

Investigation on Revaporization from CsI Deposited Particles in the Primary Circuit in Nuclear Severe Accident Conditions

Mélany Gouëlle and Teemu Kärkelä

VTT Technical Research Centre of Finland Ltd

P.O. Box 1000

FI-02044 VTT, Finland

Melany.gouello@vtt.fi, Teemu.karkela@vtt.fi

ABSTRACT

Since the Fukushima Dai-Ichi (1F) Nuclear Power Station accident, a renewed attention has been posed on the evaluation of delayed source terms, especially from Reactor Coolant System (RCS) surface deposits and on the boron carbide control rods behaviour. After fission products have been released from the overheated and molten fuel, they are transported through the reactor coolant system and fission products will reach areas at lower temperature. Therefore, vapour condensation and particle nucleation processes take place in the gas flow. If vapour condensation takes place close to the surfaces of the primary circuit, a layer of condensate can be formed on it. Particles in the gas flow may also deposit on the circuit surfaces together with control rod and structural materials.

The objectives of the work was to investigate the behavior of deposited caesium iodide particles in the RCS and to assess the effect of gaseous boric acid with the deposited particles.

Caesium iodide particles were generated by nebulization of a concentrated caesium iodide aqueous solution and then passed through a Thermal Gradient Tube (TGT). The gaseous boric acid was generated by vaporization from a crucible placed inside the furnace. Aerosols and gaseous species were sampled at 150°C on filters and liquid scrubbers and analysed with HR-ICP-MS. Aerosol number size distributions were measured with TSI Scanning Mobility Particle Sizer (SMPS), with series 3080 platform, series 3081 Differential Mobility Analyzer (DMA) and series 3775 Condensation Particle Counter (CPC). The aerosol mass concentration was monitored by Tapered Element Oscillating Microbalance Series 1400a (TEOM).

The study showed that the deposited caesium iodide particles were subject to revaporization process in Ar/H₂ atmosphere; gaseous iodine was released from the deposits. When gaseous boric acid was present in the carrier gas (Ar/H₂), the percentage of gaseous iodine released was higher. The interpretation of the SMPS and TEOM results also suggested that the presence of gaseous boric acid would then have an influence on the transport of the deposited caesium iodide particles as it showed different behaviour than during revaporisation/resuspension under Ar/H₂.

1 INTRODUCTION

Previous investigations [1;2] on the primary circuit chemistry of iodine and caesium, have suggested that condensed phase reactions, between boric acid and caesium iodide, could lead to a significant release of gaseous iodine. At the same time, the reactions could limit the caesium transport through the primary circuit by forming condensable caesium borates. The purpose of the present work was to determine if the observed condensed phase reactions keep their

relevance in more realistic conditions. The main goal was to investigate the condensed phase reactions of deposited caesium iodide particles (instead of powdery precursor), which is more representative of reactor's conditions. The choice of introducing caesium iodide in the form of particles is motivated by the results of the FPT2 test, for which sampling data indicated that at 700°C, iodine as aerosol ranged between 11 % and 44 % of the total amount of iodine (gas and aerosol) [3]. The second objective was to determine the effect of boron on caesium iodide behaviour in the primary circuit conditions. Depending on the accident scenario, the boron species can then react with fission products (gas, vapour and/or aerosols) and consequently affect the source term¹. Literature review on the effect of boron on the caesium iodide chemistry in the RCS was described in Gouëlle *et al.* [1] and has pointed out the lack of experimental data concerning the reaction between boron and condensed caesium iodide. As the formation of solid caesium borate (possible compound for the formation of blockages in the circuit) was observed with the boron oxide (B_2O_3) precursor [1], the observation will be verified by using boric acid (H_3BO_3) precursor, which is a representative boron compound in the primary circuit.

First, the transport and decomposition of caesium iodide particles in the Thermal Gradient Tube (TGT) are investigated in an Ar/ H_2O (80/20 vol.%). Then, a carrier gas of Ar/ H_2 (95/5 vol.%) is flowed over the deposited and condensed species. The similar test was performed with a carrier gas of Ar/ H_2 (95/5 vol.%) containing boric acid. The size number concentration and mass concentration of the particles monitored at the outlet of the TGT are compared. In addition, the ratio of gaseous species/aerosols are reported.

1 MATERIAL AND METHODS

1.1 Test facility and characterization

A modified version of the EXSI-PC facility was used [1].

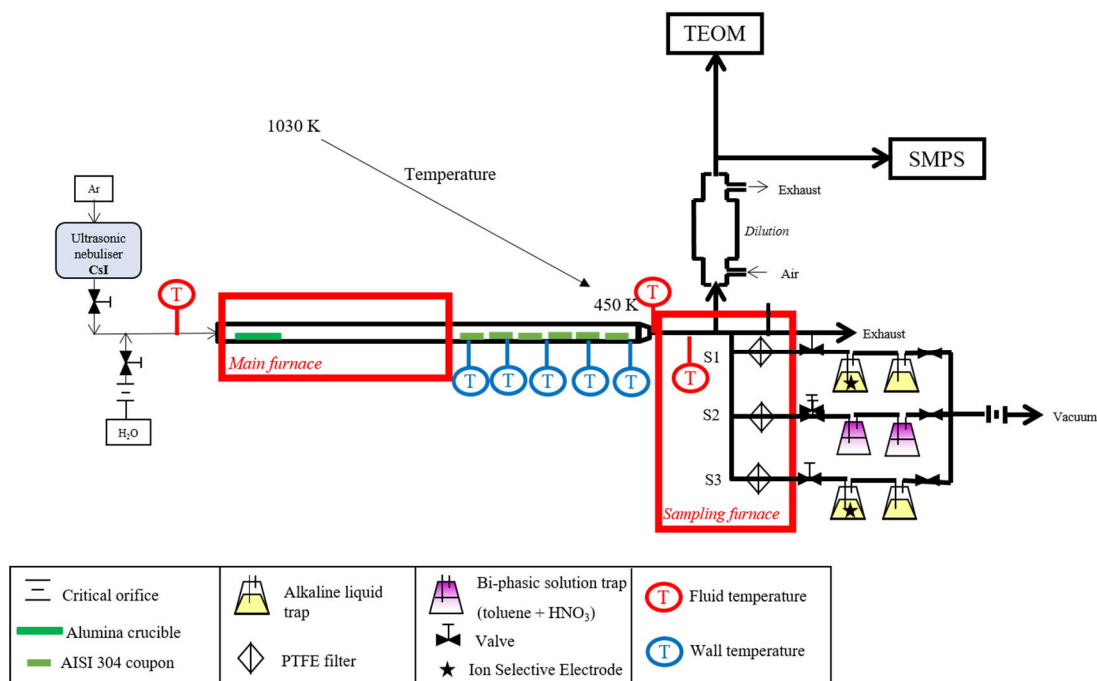


Figure 1: Schematic figure of the experimental facility EXSI-PC [1]

¹ The source term is defined as the magnitude, the chemical and physical form of the fission product source distribution in the containment atmosphere, during severe accident conditions [4].

The caesium iodide particles were generated by nebulization of a concentrated caesium iodide aqueous solution (10 g/l of caesium iodide powder 99.9 wt%, provided by SigmaAldrich®) at room temperature and atmospheric pressure. The generated aerosols passed through a pre-oxidized stainless steel TGT (AISI 304, inside diameter 25 mm and 1100 mm length provided by Restek Corporation®) from 750°C to 170°C. The boric acid (99.97% trace metals basis provided by SigmaAldrich®) was generated by vaporisation from a crucible. The carrier gas, a mixture of argon/steam (80/20 vol.%) or argon/ hydrogen (95/5 vol.%) was passed through the system. In the sampling furnace, the main flow was split into four lines:

- (1) A first line headed for aerosol on-line measurement. Upstream from the online aerosol measurement devices, the flow was diluted (dilution factor of 7.5) in order to decrease the concentration of the produced particles low enough for the instrumentation as well to decrease the temperature of the flow below 313 K. The particle number size distributions were measured with a TSI Scanning Mobility Particle Sizer (SMPS), with series 3080 platform, series 3081 Differential Mobility Analyser (DMA) and series 3775 Condensation Particle Counter (CPC). The aerosol mass concentration was monitored by Tapered Element Oscillating Microbalance Series 1400a (TEOM).
- (2) A second line was used to sample particles and gaseous species. The line was equipped with a polytetrafluoroethylene (PTFE) membrane filter (hydrophobic, poral grade 5.0 µm, 47 mm, Mitex®) and two liquid traps assembled in series. They were filled with a solution of 0.1 M sodium hydroxide (NaOH) in water (150 ml). During the test, the first liquid trap was equipped with the Ion Selective Electrode (ISE)² in order to monitor on-line the concentration of iodine. After the test, the solutions and the leachants from filters (50 ml) will be analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The analyses will be performed with a Thermo Fisher Scientific HR-ICP-MS Element2 apparatus. This line was used for the first 20-minute sampling (S1).
- (3) A third line was used, with a similar configuration as the second line, except the nature of the liquid traps. The liquid traps were filled with an immiscible solution composed of aqueous phase (nitric acid, pH=3; 50 ml) and an organic phase (toluene; 100 ml) in order to selectively separate hydrogen iodide (HI) from molecular iodine (I₂). Due to its non-polarity, molecular iodine is expected to be trapped in the organic phase while hydrogen iodide would stay in the aqueous phase. This line was used for the second 20-minute sampling (S2). The quantification of molecular iodine in toluene was carried out by UV-visible spectroscopy using a PerkinElmer spectrophotometer model Lambda 900³. In toluene, the absorption curve of molecular iodine presents two peaks at 306 nm and 497 nm, giving respective molar extinction coefficients of 7901.0 l·mol⁻¹·cm⁻¹ and 1064.8 l·mol⁻¹·cm⁻¹.
- (4) The last line had the same configuration as the second line. This line was used for the third 20-minute sampling (S3).

1.2 Test matrix

In the present study, the absolute pressure in the facility was fixed at 1 bar. Gas flow rate was set under Standard Temperature and Pressure (STP). The carrier gas was a mixture of argon and steam for the deposition phase and a mixture of argon and hydrogen for the revaporisation

² The LOD of I⁻ was assessed to be 6.7·10⁻⁷ mol/l in sodium hydroxide solution.

³ The LOD of I₂ in toluene was measured to be 4.7·10⁻⁷ mol/l.

phase. There are two main experiments and each experiment were performed in two separate steps (as minor experiments). In the first step, CsI particles were introduced and transported through the TGT in Ar/H₂O atmosphere (total flow rate 4 l/min). In the next step, the deposited CsI particles were heated up to 750°C under Ar/H₂ atmosphere (total flow rate 4 l/min). The second experiment aims to determine the effect of boron on caesium iodide behaviour in the primary circuit conditions. After the deposition phase, gaseous boric acid was introduced in the TGT in Ar/H₂ atmosphere (total flow rate 4 l/min). The CsI-1 and CsI-2 tests were performed in same conditions. The matrix of tests is presented in Table 1.

Table 1: Experimental matrix and test conditions

Exp	Precursor	Gas	
H₃BO₃-0	H ₃ BO ₃ gas	Ar/H ₂	Blank behaviour
CsI-1	CsI particles	Ar/H ₂ O	Deposition phase (i.e. "phase 1")
CsI-1_Re	Deposited CsI	Ar/H ₂	Reaction/vaporisation phase (i.e. "phase 2")
CsI-2	CsI particles	Ar/H ₂ O	Deposition phase (i.e. "phase 1")
CsI-2_Re	Deposited CsI + H ₃ BO ₃ gas	Ar/H ₂	Reaction/vaporisation phase (i.e. "phase 2")

2 EXPERIMENTAL RESULTS

The analyzed mass concentrations on particle filter and in bubblers samples and the results obtained from on-line aerosol measurement devices are summarized in Table 2.

Table 2: Results obtained from measurements

Experiment number		H ₃ BO ₃ -0	CsI-1	CsI-1_Re	CsI-2	CsI-2_Re
Amount collected on filters determined by ICP-MS [10 ⁻⁷ mol]	I	N.A.	110.04	14.35	69.16	0.54
	Cs	N.A.	100.80	13.04	64.28	0.46
	B	481.04	N.A.	N.A.	N.A.	0.80
Amount in the liquid traps determined by ICP-MS [10 ⁻⁷ mol]	I	N.A.	167.64	6.60	6.55	8.36
	Cs	N.A.	0.00	0.00	0.00	0.00
	B	110.76	N.A.	N.A.	N.A.	101.36
Amount in the liquid traps determined by ISE [10 ⁻⁷ mol]		0.00	67.54	3.48	2.29	3.98
		0	42.14	0.59	19.32	0
Amount of iodine "I" in molecular iodine (I ₂) form [mol]		< LOD	< LOD	< LOD	< LOD	< LOD
Percentage of gaseous iodine		N.A.	60.37	31.51	8.66	93.89
Percentage of gaseous boron		18.72	N.A.	N.A.	N.A.	99.22
Molar ratio measured on the filter	Cs/I	N.A.	0.92	0.91	0.93	0.85
	B/Cs	N.A.	N.A.	N.A.	N.A.	1.73
SMPS [1/cm ³]		3.4·10 ⁵	3.8·10 ⁸	1.5·10 ⁸	2.5·10 ⁸	2.6·10 ⁵
GMD [nm]		50.2	67	45	59.9	42.23
GSD		1.9	1.4	1.5	1.4	1.6
TEOM [mg/m ³]		9	1065	53	829	3

2.1 Caesium iodide particles transport through the TGT

The first set of experiments was designed to study the transport of caesium iodide aerosols in the TGT. The particle size distribution of the particles passing through the TGT was similar for the two similar tests (CsI-1 and CsI-2) looking at the SMPS measurement (Figure 2). The Geometric Mean Diameter was around 65 nm ($1.3 < \text{GSD}^4 < 1.6$). The results showed a slight difference in the number concentration between the similar conditions. The results of the TEOM measurements revealed a particle mass concentration varying between 830 mg/m³ and 1065 mg/m³.

The results obtained by ICP-MS are about the double of the values measured by ISE (Table 2). The two analyses are complementary as ISE allows the measurement of iodide (I-) ions in solution, while ICP-MS can measure all the iodine species in solution. Furthermore, the ICP-MS can measure a much larger concentration range than the ISE with a better accuracy.

The transported iodine through the TGT was lower for the CsI-2 than for the CsI-1 test. Assuming that the generation from the caesium iodide generator was constant, it seems that more particles were deposited during the CsI-2 test. The UV-Visible spectrometry has a Limit of Detection (LOD)⁵ higher than the amount of sampled gaseous iodine (few ppb); it was therefore not possible to determine the percentage of generated molecular iodine.

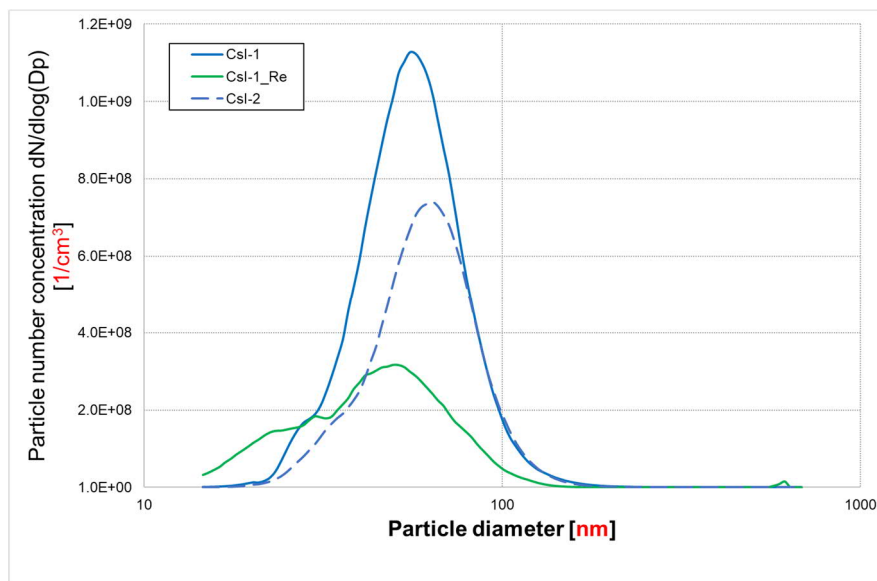


Figure 2: Number concentration of particles transported through the facility as a function of the particle electrical mobility diameter recorded with SMPS. D_p represents particle diameter. The curves represent mean values for several scans.

⁴ GSD: Geometric Standard Deviation.

⁵ The Limit Of Detection of molecular iodine in toluene was measured to be 1 ppm.

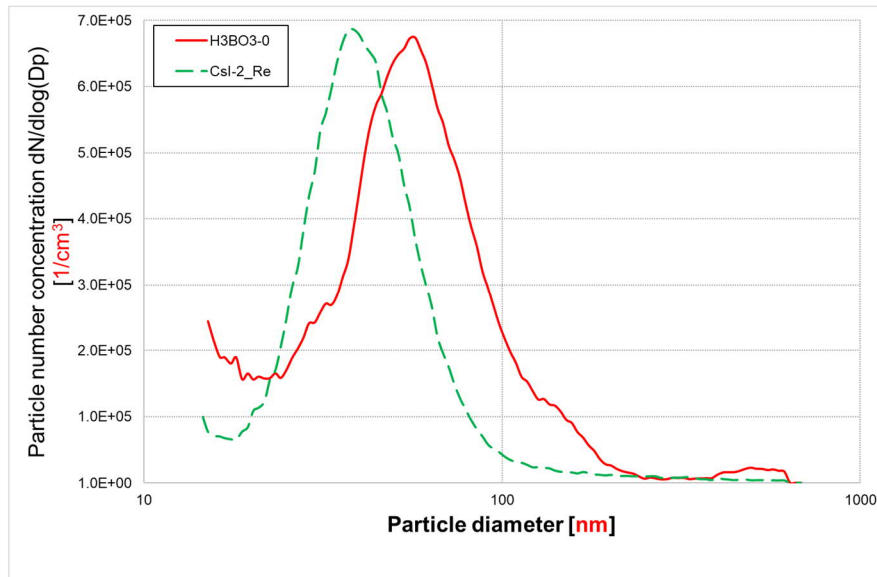


Figure 3: Number concentration of particles transported through the facility as a function of the particle electrical mobility diameter recorded with SMPS. D_p represents particle diameter. The curves represent mean values for several scans.

2.2 Caesium iodide resuspension and revaporization processes

The second phase of the experiment aimed at highlighting the possible revaporization or/and resuspension processes. The particles removed from what was deposited on the surface walls of the TGT during the first phase exhibited a GMD of 45 nm (Figure 2 see CsI-1_Re full green curve; $1.4 < \text{GSD} < 1.6$) and 50 nm (Figure 3 see CsI-2_Re dashed green curve; $1.7 < \text{GSD} < 2.0$). The particles were smaller and in lower amount than the particles measured during the caesium iodide generation.

The test performed in presence of boric acid (CsI-2_Re) showed very low amount of particles with a small diameter. The measured particles distribution during the resuspension/revaporisation phase in presence of boric acid looked similar to the one measured during the transport of gaseous boric acid (see red curve on Figure 3). This would suggest that mostly particles issued from the nucleation of gaseous boric acid were transported through the TGT and that the caesium iodide compound, which was deposited/condensed during the phase 1 was not transported during phase 2. The presence of gaseous boric acid would then have an influence on the transport of the deposited/condensed caesium iodide as it showed different behaviour than during revaporisation/resuspension under Ar/H₂. This is also highlighted by the measured mass concentration (3 mg/m³ for the revaporisation/resuspension phase with boric acid in Ar/H₂ by comparison to 53 mg/m³ for the revaporisation/resuspension phase in Ar/H₂). Besides, the amount of gaseous iodine trapped in solution downstream the TGT was higher during the CsI-2_Re than during CsI-1_Re.

3 CONCLUSIONS

Having become especially topical nowadays, the delayed fission products reemission from the RCS surface deposits are an important subject of investigation, not only for the decommissioning of Fukushima Dai-Ichi (1F) Nuclear Power Station accident but also performing Probabilistic Safety Analysis (PSA). For instance, the OECD/NEA project, denominated Experiments on Source Term for delayed Releases (ESTER) and following on from Source Term Evaluation and Mitigation (STEM2), is aiming to conduct experiments on

source term evaluation in case of a severe accident, in specialised facilities, to focus on the evaluation of delayed source terms.

The work initiated in this study deepened the research on possible late release of gaseous iodine from caesium iodide deposits in the RCS.

The preliminary results would tend to indicate that an interaction between caesium iodide deposited or/and condensed and deposited boric acid is possible in the studied conditions.

Further experiments are required in order to confirm the late release of iodine due to reactions from the deposits in the RCS or in the upper structure of the reactor vessel. First, experiments need to be repeated in order to verify the results. Secondly, the amount of deposited and condensed material should be assessed.

ACKNOWLEDGMENTS

This work was supported by the Finnish Research Programme on Nuclear Power Plant (SAFIR2022).

REFERENCES

- [1] M. Gouëlle, J. Hokkinen, T. Kärkelä, A. Auvinen, A Scoping Study of Chemical Behaviour of Caesium Iodide in Presence of Boron in Condensed Phase (650 °C and 400 °C) under Primary Circuit Conditions, *Nuclear Technology* 203 (2018) 66–84. doi:<https://doi.org/10.1080/00295450.2018.1429111>.
- [2] M. Gouëlle, J. Hokkinen, E. Suzuki, N. Horiguchi, F. Cousin, M. Barrachin, Interaction between Caesium Iodide Particles and Gaseous Boric Acid in Flowing System through a Thermal Gradient Tube (1030 K to 450 K) and Analysis with ASTEC/SOPHAEROS, *Progress in Nuclear Energy* 138 (2021) 103818. <https://doi.org/10.1016/j.pnucene.2021.103818>
- [3] N. Girault, F. Payot, Insights into Iodine Behaviour and Speciation in the Phébus Primary Circuit, *Annals of Nuclear Energy* 61 (2013) 143–156. doi:10.1016/j.anucene.2013.03.038.
- [4] B.R. Sehgal, Accomplishments and Challenges of the Severe Accident Research, *Nuclear Engineering and Design* 210 (2001) 79–94. doi:10.1016/S0029-5493(01)00433-2.