



Experimental Study of the [B, Cs, I, O, H] and [Mo, Cs, I, O, H] Systems in the Primary Circuit of a Pwr in Conditions Representative of a Severe Accident

Anne-Cécile Gregoire

Institut de Radioprotection et de Sécurité Nucléaire (IRSN)

PSN-RES/SEREX/L2EC

Cadarache, Saint Paul-lez-Durance

13115, France

anne-cecile.gregoire@irsn.fr

Hervé Mutelle

hervé.mutelle@irsn.fr

ABSTRACT

One important issue in the evaluation of the radiological consequences of a severe nuclear accident is the determination of the amount of radioactive iodine in the environment, released from the damaged reactor core and transported through the reactor primary coolant system. IRSN has launched an experimental program to study the kinetic of the chemical reactions that take place in the circuits, as some of these reactions are supposed to lead to the existence of iodine under gaseous form, which has a great potential to be released in the environment. This program consists of tests performed in a horizontal line simulating the primary circuit with representative thermal hydraulic conditions and a simultaneous injection of gaseous iodine and several elements simulating the volatile fission products (Cs, Mo) and/or the control rod material (Ag, In, Cd, B) and/or the structure material released during the reactor core meltdown.

The results of two tests will be presented and discussed here. The first test studies the persistence of gaseous iodine at the circuit outlet in presence of caesium and boron in excess relative to iodine. The second test concerns the influence of molybdenum on the persistence of gaseous iodine – still in presence of a large excess of caesium compared to iodine.

1 INTRODUCTION

In case of an accident with fuel meltdown, iodine release in the environment is a crucial nuclear safety issue. Iodine, due to its high volatility can be completely released from the reactor vessel and transported by carrier gas through the reactor coolant system (RCS) to reach the containment. With the present models implemented in severe accident simulation codes like the SOPHAEROS module of the integral ASTEC code [1], the iodine behaviour in the RCS is not satisfactorily simulated because it is not possible to predict with accuracy the fraction of iodine in gaseous form which can be released in the containment. There is also uncertainty on iodine speciation at the outlet of the RCS, which can influence subsequently the amount of volatile iodine inside the containment.

Based on PHEBUS-FP experiments, the presence of early gaseous iodine in the containment can be attributed on pre-existing gaseous iodine in the primary circuit [2]. CsI is not the only iodine condensable species formed in the primary circuit as usually assumed in

the past. It is worth noticing that iodine speciation predicted at the break by thermodynamic computations can change, according to remaining uncertainties on available thermodynamic data. Besides, under these conditions, kinetic limitation of reactions can also occur, but very few kinetic data are available in the literature [3].

In order to develop and validate models relative to FP behaviour in the primary circuit, CHIP experimental program (Chemistry Iodine Primary Circuit) was launched to obtain more information on iodine speciation in different boundary conditions and so to derive/validate thermo-kinetic models from experimental results. It consists of tests performed in a horizontal line simulating the primary circuit with representative thermal hydraulic conditions and a simultaneous injection of gaseous iodine and several elements simulating the volatile fission products (Cs, Mo) and/or the control rod materials (Ag, In, Cd, B) and/or the structure material released during the reactor core meltdown. Experimental challenges are the detection and the quantification of gaseous forms of iodine at the circuit exit as a function of the parameters involved in chemical reactions: residence time, temperature gradient, composition of the carrier gas ($\text{H}_2\text{O}/\text{H}_2/\text{Ar}$), nature and concentration of injected elements.

A first series of tests was performed on a small-scale test loop with the concomitant injection of I_2 and CsOH vapours in conditions representative of a RCS in a severe accident (steam, strong temperature gradient from 1600°C - 150°C and residence time of 8 s). The reactants were mixed together in the high temperature zone with a low excess of Cs relative to I (Cs/I molar ratio ~ 2 -3). No gaseous iodine could be evidenced in the 150°C temperature zone (representative of a cold leg break), as expected from thermodynamic computations-iodine being exclusively released as CsI. It was thus decided to study more complex systems involving one or two additional elements to the initial [Cs, I, O, H] system. The aim is to identify the systems leading to the persistence of significant gaseous iodine fraction at the break. Boron and molybdenum are known to react with caesium to form respectively stable caesium borates [4] and caesium molybdates [5] in the temperature range prevailing in the RCS. They could thus act as caesium sinks and enhance the release of gaseous iodine species. Two tests were performed in the CHIP Phenomenological Line (CHIP PL), the first one involving the [B, Cs, I, O, H] system and the second one the [Mo, Cs, I, O, H] system.

2 EXPERIMENTAL

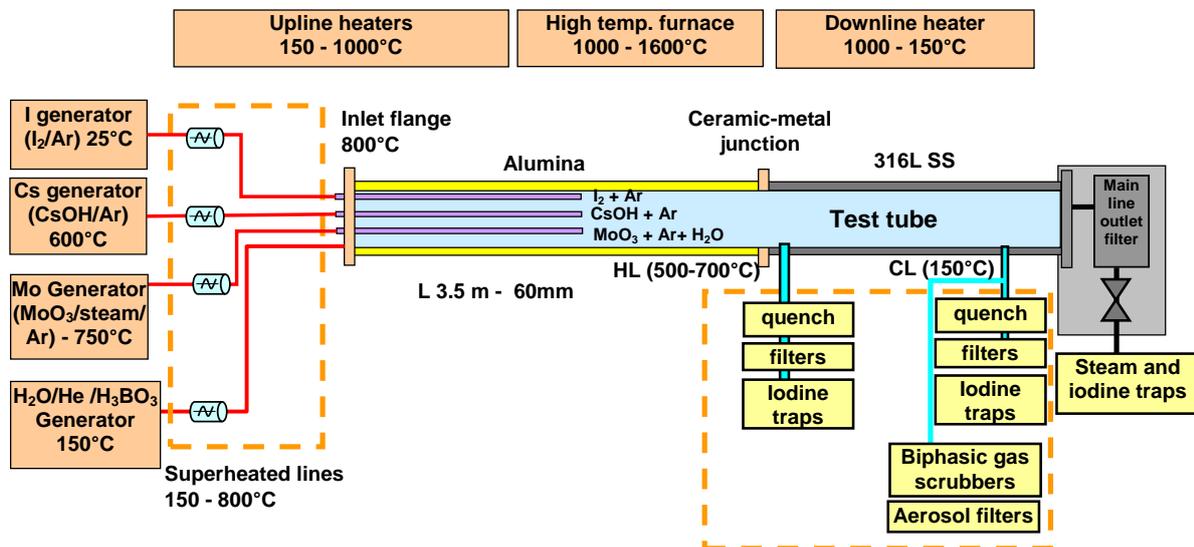
The CHIP Phenomenological Line has been designed as an open system with a continuous flow of reagents. The chemical elements including the carrier gas ($\text{H}_2/\text{H}_2\text{O}/\text{inert}$ gas) are heated at 1600°C in a High Temperature (HT) zone. At this temperature, all the species are supposed to be under gaseous form at thermodynamic equilibrium. Downstream, the fluid is cooled down in the so-called “transport zone” where chemical reactions take place producing aerosols and gases. The transport zone must be representative of the material of the RCS. Particles and gases are then collected and separated before being analysed by offline chemical techniques. The main parameters that define one test are:

- the molar flow rate or the concentration of the elements injected in the loop;
- the residence time of the flow and the thermal profile of the fluid in the transport zone;
- the composition of the carrier gas (mixture of steam/He or steam/He/ H_2).

2.1 CHIP Phenomenological Line – description of the test loop

The test loop is composed by a straight line 3.5 m long and 62.7 mm in internal diameter, composed of only two tubes assembled by a specific junction (see figure 1). The central tube located in the high temperature zone is made of alumina (2 m) and the

downstream tube located in the transport zone is made of stainless steel (1.5 m) to be representative of the RCS. The thermal profile along the test loop is obtained by means of a high temperature oven located at the centre of the test loop and of heated sections upline and downline.



Caesium injection: vaporization of dehydrated CsOH at 600°C under a low argon flow in an external generator – caesium injection directly in the high temperature zone

Molybdenum injection: vaporization of MoO₃ powder at 750°C under a steam/argon flow in an external generator – molybdenum injection directly in the high temperature zone

Main line Outlet Filter: Quartz – porosity 0.9 μm – length 145 mm, thickness ~3 mm

Figure 1: Principle of the CHIP PL test loop - general design

Boron is delivered by a steam generator producing either a mixture of steam/carrier gas or a mixture of steam/H₃BO₃/carrier gas by vaporization of a boric acid aqueous solution. Gaseous iodine is obtained by sublimation of molecular iodine pellets. Caesium vapours are produced by vaporization of dehydrated caesium hydroxide placed in an external generator. Temperatures in the range 550-650°C are necessary to generate significant amounts of CsOH vapours. Molybdenum vapours are also generated in an external generator by vaporization of molybdenum trioxide. Due to the low volatility of MoO₃, heating up to 750°C in presence of steam was necessary to get a significant molybdenum vapour flow rate.

The steam/carrier gas or steam/H₃BO₃/carrier gas mixture is directly fed up at the inlet of the high temperature alumina tube. The other reagents are transported in a low argon flow up to the high temperature zone where they are mixed together. They are transported in separate heated lines (C22 alloy tube for CsOH/Ar and MoO₃/steam/Ar flow and alumina coated SS tube for I₂/Ar flow) extended beyond the inlet flange by separate alumina nozzles.

The outlet of the main tube is equipped with an integral quartz aerosol filter. The pressure in the CHIP line is regulated by the means of a control valve located downstream the main filter. The main outlet filter is completed by two gas scrubbers filled with a sodium hydroxide solution (1 M) in order to trap the gaseous iodine species.

2.2 The Sampling Lines

Two sampling lines have been implemented on the test loop: the Hot Leg sampling line (HL) devoted to fluid sampling at the inlet of the downstream tube at 500-700°C and corresponding to hot leg break conditions and the Cold Leg sampling line (CL) devoted to fluid sampling in the 150°C temperature zone of the downstream tube and corresponding to cold leg break

conditions. These two lines are composed of an iso-kinetic sampling probe implemented in the main line¹ followed by a dilution system² (figure 2). Downstream, they are divided into an integral line where the flow is directed all the time when the corresponding sampling line is operated and a sequential line that can be operated for a given duration (15 minutes) and provided with three membrane filters. Each line is then terminated by gas scrubbers filled with a diluted alkaline solution (0.1M NaOH) to trap gaseous iodine species. The flow rates in the integral and the sequential lines are set by critical orifices so that the sampled fraction of main flow is 8% in the integral line and 2% in the sequential line.

An additional organic line (CL-OL) was implemented as a branch of the Cold Leg sampling line, directly after the isokinetic probe. It can be operated independently by means of isolation valves. It is composed of two biphasic gas scrubbers in series dedicated to the separation of gaseous molecular iodine (trapped in the organic phase - toluene) from the other iodinated gaseous species and aerosols transported in the flow (trapped in the aqueous phase - diluted nitric acid solution). The final integral filter is dedicated to trap the remaining aerosols. This line has been developed to enhance the separation efficiency between gaseous molecular iodine and aerosols, especially in presence of reactive aerosols such as CsOH [1]. Given the low sensitivity of molecular iodine detection in toluene (Ultra Violet-visible absorption spectroscopy at 309 and 498 nm), this line has been designed to collect about 10% of the main fluid flow and must be operated for at least ½ hour.

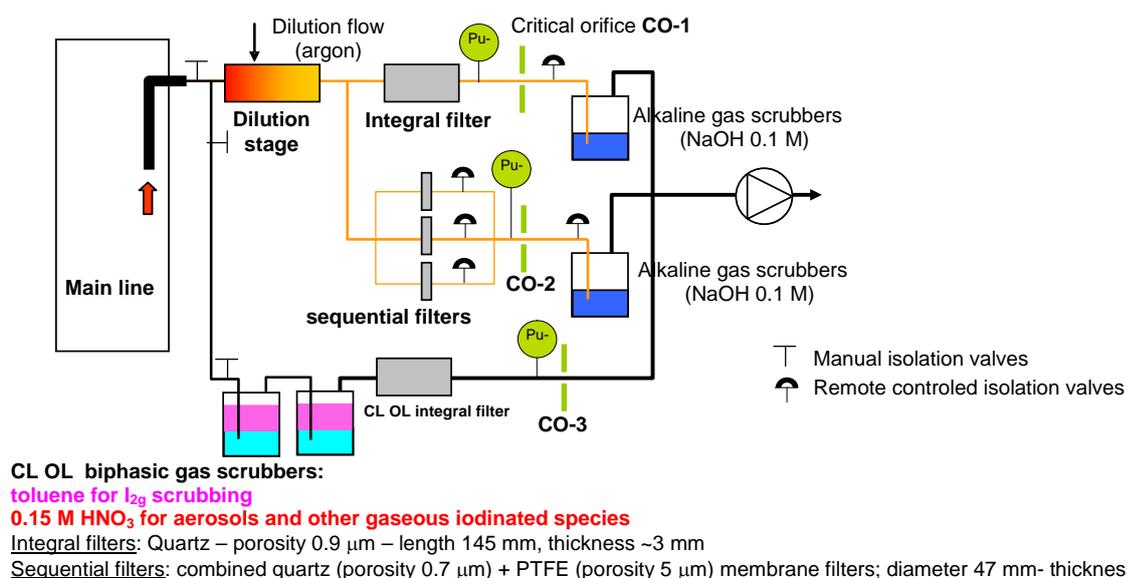


Figure 2: Scheme of the CL sampling line including the CL-OL line

To avoid steam condensation, the whole sampling system is heated at 150°C from the isokinetic sampling down to the gas condensation stages.

¹ The sampling probes are j-shaped pipes pointing upstream designed to sample about 5 to 10% of the flow from the CHIP line. The sampling is considered as iso-kinetic in the full range of the main line working conditions.

² The aim of the dilution stage is to quench all aerosol and gaseous dynamics (nucleation, coagulation...) and chemistry to obtain as much as possible a representative measurement. In the cold leg, the dilution is performed by injecting argon heated at 150°C through the wall of a porous tube. To avoid steam condensation, the lines are then heated at 150°C up to the gas scrubber stage.

2.3 Test Conduct and post test operations

The whole test loop is slowly heated (~24 h) in order to match the required thermal hydraulic boundary conditions, both in the main line and in the upstream injection zone including the external Cs and Mo-generators³ and the transport lines (overheated by ~50°C to avoid vapour condensation) up to the inlet flange (see table 1). During this transition period, the outlet of the main line is by-passed into specific steam traps and the sampling lines are kept closed to avoid possible pollution.

As soon as the desired thermal hydraulic conditions have been obtained, the outlet of the main line is connected to the iodine traps and the different elements are injected in the main line: the iodine generator is connected to the main line and the carrier gas flows in the Cs and Mo-generators are set to their nominal values. Concomitant element injection lasts up to 6-7 hours, so that each sampling line can be operated successively. The test ends by stopping the reagent injection (the iodine generator is by-passed, boron injection can be stopped by switching to pure steam injection and the CsOH and MoO₃ injection are stopped by setting the carrier gas flow in the external generators to its lowest level) and by cooling down the whole test loop for 12 hours under a low argon flow (2 Nl/min).

After the test, the facility is dismantled and each part is leached to be able to establish a reliable element distribution from the high temperature mixing zone down to the outlet gas scrubbers. As iodine can only be stabilised in alkaline media, the leaching is performed with diluted NaOH. Caesium and boron species are also quantitatively recovered by these operations but molybdenum oxides are only partly recovered. The solutions are then analysed by ICP MS (Inductively Coupled Plasma – Mass Spectrometry) for elemental quantification. A selection of samplings (sequential filters and aerosols deposits in the main line) is preserved for aerosol characterisation (determination of morphology, composition and speciation).

3 RESULTS AND DISCUSSION

A first test was performed in the CHIP phenomenological line with simultaneous injection of iodine, caesium and boron (PL_BC*s*I_1 test). A second test was performed, with molybdenum injection (as MoO₃) instead of boron injection (PL_MoCsI_1 test). This second test completes also the series of tests performed on a small-scale test loop with concomitant injection of CsI and MoO₃ that highlights high gaseous iodine fraction [6].

These two tests were performed with similar thermal hydraulic conditions and carrier gas composition (mixture of steam/helium). To be representative of a reactor case, low element concentrations were achieved in the high temperature zone, caesium (as CsOH) was injected in excess relative to iodine (as I₂) and boron, respectively molybdenum, were injected in excess relative to caesium.

3.1 Thermal hydraulic test boundary conditions

The thermal hydraulic boundary conditions of the PL_BC*s*I-1 and PL_MoCsI-1 tests are reported in table 1. They were chosen so as to promote kinetic limitations, if any, with high thermal gradient and very short residence time between the high temperature zone and the main line outlet.

³ During this preheating phase, the Cs and Mo-generators are continuously swept by a very low argon flow (0.05 Nl/min). The CsOH in the Cs-generator is firstly dehydrated for 12 hours at 180°C and then melted at 350°C for one hour before the heating up to the vaporisation temperature.

Table 1: Thermal Hydraulic conditions of the PL_MoCsI and PL_BCsl tests

Main test loop:	Test boundary conditions (main phase)
H ₂ O mass flow rate	$2.2 \cdot 10^{-4}$ kg/s (800 g/h, 16.6 NL/min)
He mass flow rate	$4.5 \cdot 10^{-5}$ kg/s (15.125 NL/min)
Ar mass flow rate (external generator)	$4.6 \cdot 10^{-5}$ kg/s (PL_BCsl_1 test) to $5.2 \cdot 10^{-5}$ kg/s (PL_MoCsI_1 test)
Steam volumetric fraction	~50%
HT zone to outlet filter temperature profile	High temperature drop from 1600°C down to 150°C
Residence time from HT zone to outlet	11-12 s
Pressure (Pa)	$2 \cdot 10^5$
Element injection:	Test boundary conditions (main phase)
Iodine Generator	T: 25°C, carrier gas : Ar 0.55 NL/min , P : $2.7 \cdot 10^5$ Pa
Boron injection (PL_BCsl_1 test only)	Main Steam generator, H ₃ BO ₃ concentration 2 g/L
Cs-Generator	T: 600°C, carrier gas : Ar 1 NL/min, P : $2 \cdot 10^5$ Pa
Mo-Generator (PL_MoCsI_1 test only)	T : 750°C, carrier gas : Ar/steam 0.2 NL/min/0.8 NL/min , P: 10^5 Pa

3.2 Main results of the PL_BCsl_1 test

The injected flow rates were close to the test specification for each element; in the high temperature zone, the following concentrations could be achieved: $9.4 \cdot 10^{-8}$ mol/L for I, $2.2 \cdot 10^{-7}$ mol/L for Cs and $4.1 \cdot 10^{-6}$ mol/L for B, with a low Cs/I molar ratio (2.3) and a high B/Cs ratio (19). The element distribution in the test loop is reported in figure 3.

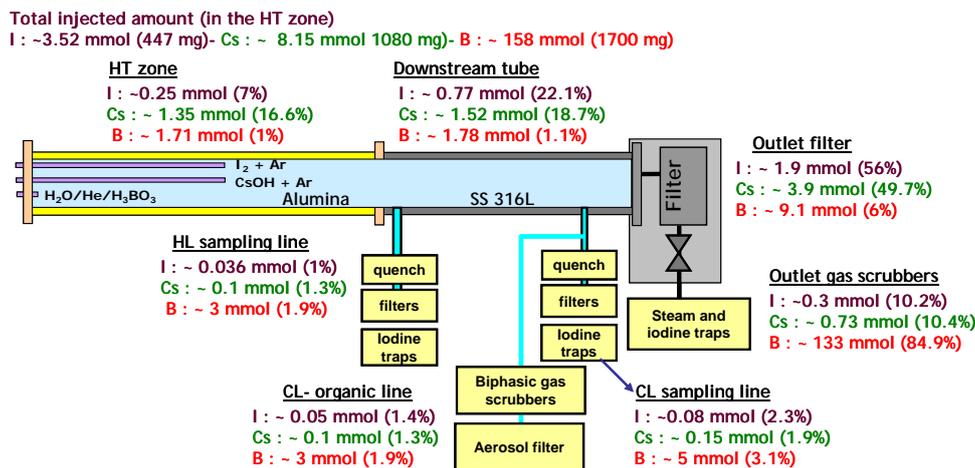


Figure 3: PL_BCsl_1 test – I, Cs and B distribution in the CHIP PL (HT zone to outlet)

The accumulation of Cs in the main outlet gas scrubbers is due to a failure of the main line outlet filter during the test. As a consequence no reliable data on gaseous iodine accumulation can be inferred from these gas scrubbers, as material accumulation accounts for both gases and aerosols. On the contrary the filters of the sampling lines worked as expected. Boron accumulation in the gas condensation stage indicates that, at 150°C, a large fraction of boron is still transported as gaseous species (possibly as a trimer of metaboric acid [7]). A low fraction of gaseous iodine could be unambiguously identified both in the Hot Leg sampling line (0.8% - referring to the total iodine mass collected in the filter stage and the outlet gas scrubbers), in the Cold Leg sampling line (0.45%) and in the organic line (1.4%, only gaseous molecular iodine as other gaseous iodine species cannot be distinguished from the aerosols trapped in the aqueous phase).

3.3 Main results of the PL_MoCsI_1 test

As for the PL_BCsl_1, the element injection was close to the test specification for iodine and caesium; as the molybdenum oxide deposits were not completely recovered by the

leaching operations, the experimental mass distribution in the CHIP PL test loop can be considered as a lower bound. The following concentrations could be achieved in the high temperature zone: $6.3 \cdot 10^{-8}$ mol/L for I, $2.1 \cdot 10^{-7}$ mol/L for Cs and a minimal value of $4.1 \cdot 10^{-7}$ mol/L for Mo, with a low Cs/I molar ratio (3.3) and a minimal Mo/Cs ratio (>2). The element distribution in the test loop is reported in figure 4.

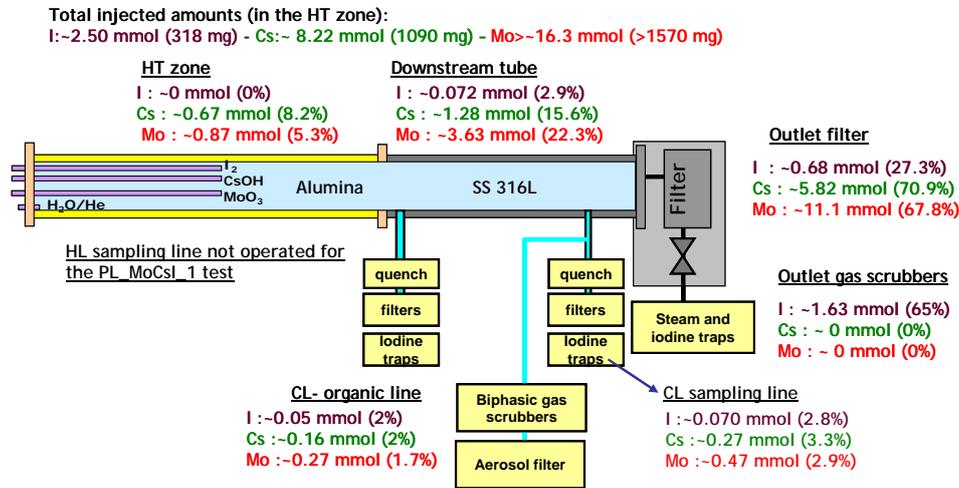


Figure 4: PL_MoCsI_1 test – I, Cs and Mo distribution in the CHIP PL (HT zone to outlet) -

A significant gaseous iodine fraction could be evidenced both at the outlet of the main line (70% - referring to the total iodine mass collected in the filter stage and the outlet gas scrubbers), at the outlet of the cold leg sampling line (57% for the integral line and 56% for the sequential line) and in the organic line (40%, molecular iodine). Though of the same order of magnitude, the gaseous iodine fraction determined in the sampling lines is lower than in the main line outlet. This feature can be due to gaseous iodine retention in the transfer lines (made of stainless steel tubing for some sections) and on the filtering media themselves⁴. For the organic line, dedicated to the detection of molecular iodine only, the difference may be also explained by the presence of a significant fraction of the gaseous iodinated species as HOI or HI (soluble in aqueous media as most of the generated aerosols) which could not be evidenced with this line configuration. A tentative repartition between molecular iodine and other gaseous iodinated species of about 60-70/40-30 can be proposed based on these results.

The characterisation of aerosols collected at 150°C (Micro Raman and X-ray Photoelectron Spectroscopy) indicates the presence of caesium molybdates ($\text{Cs}_2\text{Mo}_2\text{O}_7$, $\text{Cs}_2\text{Mo}_3\text{O}_{10}$ and possibly $\text{Cs}_2\text{Mo}_5\text{O}_{13}$), molybdenum oxides (MoO_3 , $3\text{H}_2\text{O}$) and caesium iodide particles, as already observed in similar tests with concomitant CsI and MoO_3 injection [6].

3.4 Discussion/Conclusion

These results show that in our conditions, molybdenum acts as a stronger “caesium sink” than boron. With a low excess of Mo relative to Cs, up to 70% of I is released as gaseous species. On the contrary, the large excess of B leads to the release of only ~1% of gaseous iodine. Molecular iodine has been identified as the main species, but the existence of other gaseous species (HI, HOI) can not be excluded.

The weak influence of B on gaseous iodine persistence at the cold leg break was also observed during the Phébus FPT2 test, performed with a boric acid injection in excess relative

⁴ A higher gaseous iodine retention (representing 30% of injected gaseous molecular iodine) was already observed on the integral filter stage of the samplings lines compared to the main outlet filter device (less than 20%). It is owed to a longer residence time.

to Cs ($B/Cs \sim 14$), though the release of Ag and Cd^5 may also contribute to a strong lowering of gaseous iodine at the circuit cold leg break [3]. It seems that only very large release of boron ($B \gg Cs$) may lead to a significant gaseous iodine fraction at the cold leg break – for instance during the degradation of a B_4C control rod as in the Phébus FPT3 test [3]. Concerning the role of Mo, the results are consistent with those obtained on the small-scale GAEC test loop [6].

Further work with the [Mo, Cs, I, O, H] system will focus on the influence of the carrier gas composition (mixture of steam and hydrogen) on the gaseous iodine fraction and speciation. The determination of the deposits and aerosol composition as a function of the temperature will be also an important issue. The study of the [B, Cs, I, O, H] system is currently progressing in the GAEC test loop, with a concomitant CsI and boric acid injection in the presence of steam.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the partners of the International Source Term Program (Electricité de France, the Commissariat à l’Energie Atomique, the Commission of the European Communities, the US Nuclear Regulatory Commission, the Atomic Energy of Canada Limited, Suez-Tractebel and the Paul Scherrer Institute).

REFERENCES

- [1] F. Cousin *et al.*, “New capabilities of simulating fission product transport in circuits with ASTEC/SOPHAEROS”, Nucl. Eng. Des., 238, 2008, pp-2460-2438.
- [2] N. Girault *et al.*, “Towards a better understanding of iodine chemistry in RCS of nuclear reactors” Nucl. Eng. Des., 239, 2009, pp-2162-2170.
- [3] L. Cantrel *et al.*, “Reaction Kinetics of a fission product mixture in a carrier gas in the Phébus Primary Circuit”, Nucl. Technol., 144, 2003, pp 1-15.
- [4] B., R. Bowsher and S. Dickinson, The interaction of caesium iodide with boric acid vapour phase and condensed phase reactions, Atomic Energy Establishment of Winfrith, 1986, Unclassified Report AEEW-2102.
- [5] J. McFarlane *et al.* “Chemical speciation of Iodine Source Term to Containment”, Nucl. Technol., 183, 2002, p162
- [6] M. Gouello *et al.*, “Chemistry of iodine and aerosol composition in the primary circuit of a nuclear power plant”, Proc. 21st Int. Conf. Nuclear Energy for New Europe , Ljubljana, Slovenia, September 5-7, Nuclear Society of Slovenia, 2012, paper 509.
- [7] S.Wery *et al.*, “Etude thermodynamique des systèmes BHO et BSi-HO : modélisation de la vaporisation de B_2O_3 ” Proc. Matériaux 2006, Dijon, France, 13-17 November.

⁵ Test performed with a Silver-Indium-Cadmium control rod in the test bundle.