figures S10,  
497 S11 and S12). Additional particles composed of Cs-Cd mixed compounds as  $\text{Cs}_{2x}\text{Cd}_y(\text{MoO}_4)_{x+y}$  are  
498 hypothesized regarding their typical Raman line shifts but these intermediates are not described in the  
499 literature. Cs-Cd molybdates may result from the reaction at high temperature between  $\text{MoO}_{3(g)}$  and  
500  $\text{Cd}(\text{OH})_{2(g)}$  and/or  $\text{Cd}_{(g)}$  and  $\text{CsOH}_{(g)}$ . Above 600°C, the morphology of  $\text{CdMoO}_4$  is octahedral (Shahri *et*  
501 *al.*, 2013) that is consistent with RMS results. With decreasing temperature, the overall particle size  
502 decreases and the particle shape changes from octahedral to spherical. Mixed Cs-Cd molybdates are  
503 observed in a cement like deposit (see Figure 3b). Cadmium silicates are identified at lower  
504 temperatures (below 540°C) by EDX and XRD (Figure S12) in plate-shaped particles or rods. Reaction  
505 between Cd with quartz plate substrate may account for the formation of such species.

506 The aerosols collected at 150°C are composed of aggregates of submicron particles mixed with larger  
507 spherical particles (1-3  $\mu\text{m}$ ).  $\text{CdMoO}_4$  and  $\text{Cs}_2\text{Cd}_2(\text{MoO}_4)_3$  are the main compounds of aggregates.  
508 Besides spherical particles of Cd metal, part of Cd may be also oxidized in the steam flow as  $\text{Cd}(\text{OH})_2$   
509 and CdO forms were detected by XRD (Figure S13). Additionally, traces of  $\text{MoO}_2$  were also detected at  
510 150°C by RMS (Figure S14). As stated in section 3.1.2, the formation of molybdenum dioxide results  
511 indirectly from the oxidation of Cd metal exposed to the high temperature steam condition and  
512 producing hydrogen capable of reducing  $\text{MoO}_3$  to  $\text{MoO}_2$  (Grégoire *et al.*, 2015). Although only  
513 evidenced at the line outlet, partial reduction of Mo(VI) to Mo(IV) is consistent with high amount of  
514 Mo found deposited in the high temperature zone consecutively to the formation of the less volatile  
515 Mo (IV)-oxide.

516 No isolated caesium molybdate compounds are identified on any samples. The absence of such species  
517 in the deposits or in the transported aerosols can result from the competition between Cs and Cd when  
518 reacting with molybdenum which is in favour of the later one, since cadmium was injected in very large  
519 excess with respect to Cs and Mo. Indeed, cadmium molybdate is stable in the  $\text{MoO}_3$ -Cd system below  
520 700°C with a low formation standard enthalpy (-1034 kJ/mol at 25°C - Ali *et al.*, 2005).

521 As far as iodine is concerned, no iodine containing species (such as CsI ou  $\text{CdI}_2$ ) are evidenced in the  
522 670°C-430°C temperature range. Low amounts of iodine are detected at 150°C by XPS (Figure S15)  
523 with I 3d<sub>5/2</sub> binding energy (BE) at 619.9 eV assigned to I-I bonds energy. Indeed, this BE is  
524 higher than the ones expected for Cs-I or Cd-I bonds. This last feature states for  $\text{I}_2$  likely adsorbed on  
525 particles (Dillard *et al.*, 1984). Nevertheless, in presence of large amounts of Cd, the I3d<sub>5/2</sub> XPS peaks  
526 at 619 eV can be interfered by that of Cd3p<sub>3/2</sub> (618.4 eV) so that chemical shift interpretation should  
527 be considered with caution; the I 3d<sub>3/2</sub> peak (631.5 eV) remains free of interference but is less  
528 documented in the literature (NIST database). The characterization of the condensed material is  
529 consistent with results gained from gaseous phase (organic line) strengthening the fact that interaction  
530 between iodine and cadmium seems to be weaker than inferred from the Phébus FP tests (Girault and



531 Payot, 2013), even for very large excess of Cd relative to I. Table 4 summarizes the main identified  
 532 species in the [Cd+MoCsI] test.

533 *Table 4: [Cd+MoCsI] test - Summary of the main identified species in the deposits and aerosols collected in*  
 534 *the 800-150°C temperature range. Dominant species are in bold characters.*

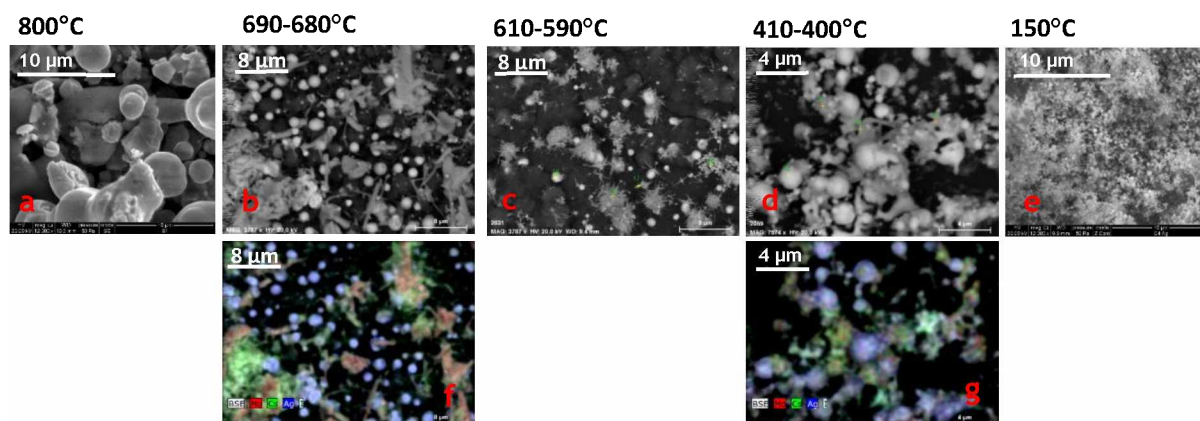
Analysis	~670°C	~640°C	~530°C	~465°C	~445°C	150°C
SEM-EDX	<b>Octahedra</b> Mo/Cd=1.0 <b>CdMoO<sub>4</sub></b>	<b>Octahedra</b> Mo/Cd=0.9 <b>CdMoO<sub>4</sub></b>	<b>Sphere</b> Mo/Cd=1.0 <b>CdMoO<sub>4</sub></b>	<b>Sphere</b> Mo/Cd=1.4 Mo/Cs=1.3 Cd/Cs=1.0 <b>Cs<sub>2</sub>Cd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub></b>	<b>Sphere</b> Mo/Cd=0.9 <b>CdMoO<sub>4</sub></b>	<b>Sphere</b> Mo/Cd=0.1 Mo/Cs=1.6 Cd/Cs=14-21
Morphology	<b>"Cement"</b> Mo/Cd=1.9 Mo/Cs=2.2	<b>"Cement"</b> Mo/Cd=1.5 Mo/Cs=1.6	<b>Rod</b> Cd/Si=0.9 <b>CdSiO<sub>3</sub></b>	<b>Plate</b> Cd/Si=1.9 <b>Cd<sub>2</sub>SiO<sub>4</sub></b>	<b>Plate</b> Cd/Si=1.0 <b>CdSiO<sub>3</sub></b>	<b>Cd</b>  <b>Aggregate</b>
Elemental atomic composition and ratio	Cd/Cs=1.5 <b>Cs<sub>2x</sub>Cd<sub>y</sub>(MoO<sub>4</sub>)<sub>x+y</sub></b>	Cd/Cs=1.0 <b>Cs<sub>2</sub>Cd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub></b>	<b>"Cement"</b> Mo/Cd=1.6 Mo/Cs=1.6 Cd/Cs=1.0 <b>Cs<sub>2</sub>Cd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub></b>	<b>Cd<sub>2</sub>SiO<sub>4</sub></b>	<b>Sphere</b> Mo/Cd=1.6 Mo/Cs=1.6 Cd/Cs=1.0 <b>Cs<sub>2</sub>Cd<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub></b>	Mo/Cd=0.2-0.4 Mo/Cs=1.7-2.2 Cd/Cs=4.2-17 <b>Mix</b>
Species		<b>Cs<sub>2x</sub>Cd<sub>y</sub>(MoO<sub>4</sub>)<sub>x+y</sub></b>				
RMS	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>  CdSiO <sub>3</sub> or Cd <sub>2</sub> SiO <sub>4</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>  MoO <sub>2</sub>
XRD	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>  CdSiO <sub>3</sub> Cd <sub>2</sub> SiO <sub>4</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>  CdSiO <sub>3</sub> Cd <sub>2</sub> SiO <sub>4</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>  CdSiO <sub>3</sub> Cd <sub>2</sub> SiO <sub>4</sub>	CdMoO <sub>4</sub> Cs <sub>2</sub> Cd <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>  Cd CdCO <sub>3</sub> Cd(OH) <sub>2</sub>

535  
 536 **3.2.3 Results for the [Ag+MoCsI] test**  
 537 Various particle morphologies are identified by SEM (see Figure 4) that are observed over almost all  
 538 the temperature range (800-150°C):

- 539 • Large Ag-rich spherical particles (> 10 μm) are observed both partly coalesced at high temperature  
 540 and then isolated with size decreasing along with sampling temperature to reach submicronic sizes  
 541 (~100 nm) at 150°C.
- 542 • Parallelepipedic crystallites (not shown) with size decreasing from ~10 μm to less than 1 μm are seen  
 543 from 800°C to 150°C. EDX analyses reveal that these particles are Mo-enriched above 600 °C and  
 544 featured also Ag below 600°C;
- 545 • Needle like particles are observed only when the temperature is below 700°C. The particle size  
 546 varies from initially 3-4 μm long at T= 700°C to < 1μm at the temperature sampling. The needles  
 547 contain mostly Mo and Ag;
- 548 • Aggregates of very fine particles are seen below 700°C, in which Cs is detected.

549 Table 5 summarizes the main identified species by combination of SEM-EDX and RMS analyses. Note  
 550 that with decreasing temperature, fine particles agglomerate to form larger structures in which single  
 551 components are difficult to identify. Consistently with its refractive properties, silver metal condenses  
 552 early in the transport zone and is found as the main deposited species above 750°C (EDX) in the large

553 and partly coalesced droplets. Silver metal is then transported/deposited in the line as spherical  
554 particles as confirmed by EDX and XRD analyses (Figure S16).



555  
556 *Figure 4: [Ag+MoCsI] test - SEM-BSE (a-e) and EDX (f,g) images of deposits and aerosols collected in the*  
557 *800-150°C temperature range. (on elemental images f and g: red is Mo, blue is Ag and green is Cs).*

558 In the 700-400°C temperature region, molybdenum(VI) and (IV) oxides are found by RMS as  
559 predominant species. The presence of reduced forms of Mo is confirmed by XPS in the same  
560 temperature range (Figure S17). The formation of MoO<sub>2</sub> is consistent with the injection of a low  
561 amount of hydrogen and the presence of important amount of silver metal which can be considered  
562 as a reducing agent. The presence of the less volatile Mo(IV) species is also consistent with enhanced  
563 Mo deposition at high temperature (as stated in section 3.1). Silver molybdates (Ag<sub>2</sub>MoO<sub>4</sub> as a major  
564 compound and Ag<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, Ag<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub>) are also identified by RMS (Beltran *et al.*, 2014) in this  
565 temperature range (Figures S18 and S19). Molybdenum oxide and silver molybdates are mostly found  
566 in the needle and parallelepiped-shaped particles. In a lesser extent caesium molybdates are also  
567 identified and found as amorphous structure. Caesium molybdates account for the dominant species  
568 only below 500°C. Competition between the formation of silver and caesium molybdates may explain  
569 the delayed deposition of caesium molybdate species when comparing with tests featuring only the  
570 Mo-Cs-I-O-H chemical system (Gouello, 2012). The distinction between silver and caesium molybdates  
571 remains challenging as Raman spectra of such compounds exhibit typical Raman bands related to Mo-  
572 O vibrational modes in the same spectral range (i.e. 800-100 cm<sup>-1</sup>).

573 Only few single particles featuring either CsI or AgI are observed in deposits between 350°C and 400°C  
574 as seen on the SEM-EDX images (Figure S20). Because iodine is injected with an elemental flow rate  
575 ~50 times lower than silver one, metallic iodide (if formed) would account for a minor compound.

576  
577

Table 5: [Ag+MoCsl] test - Summary of the main identified species in the deposits and aerosols collected in the 800-150°C temperature range. Dominant species are in bold characters.

Analysis	800-765°C	690-680°C	610-590°C	520-500°C	410-400°C	~350-340°C	150°C
SEM-EDX	Large spherical particles (> 5-10 µm) : <b>Ag(0)</b>	spherical particles (1-2 µm): <b>Ag(0)</b>	spherical particles (1-2 µm) : <b>Ag(0)</b>	Not analysed	spherical particles (1-2 µm): <b>Ag(0)</b>	Same as 410-400°C plate plus some Mo Rich large plates	Submicronic spherical particles (100 nm) : <b>Ag(0)</b>
Morphology		fine needles (~5 µm) and parallelepipedic plates (2-10 µm) : Mo rich	fine particles (<1) µm		fine particles (<1) µm		
Elemental atomic Composition		MoO <sub>3</sub> , MoO <sub>2</sub> and Ag <sub>2</sub> MoO <sub>4</sub>	aggregates of fine particles around the spherical one's		aggregates of fine particles around the spherical one's		Submicronic particles difficult to characterize
Species		amorphous structure ("cement" like): Cs rich (Cs <sub>x</sub> Mo <sub>y</sub> O <sub>z</sub> ?)			sparse AgI particles	sparse AgI particles	
RMS	<b>Ag<sub>2</sub>MoO<sub>4</sub></b> Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> Ag <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub>	<b>Ag<sub>2</sub>MoO<sub>4</sub></b> Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub>	<b>Ag<sub>2</sub>MoO<sub>4</sub></b> Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> / Cs <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> Ag <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub> / Cs <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub>  (Cs/Ag) <sub>x</sub> Mo <sub>y</sub> O <sub>z</sub>	<b>Ag<sub>2</sub>MoO<sub>4</sub></b>  (Cs/Ag) <sub>x</sub> Mo <sub>y</sub> O <sub>z</sub>	Ag <sub>2</sub> MoO <sub>4</sub>	Ag <sub>2</sub> MoO <sub>4</sub> Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> (p)	<i>Ag<sub>2</sub>MoO<sub>4</sub></i> Ag <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub>  Cs/Ag <sub>x</sub> Mo <sub>y</sub> O <sub>z</sub>
		Cs <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> Cs <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub>		Cs <sub>2</sub> Mo <sub>2</sub> O <sub>7</sub> Cs <sub>2</sub> Mo <sub>3</sub> O <sub>10</sub>	<b>Cs<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub></b> <b>Cs<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub></b> <b>Cs<sub>2</sub>Mo<sub>5</sub>O<sub>16</sub></b>	<b>Cs<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub></b> <b>Cs<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub></b> <b>Cs<sub>2</sub>Mo<sub>5</sub>O<sub>16</sub></b>	<b>Cs<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub></b> <b>Cs<sub>2</sub>Mo<sub>3</sub>O<sub>10</sub></b> Cs <sub>2</sub> Mo <sub>4</sub> O <sub>13</sub> Cs <sub>2</sub> Mo <sub>5</sub> O <sub>16</sub>
	MoO <sub>2</sub>	<b>MoO<sub>3</sub>xH<sub>2</sub>O</b> <b>MoO<sub>2</sub></b>	<b>MoO<sub>2</sub></b> <b>α-MoO<sub>3</sub></b>	<b>MoO<sub>2</sub></b> MoO <sub>3</sub> xH <sub>2</sub> O	MoO <sub>3</sub> (p) MoO <sub>2</sub> (p)	MoO <sub>3</sub> (p) MoO <sub>2</sub> (p)	Mo <sub>x</sub> O <sub>y</sub>

578

#### 579 4. Discussion

580 In the presence of SIC control rods, the behaviour of iodine may be contrasted. Iodine is transported  
581 in the gaseous phase when indium is injected, but maintaining an excess of Mo with respect to Cs.  
582 Whereas silver and cadmium injection in large excess induce the formation of iodide aerosols. AgI  
583 formation seems to be limited despite a large excess of silver, with a formation rate lower than 10%  
584 with respect to iodine ([Ag+MoCsl] test). This point confirms that AgI is less stable than CsI and CdI<sub>2</sub>  
585 consistently with thermodynamic data (Table 6). More specifically, the three tests exhibited some  
586 significant differences as for iodine behaviour:

- 587 • For the [In+MoCsl] test, a part of the injected indium preferentially reacts with MoO<sub>3</sub> rather than  
588 iodine to form indium molybdates so that InI<sub>x</sub> formation was not observed. As Mo was injected in  
589 excess of In and Cs, the molybdenum still acts as a Cs sink preventing CsI formation and thus allows  
590 the existence of gaseous iodine at 150°C. It is not excluded that the injection of In<sub>2</sub>O<sub>3</sub> in larger  
591 amounts (e.g. larger than Mo as for the tests with Cd and Ag) could result in an increased  
592 consumption of MoO<sub>3</sub> to form In-molybdate competing with Cs-molybdate formation and thus  
593 favouring caesium iodide formation, but in any case this is not very representative of the SA case  
594 (In is still in lower amount than Mo).  
595
- 596 • For [Ag+MoCsl] and [Cd+MoCsl] tests, despite the injection of a huge excess of cadmium or silver  
597 relative to all the other elements, the formation of metallic iodide other than CsI seems not to be  
598 the main reaction pathways leading to the reduction of gaseous iodine release. Two reaction



599 pathways are put forward. Firstly, the reactivity of cadmium and silver with molybdenum oxides  
 600 may contribute to significantly reduce the Cs-scavenging role of Mo by preventing the formation  
 601 of caesium molybdates with Mo(VI) oxidation state. Secondly, the oxidation of the injected  
 602 metallic species (Cd, Ag) may indirectly promote the formation of less reactive MoO<sub>2</sub> oxide. This  
 603 second reaction pathway should remain limited, however, as at most 10% of injected Mo(VI) could  
 604 be reduced (XPS data, see section 3.2). As a result, the formation of CsI is favoured preferentially  
 605 to AgI (observed) or CdI<sub>2</sub> (hypothesized) in agreement with the relative stability of these  
 606 compounds. Indeed, available thermodynamic data tends to show that caesium iodide is the most  
 607 stable metallic iodide to be considered here both in gaseous and condensed phases.

608 *Table 6: Standard Enthalpy of formation of metallic iodide of interest taken from literature*

<i>Chemical species</i>	standard formation enthalpy for condensed species (kJ/mol)@298K	standard formation enthalpy for gaseous species (kJ/mol)@298K
<i>CsI</i>	-348.1 (Cordfunke and Prins, 1985)	-153.3 ± 1.8 (Roki <i>et al.</i> , 2014)
<i>CdI<sub>2</sub></i>	-205 (Konings <i>et al.</i> , 1993)	-58.8 ± 2.5 (Shugurov <i>et al.</i> , 2021)
<i>AgI</i>	-61.8 (Taylor and Anderson, 1921)	125.3 (Barin, 1989)
<i>InI</i>	-102 (Vasil'ev <i>et al.</i> , 1987)	26.4 (Gurvich <i>et al.</i> 1989)
<i>InI<sub>3</sub></i>	-223 (Vasil'ev <i>et al.</i> , 1987)	-105.4 (Gurvich <i>et al.</i> 1989)

609  
 610 Characterization of the main compounds deposited in the CHIP line allowed for identifying several  
 611 metallic polymolybdates in addition to the caesium molybdates already characterized in similar  
 612 thermal hydraulic conditions (Lacoue-Nègre, 2010; Gouello *et al.*, 2013; Grégoire *et al.*, 2015). Such  
 613 species were not mentioned for the VERCORS nor Phébus tests. Nevertheless, deposition profile of In,  
 614 Cs and Mo obtained in a 800-200°C thermal gradient for the VERCORS HT tests (deposition along  
 615 Thermal Gradient Tube as reported by Pontillon and Ducros, 2010) showed concomitant deposition in  
 616 the ~800°C (HT2 test), ~675-725°C (HT3 test) and ~640°C (HT2 test) temperature zones, so that  
 617 deposition of metallic molybdates involving Cs and/or In cannot be excluded. Silver deposition is much  
 618 more complex to discuss featuring a low homogeneous deposition detected below 700°C (HT3 test)  
 619 and 600°C (HT2 test) and no data for Cd deposition is available. As only I and Cs deposition profiles  
 620 were determined for the Phébus Thermal Gradient Tube (700-200 °C) during the FPT1 and FPT2 tests  
 621 (Girault and Payot, 2013), it will be difficult to infer any comparison with our results.

622 The formation of various metallic polymolybdates entering in competition with the formation of  
 623 caesium polymolybdates is clearly evidenced in the three tests. Indeed, deposits containing pure  
 624 caesium molybdates were detected at a lower temperatures (below 600°C for [In+MoCsI] and  
 625 [Ag+MoCsI] tests) than observed when only Mo oxide and Cs species are reacting together (1000°C, as  
 626 reported in Gouello *et al.*, 2013). Cd and Ag are injected both in large excess relative to Mo and Cs, so  
 627 that a direct comparison of the two tests in terms of molybdate formation can be put forward. Pure  
 628 caesium molybdates are still observed in [Ag+MoCsI] test, as well as MoO<sub>2</sub> and MoO<sub>3</sub> species. On the  
 629 contrary, cadmium-containing molybdates are the dominant species in the [Cd+MoCsI] test featuring  
 630 only mixed CdCs molybdates and traces of MoO<sub>2</sub> (aerosols collected at the line outlet). These features  
 631 indicate that the formation silver molybdates seem less favoured compared to that of cadmium  
 632 molybdates in our test condition. Even if In<sub>2</sub>O<sub>3</sub> was injected in lower amount (in default relative to Mo  
 633 but in excess compared to Cs), the formation of indium molybdates seem favoured at high  
 634 temperature, compared to that of pure caesium molybdates, as CsIn(MoO<sub>4</sub>)<sub>3</sub> and In<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> are the  
 635 dominant species in the 500-750°C temperature range. Caesium was found mainly as a mixed InCs  
 636 molybdate compounds over all the temperature range, pure caesium molybdates appearing less  
 637 abundant. In the oxidative atmosphere of this test (steam injection and no reducing species), the



638 excess Mo was found mainly as  $\alpha$ -MoO<sub>3</sub> from 500°C down. It is nevertheless difficult to know exactly  
 639 if the species are formed in the gas phase and/or in the solid phase after condensation of In, Mo and  
 640 Cs species in oxide or hydroxide forms.

641 Formation enthalpies referenced in the literature show that caesium molybdates are most stable  
 642 compared to cadmium, silver and indium molybdates even if the thermodynamic data are uncomplete  
 643 with no mixed elements (see Table 7). In our conditions the large excess of Cd, Ag and In reagents  
 644 compared to Cs may have displaced equilibrium in favour of Cd, Ag or In-molybdates in the high  
 645 temperature zone. Consumption of these elements results in the formation of the more stable Cs  
 646 molybdates at lower temperature as experimentally observed. In this discussion, possible kinetic  
 647 limitations in the thermal-hydraulic transient are not taken into account and thermodynamic data are  
 648 nevertheless not all available in the literature.

649 *Table 7: Standard Enthalpy of formation of molybdates of interest taken from literature*

<i>Chemical species</i>	standard formation enthalpy for condensed species (kJ/mol)@298K	standard formation enthalpy for gaseous species (kJ/mol)@298K
$\alpha$ -MoO <sub>3</sub> (s) and MoO <sub>3</sub> (g)	-745.5 (Crouch-Baker and Dickens, 1984)	-364.4 ± 20.0, (Cordfunke and Konings, 1990)
Cs <sub>2</sub> MoO <sub>4</sub>	-1514.4 (Gamsjäger and Morishida, 2015)	-1179.2 (Tangri <i>et al.</i> , 1989)
In <sub>2</sub> MoO <sub>4</sub>	Not available	-855 ± 33 (Lopatin <i>et al.</i> , 2013)
Ag <sub>2</sub> MoO <sub>4</sub>	-838.2 (Gamsjäger and Wiessner, 2018; Gamsjäger and Morishita, 2015)	-459.6 (CCSD(T)/CBS(TZ-QZ) value, method described in Saab and Souvi, 2018)
CdMoO <sub>4</sub>	-1034 ± 5.7 ; -1015.4 ± 14.5 Ali <i>et al.</i> , 2005 ; Mishra <i>et al.</i> , 2006	-606.0 (CCSD(T)/CBS(TZ-QZ) value, method described in Saab and Souvi, 2018)
SnMoO <sub>4</sub>	Not available	-699 ± 29 (Shugurov <i>et al.</i> , 2015)

650  
 651 Even if trends could be inferred from a direct comparison of stability of the identified compounds, a  
 652 full understanding of the main reactions which occurred in the CHIP line with these chemical systems  
 653 will be gained by simulation of the experiments with severe accident calculation codes as  
 654 ASTEC/SOPHAEROS (Cousin *et al.*, 2008; Cantrel *et al.*, 2013). Nevertheless, up to date, thermodynamic  
 655 data of some metallic molybdates evidenced in these experiments are not available in the literature  
 656 and cannot be accounted in the thermodynamic database of the simulation tools. Density Functional  
 657 Theory calculations may help to provide some of the missing thermodynamic data for gaseous species.

## 658 659 **5. Conclusion**

660 A series of tests performed in the CHIP line with the Mo-Cs-I-O-H chemical system and CR elements  
 661 revealed that the behaviour of each component (Ag, In and Cd) of the SIC control rod considered  
 662 separately is much more complex than initially expected. Indeed, combined on-line sampling,  
 663 elemental post-test analyses and an extended characterization of deposits allow for identifying most  
 664 of formed compounds during the transport in the thermal gradient (1600-150°C) of the CHIP line.  
 665 These species could not be evidenced in the larger scale Phébus tests or VERCORS HT tests.

666 In the case of indium injection, a release of gaseous iodine similar to the [PL\_MoCsI\_3] reference test  
 667 is observed. Indium iodide formation is not observed as expected from the low stability of InI<sub>x</sub>(g). The  
 668 fully oxidative conditions contribute to maintain Mo in the +VI oxidation state and thus its capabilities  
 669 to easily form metallic molybdates. Beside, significant deposition of In<sub>2</sub>O<sub>3</sub> at high temperature (>750°C)  
 670 owing to the refractive behaviour of this species, the main contribution of In injection is the formation

671 of indium and mixed In-Cs molybdates likely in the condensed phase. Owing to the large excess of Mo  
672 relative to both In and Cs, Mo still plays a Cs-sink role with a large fraction of gaseous iodine  
673 transported at low temperature.

674 In the case of both cadmium and silver injection, the formation of metallic iodide other than CsI seems  
675 not to be the main reaction pathways leading to a strong reduction of gaseous iodine release despite  
676 the injection of a very large excess relative to all the other elements (I, Cs and Mo). The formation of  
677 various metallic silver or cadmium molybdates entering in competition with caesium molybdates  
678 contribute to significantly reduce the Cs-scavenging role of Mo.

679 It can be stated that due to the high stability of caesium iodide, only the absence of Cs can prevent its  
680 formation but if caesium molybdates are formed, as detailed before, caesium cannot be totally  
681 consumed by molybdenum in presence of control rod materials.

682 It is worth noting that all these results apply to the CHIP conditions where molybdenum is injected in  
683 slight excess and silver and cadmium in large excess with respect to representative conditions of a  
684 severe accident.

685 Efforts are ongoing to improve the ASTEC/SOPHAEROS modelling to reproduce as much as possible all  
686 the trends experimentally observed in terms of iodine chemical reactivity and also FPs deposits, to be  
687 at least capable to deepen the understanding of the FP's chemistry observed during the Phébus tests  
688 (Girault and Payot, 2013) and later on perform SA simulations

689

690 CRediT authorship contribution statement

691 Grégoire A.C.: Investigation, Writing - original draft; Sobanska S : Investigation, Writing - original draft,  
692 Tornabene C.: Investigation; Talaga D.: Investigation; Mamede A.S.: Investigation; Morin S.:  
693 Investigation; Cantrel L. : Writing, original draft.

694 Declaration of Competing Interest:

695 The authors declare that they have no known competing financial interests or personal relationships  
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697

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710

- 711 Glossary:
- 712 ASTEC: Accident Source Term Evaluation Code
- 713 BSE : Back Scattering Electron imaging
- 714 CHIP : Chemistry Iodine Primary circuit
- 715 EdF : Electricité de France
- 716 ESEM-EDX: Environmental Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy
- 717 FD NPP: Fukushima Daiichi Nuclear Power Plants
- 718 FP: Fission Product
- 719 FPs : Fission Products
- 720 GAEC : Generation of AErosols in the reactor Coolant system
- 721 ICP AES: Inductively Coupled Plasma – Atomic Emission Spectroscopy
- 722 ICP MS: Inductively Coupled Plasma – Mass Spectrometry
- 723 LWR : Light Water Reactor
- 724 PWR: pressurised Water reactor
- 725 RCS: reactor Coolant System
- 726 RMS : Raman Micro Spectrometry
- 727 SA: Severe Accident
- 728 SE : Secondary Electron imaging
- 729 SIC CR : Silver-Indium-Cadmium Control Rod
- 730 XRD: X-Ray Diffraction
- 731

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