

Source Term Issues, S4-5**Towards a better understanding of iodine chemistry in RCS of nuclear reactors**N. Girault¹, C. Fiche¹, A. Bujan², J. Dienstbier³

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Summary

Phebus FP tests provided new insights into iodine transport through the primary circuit. Indeed, in these tests transported iodine was often found not associated with caesium as generally postulated up to now. Several iodine species were experimentally shown to have circulated in the hot leg at 700°C, while a fraction was also suspected to be in a gaseous form in the cold leg at 150°C. For a better estimate of the iodine source term in the containment, both in terms of speciation and quantity, it becomes thus necessary to reconsider iodine species behaviour along their pathway in the reactor coolant system (RCS).

This paper presents a current understanding, mainly based on SOPHAEROS equilibrium chemistry calculations of Phebus FP tests performed within the I-RCS SARNET circle. The suspected connection existing between Cs, Mo, Cd and I chemistry and the strong influence of both their release kinetics and related species thermodynamic properties on the iodine speciation in different environments (reducing/oxidizing) are highlighted. Potential explanations for the predicted iodine volatility and the level of association of I to Cs are also discussed in the present paper.

A. INTRODUCTION

The main objective of the I-RCS SARNET circle is to predict the iodine behaviour in a Reactor Cooling System (RCS) under severe accident transient conditions. This objective can be reached only with a step-wise process, and the first step is to explain the iodine behaviour in Phebus FP tests by its speciation in the RCS and the speciation of elements that could directly or indirectly influence it. Iodine was indeed found to be very important as it was the only element, except for noble gases, observed in the Phebus FP tests in a gaseous form in the containment. There is an indication that the largest part in FPT-3 and some other fraction in the other tests came as volatile iodine already from the circuit.

The present work on Phebus tests mainly concerns analysis of the iodine experimental results in the primary circuit in terms of iodine retention, gaseous iodine fraction and iodine vapour speciation. The primary circuit in Phebus tests is characterised by gas temperatures reaching nearly 1600°C at its entrance and cooling down to 150°C at its outlet, just before entering into the containment. The main phenomena arising in the RCS are chemical transformation of vapours, vapour condensation on structures as well as nucleation into aerosols or onto aerosols, aerosol agglomeration and deposition due to thermophoresis.

Source Term Issues, S4-5**B. EARLIER WORK**

Earlier work was essentially based on applications of a standard FP transport code, SOPHAEROS. These calculations could reproduce some important aspects of the first two Phebus tests, FPT-0 and FPT-1 (principally vapour/aerosol behaviour and total retention in the primary circuit (Ref.[1])). Nevertheless, significant disagreements with experimental results were identified as for example for the FP deposition in the vertical hot leg or in the steam generator. The most likely explanations for these latter disagreements were put forward. Underestimation of fission product in the vertical line inlet was shown to be both accounted for by the effect of simultaneously developing flows (because in this region flows are neither developed thermally nor hydro-dynamically) and for the non-uniform geometry at the bundle exit. Others topics that were also earlier investigated, such as iodine vapour phase chemistry and gaseous iodine formation are discussed later in the present paper.

C. CURRENT PROGRAMME

The most striking experimental finding in all Phebus tests, not anticipated by thermodynamic pre-calculations, was that significant fractions of the transported iodine remained in gaseous form (i.e. did not condense at 150°C). That was why, in the continuation of earlier work (Ref.[1]), analyses were performed with an updated version of the transport code SOPHAEROS developed by IRSN as part of the IRSN-GRS integral code ASTEC (Ref.[2]). This fission product transport code, which models a variety of vapour and aerosol phenomena, assumes chemical reactions only among gases. Besides, equilibrium chemistry is assumed (the chemical equilibrium being calculated by the species Gibbs free energy), which means that the reaction kinetics are not taken into account. This is correct for reactions much faster than the transport velocity between volumes. All the physical properties and chemical constants used are those included in the Material DataBase (MDB), a part of ASTEC used by SOPHAEROS. This database comprising nearly 800 vapour species stable in steam- or hydrogen rich atmospheres between 450 and 3000 K was built from a systematic assessment of significant species in accident reactor conditions (Ref.[4]).

The four Phebus FP tests in fuel rod geometry were investigated (FPT-0/1/2/3). The iodine vapour speciation was only measured in FPT-2 and FPT-3 tests for which specific sampling devices were used (namely Thermal Gradient Tubes (TGT) and Transitions Lines (TL) connecting, in the hot zone, 700 to 150°C aerosol filters). All input data needed for the calculations were preferentially determined on the basis of experimental reports (Ref.[6,7]), supplemented by the Phebus database. Calculations were performed with a fine nodalisation of the Phebus primary circuit, comprising a virtual volume at high temperature for the initial speciation in the fuel and 20 control volumes downstream (volumes being concentrated in zones of rapid temperature change as at the bundle exit and steam generator entrance). For the TGT and TL a very fine nodalisation was used (40 control volumes for respectively 1 m and 0.45 m long tube). Meanwhile, near to the wall fluid and wall temperatures in the TGT and TL were very precisely calculated by the means of a CFD code. In TL, in which non-stationary conditions prevailed, evolution of these temperatures against time was also calculated.

Finally, along with an exhaustive exploration of known iodine species, non-equilibrium chemistry models are also being investigated (Ref.[3]), but this work will not be described in this paper.

Source Term Issues, S4-5**D. MAIN ACHIEVEMENTS**

In Phebus FP tests, most elements are expected to be released in vapour form from the fuel, given the high temperature in the fuel bundle. SOPHAEROS indicates that this is also the case for their compounds. Nevertheless, some of them start condensing on aerosol already in the bundle and many more in the upper plenum just above it. As the gas temperature drops in the upper plenum and reaches finally about 700°C in the hot leg, most species change from vapour to aerosol, mostly due to heterogeneous nucleation on pre-existing particles as mentioned also in Ref.[1].

D.1. Vapour phase chemistry predicted in RCS

All Phebus FP test results support the idea, found also in most SOPHAEROS FPT-1 and FPT-2 calculations (Ref.[1,5,9]) that one of the main caesium species in the primary circuit at 700°C is caesium molybdate, Cs_2MoO_4 . The source of Mo (mainly as a fission product) comparing to Cs was indeed so large during FPT-1 and in the period after 15000 s, also during FPT-2, that there must be other Mo species not containing Cs. The SOPHAEROS calculations indicate that these species are mostly molybdic acid, H_2MoO_4 , and hydrated molybdenum oxide, HMoO_2 . Besides Mo, other important “consumers” of Cs have been found namely Re (from thermocouples) and B (from boric acid in FPT-2/3 and B_4C control rod in FPT-3), by respectively forming CsReO_4 and CsBO_2 (especially the case in FPT-3). Other potential Cs traps in the calculations are structural Cr (behaving similarly to Mo) and impurities, if considered (e.g. Si). Nevertheless, part of Cs is also calculated to leave the bundle as CsOH or its dimer and even some as Cs^+ . For FPT-0 (in which trace-irradiated fuel was used), due to about two orders of magnitude smaller Cs source, almost no Cs_2MoO_4 is calculated. Note that Rb behaviour is predicted to be quite similar to that of Cs except that, from experimental measurements, Rb seems to be released in smaller quantities than Cs.

At high temperature, large part of iodine remained in elemental form and changed to hydrogen iodide, HI, in the upper plenum with only a small part reacting to form metal iodides such as CsI, RbI and AgI. Cd was released in large quantities compared to iodine, except in FPT-3, because the source from the control rod is much larger than that of fission product. Cd remained mostly in elemental form in the whole RCS. As the source of iodine is much smaller than that of caesium in all the Phebus tests (except in FPT-0), the amount of CsOH would allow formation of CsI downstream in the circuit through its reaction with HI.

The Cs_2MoO_4 or HMoO_2 change from vapour to aerosol is calculated to happen already in the upper plenum due to their lower vapour saturation pressure (Figure 1). These species are then no more taken into account in the calculations of gas phase speciation and chemistry in the circuit. The main species that are calculated to remain in vapour form in the hot leg are HI, Cd, CdI_2 , CsI, RbI, CsOH and RbOH .

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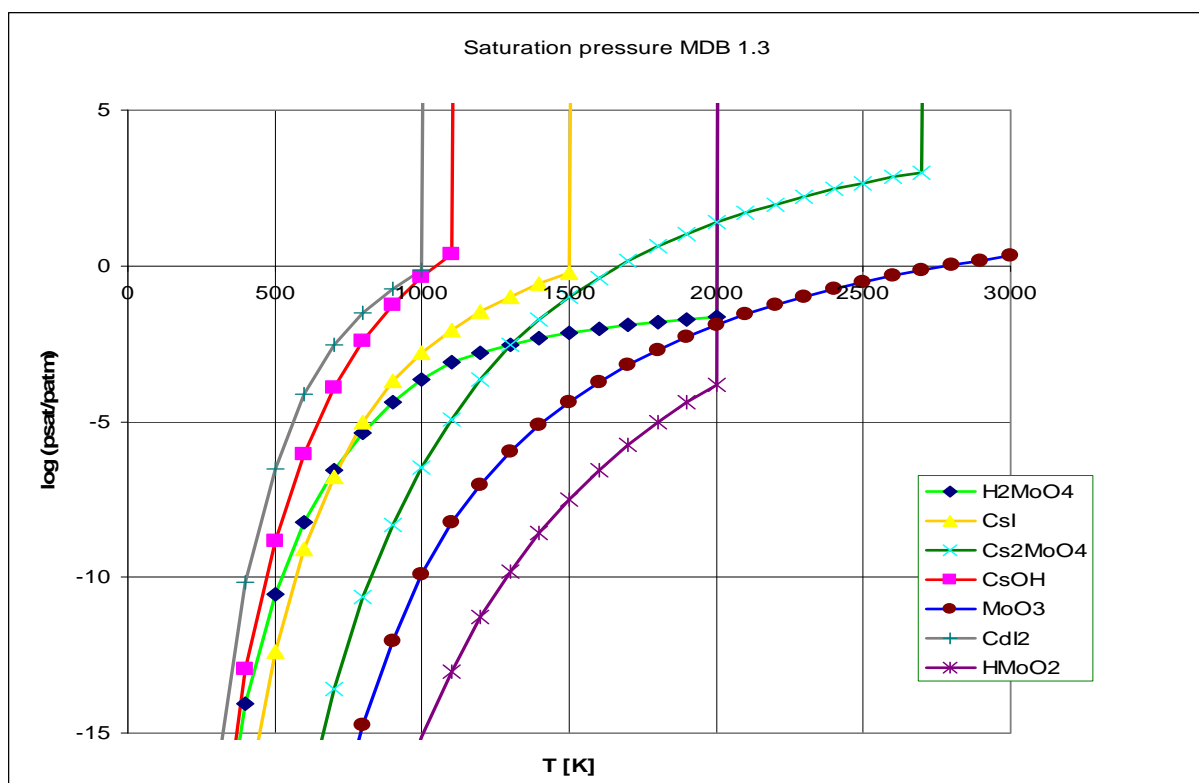


Figure 1 Saturation pressure of analysed species in ASTEC MDB v1.3

Calculations clearly indicated that the key species responsible for the volatile iodine persistence in the primary circuit of Phebus FP tests is H_2MoO_4 because a non-negligible part of it remains as vapour, according to its remarkably flat saturation pressure curve (Figure 1). Indeed, it was found in FPT-1 calculations (Ref.[9,15]), that H_2MoO_4 consumes a significant part of Cs from CsOH to form Cs_2MoO_4 and almost does not allow CsI formation, leaving thus the larger part of iodine as HI . Then, this HI reacts with other very volatile vapour element, as Cd, to form CdI_2 and to a less extent CdI . In sensitivity calculations which decreases H_2MoO_4 saturation pressure at lower temperature, the Cd vapour cannot compete with CsOH and RbOH , and practically all iodine changes to CsI and RbI (Ref.[9,15]).

From analysis of calculation results and comparison with experimental results, it is thought that either the H_2MoO_4 saturation pressure included in MDB might not have been measured correctly (according to the present MDB, H_2MoO_4 is preferred at high temperature to other relatively volatile species, as MoO_3) or that other Mo species exist in the bundle in reality such as polymolybdates (e.g. $\text{Cs}_2\text{Mo}_2\text{O}_7$) not included in ASTEC v1.3 MDB (Ref.[16,17]). The formation of such species can greatly impact the iodine speciation in the RCS as more Mo can be stored in such species, this involves a decrease in the H_2MoO_4 concentration by several times.

D.1.1. Iodine and Caesium vapour speciation

D.1.1.1. Integrated chemical speciation in RCS in calculations

Integrated chemical speciation in the circuit predicted both in condensed and gaseous phases at the end of Phebus FP test transients by the latest version of the

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SOPHAEROS/ASTEC v1.3 module for iodine and caesium is presented in the following Tables 1 and 2. Note that results for FPT-0 and FPT-1 tests were obtained by re-calculation of the base-case analyses (Ref.[10]) in which cadmium was available during the whole bundle degradation phase. As can be observed from Table 1, transformation of part of the HI to volatile species SnI_4 , SnI_2 and I_2MoO_2 is predicted, but only if no Cd is present.

Table 1 Percentage of the iodine mass released from the bundle chemically bonded in the circuit in a given species as calculated by SOPHAEROS/ASTEC v1.3

	FPT-0	FPT-1	FPT-2 Case A ⁴⁾	FPT-2 Case B ⁴⁾	FPT-3
CdI_2 (CdI)	89.6	77.4	25.6	12.7	-
CsI (Cs_2I_2)	0.04	19.2	72.8	72.7	71.7
RbI (Rb_2I_2) ¹⁾	6.6	-	1	1	1.6
AgI ²⁾	0.7	3	0.3	0.3	-
FeI_2 ³⁾	0.1	-	-	-	-
BaHIO	0.15	0.03	0.05	0.05	0.1
BaI_2	0.02		0.2	0.3	0.4
HI (gas)	2.6	0.025	0.03	2.8	4.3
SnI_2	~ 0	0.01	0.0005	2	3.7
SnI_4	~ 0	0.005	0.0015	5	11.8
I_2MoO_2	~ 0	0.01	0.004	2.9	6.2

¹⁾ Rb was not taken into account in the FPT-1 test analysis.

²⁾ Silver as a structural material is not present in the FPT-3 test.

³⁾ Iron as a structural material was taken into account only in FPT-0 test analysis.

⁴⁾ Cases A and B correspond respectively to assumed non-limited and limited Cd release kinetics

Meanwhile, as observed from Table 2, boron is predicted to act in FPT2/3 as an efficient trap for caesium just as for molybdenum, although not so strong as expected (Ref.[18]).

Table 2 Percentage of the caesium mass released from the bundle chemically bonded in the circuit in a given species as calculated by SOPHAEROS/ASTEC v1.3)

	FPT0	FPT1	FPT2 Case A ²⁾	FPT2 Case B ²⁾	FPT3
CsReO_4	98.3	60.5	20.1	20.1	15
$\text{Cs}_2\text{Si}_4\text{O}_9$ ¹⁾	1.6	-	-	-	-
Cs_2MoO_4	~ 0	29.3	24	24	29.2
BCsO_2 ¹⁾	-	-	23.6	23.6	35
CsOH	0.1	7.9	10.9	11.2	7.2
CsI (Cs_2I_2)	0.01	1.5	6.5	6.4	6.3
Cs-Te	~ 0	0.7	14.8	14.6	7.3

¹⁾ Silicon was considered only in FPT0 analysis and boron only in the FPT2-3 analyses.

²⁾ Speciation of the Cs is nearly the same as for Case A (different Cd release kinetics has negligible influence).

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A more detailed investigation of the iodine vapour speciation has been performed for the FPT-2 test by comparing experimental and calculated iodine condensation profiles in the TGT and TL (Ref.[20]). The impact of oxidizing-reducing conditions and of fission product/structural material release kinetics was especially studied. Species discrimination according to their volatility is expected to be much finer in the TGT where the wall temperature gradient was controlled and was stationary during the sampling. Moreover, there was not any upstream aerosol filter which prevents any chemisorption from occurring. For the transition line, the upstream aerosol filtration was simulated in the calculations by forcing the aerosol deposition in a control volume at their entrance of the transition line. Quite unexpectedly, and in an apparent contradiction with the TGT results, the post-test gamma scanning of the transition lines connecting 700 to 150°C filters only showed deposition of iodine, except in one transition line where iodine was partially found associated with caesium.

D.1.2.1. Iodine vapour speciation during the hydrogen release phase

Two samplings (TGT 701 and LT2) were performed during the main hydrogen release phase. The experimental deposition profiles of iodine and caesium, although disturbed, are very close together, which could be indicative of a binding of these two elements in the RCS. Calculations predict the formation of CsI and its dimer in TGT 701 in agreement with the experimental results. This is also quite consistent with a low Mo release during this phase.

In the second transition line (LT2), caesium was not detected and one single iodine condensation peak was measured corresponding to a condensation temperature increasing from 175 to 375°C throughout the sampling transient (Figure 2). The simulated iodine vapour condensation profile also exhibits one main single peak attributed to CsI corresponding to a condensation temperature in the 210-450 range (Figure 2). Although the two considered samplings (TGT 701 and LT2) were triggered 500 s apart, the Cs, Mo and Te flow rates greatly increase during this period and could be partly responsible for the difference experimentally observed. In particular, CsI species could be prevented in LT2 because of preferential formation of caesium-tellurides under reducing conditions. These latter species known to chemisorb by reaction with Cr could be retained on the upstream aerosol filter in Inconel (Ref.[19]).

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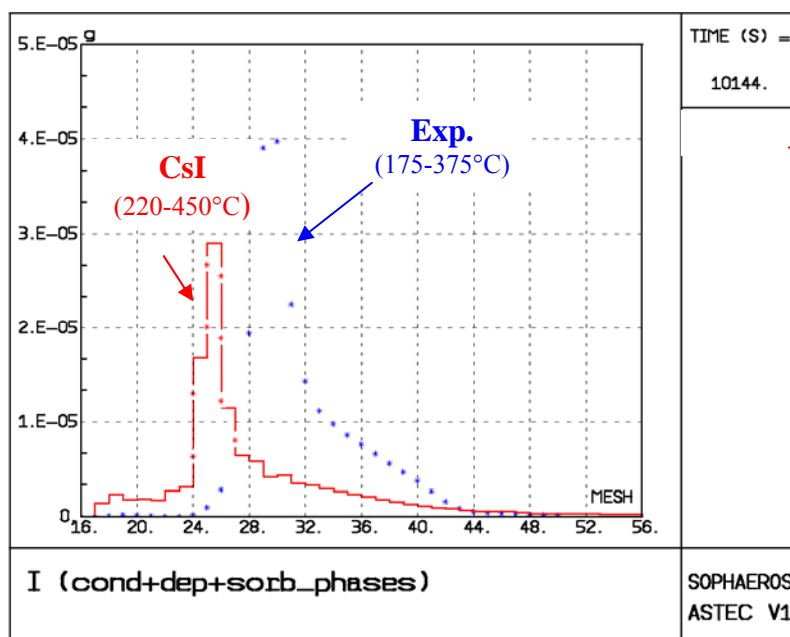


Figure 2 Calculated iodine condensation profile (red curve) in the transition line triggered during the H₂ release phase compared to measurement (blue points)

One reason why caesium-tellurides species are not predicted in samplings performed during the hydrogen release phase by SOPHAEROS could be an overestimation of Cs-Te deposits upstream the samplings. Indeed, SOPHAEROS predicts Cs-Te formation in the gaseous phase but these species chemisorb on the Inconel surface of the vertical line. Another explanation could be the potential formation of complex species of caesium-tellurides of a number of different stoichiometries not included in the ASTEC Material Databank (e.g. Cs₃Te₂, Cs₅Te₄, Cs₂Te₅...). These points are currently under investigation.

D.1.2.2. Iodine vapour speciation during the steam-rich phase

In TGT 702 triggering during the following steam-rich phase, the formation of Cs₂MoO₄ is predicted to become predominant. This is explained by a higher Mo/Cs molar ratio, leaving thus only a little Cs available for CsI formation. While the Cs₂MoO₄ deposited profile by thermophoresis in TGT 702 is consistent with the experimental Mo and Cs measured profiles, the iodine speciation is clearly not well captured by SOPHAEROS (Figure 3). The iodine species that condensed in the middle of this TGT (Figure 3) corresponds to a medium volatility species with a condensation temperature of about 575°C. A concomitant small caesium condensation peak was also observed standing out against the overall deposition profile of caesium aerosols by thermophoresis. When the formation of Cs₂MoO₄ is prevented in the calculations as a sensitivity case, CsI takes precedence resulting in a predicted condensation peak in the middle region of TGT 702 as observed (Figure 4). In this case, nevertheless any highly volatile iodine is predicted to condense at the TGT outlet as measured. This suggests that the formation of Cs₂MoO₄ is probably too much favoured in the calculations to the detriment of CsI because of the too high volatility of H₂MoO₄.

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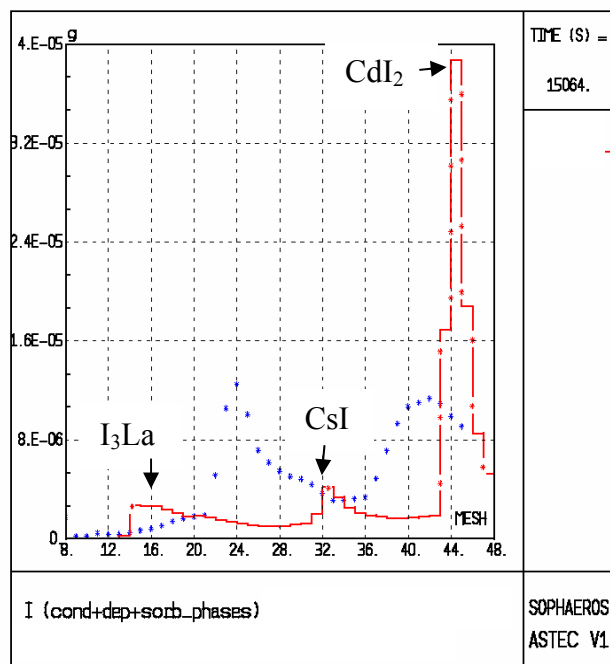


Figure 3 Calculated iodine condensation profile in TGT 702 in red (measured blue points)

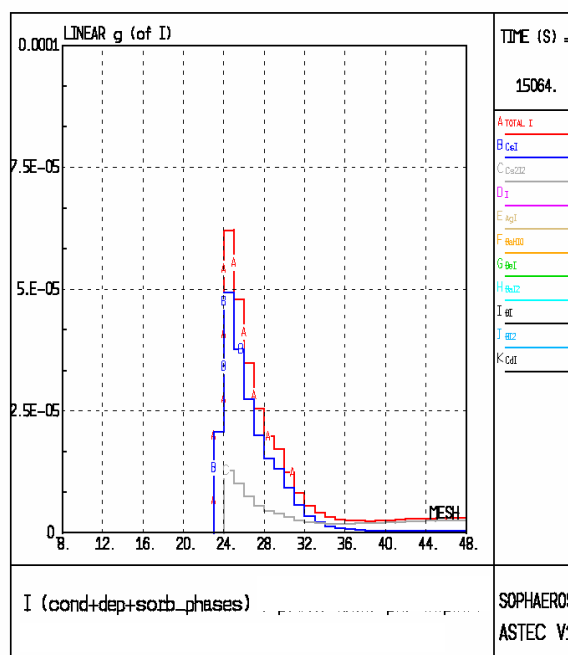


Figure 4 Calculated iodine condensation profile and speciation in TGT 702 with no Cs_2MoO_4

In comparison to TGT 702, the post-test gamma scanning of the third transition line (LT3) was also analysed. These two samplings were indeed triggered during the same steam-rich period, characterised by a relatively small variation in FP release kinetics, but 2000s apart. In this transition line, the experimental iodine vapour condensation profile partially corresponding to caesium profile is an indication that iodine at that time in the primary circuit was partly bounded to Cs. Calculations can partly reproduce this, but CsI formation is predicted to be smaller than measured. The second and third measured iodine peak attributed to an iodine species not bounded to caesium, correspond to condensation temperatures respectively in the range 350-450°C and 150-200°C. While the latter condensation peak attributed in the calculations to CdI_2 condensation could not be observed in the TGT in which the wall temperature at the end is about 200°C, the second condensation peak corresponding to a non-predicted medium volatility iodine species would correspond to the large iodine peak measured at the TGT 702 outlet.

Besides SOPHAEROS calculations, it was attempted to determine the potential iodine species that condensed both in TGT and TL. This was performed by first determining the saturation temperature and pressure corresponding to the measured condensation peaks and then by comparing these data to those included in the SOPHAEROS Material Data Bank. This is an interesting way in analysing the measurements because it can possibly highlight some deviation from equilibrium chemistry. Applying this method for instance to the third transition line (LT3) analysis shows that the measured condensation peak could correspond to iodine species not predicted by equilibrium chemistry calculations (as FeI_2 , InI_3 ...). Work is under progress to establish a list of potential iodine species that would have condensed in the different TGT and transition lines.

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D.2. Iodine behaviour in RCS

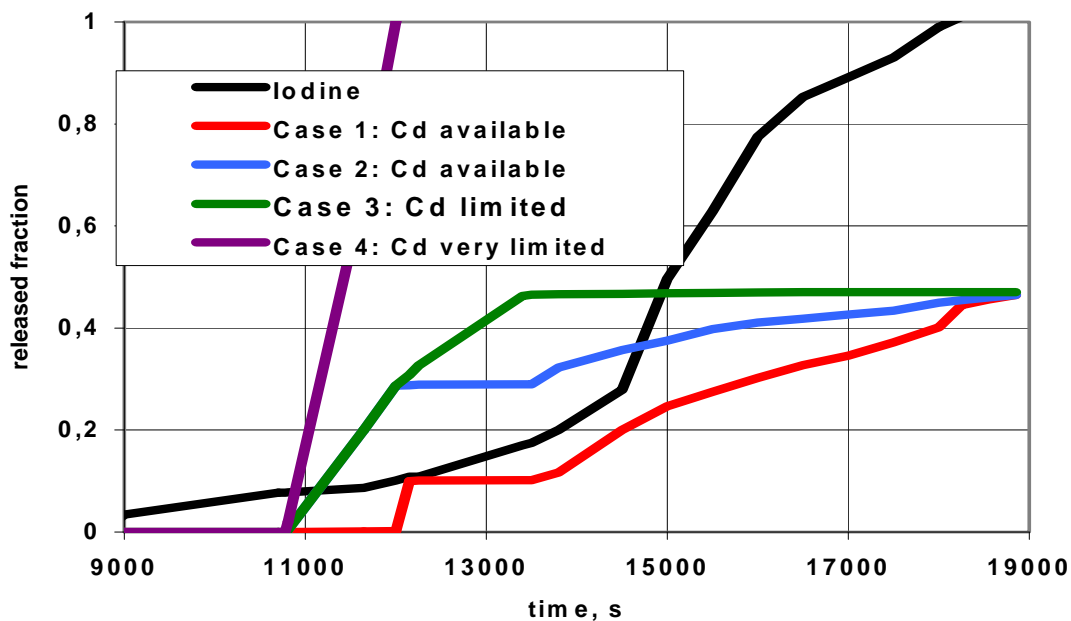
The behaviour of iodine in the circuit and its release into the containment is strongly influenced by its chemical form. Indeed, in the case where it changes mostly to CdI_2 , its retention is very high in the Steam Generator (SG) hot leg. This is due to the fact that the SG wall temperature is only slightly above $150^{\circ}C$ while the gas temperature drops from about $700^{\circ}C$ to $150^{\circ}C$ gradually in the SG hot leg. As CdI_2 is highly volatile (Figure 1), calculations predict that it mostly condenses on the SG tube wall before.

D.2.1. Iodine retention in RCS and volatile fraction at low temperature*D.2.1.1. Iodine retention in RCS*

One problem for iodine is the overestimation of the calculated deposition in the SG tube in all the Phebus FP tests, as compared to experimental data. For example, in FPT-1 base-case calculations, assuming a continuous Cd release throughout the test, a very high iodine retention was predicted (above 60% of the bundle source (Ref.[1,9]), while the measured retention was only about 28% (Ref.[7]).

Deposition in steam generator

The significant impact of Cd release kinetics on iodine retention in SG was studied in former sensitivity analyses (Ref.[1,5]) of the Phebus FPT-0/FPT-1 (Ref.[6,7]) tests (Figures 5 and 6). For these tests indeed, large uncertainties remained in the cadmium release kinetics; Cd being only measured by post-test chemical analysis of few samplings. The impact of different Cd release kinetics on deposition in steam generator was then analysed by assuming that Cd might have been released in several “puffs” (case 3 and 4 in figure 5).



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Figure 5 Cadmium cumulative fractions of initial bundle inventory calculated to be released from the bundle (cases from 1 to 4) during the FPT-0 test as compared to iodine (Ref.[5])

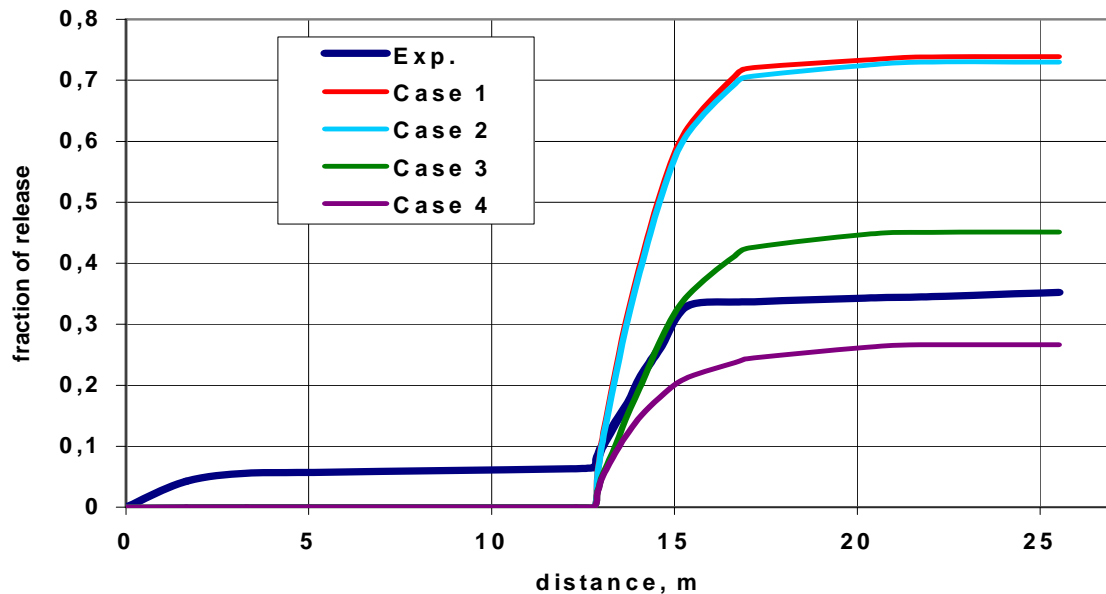


Figure 6 Iodine retention profile along the circuit for FPT-0 test (Ref.[5]) as a function of Cd release kinetics

The FPT-0/1 calculation results show, that if considerably limited or no cadmium release is assumed in the circuit during the significant iodine release from the bundle (Cases 3 and 4, figure 5), a significant fraction of iodine exists as gaseous hydrogen iodide (HI) and consequently calculated deposition of the iodine in the SG pipe is significantly reduced (figure 6) to a value comparable with the measured deposition. In turn, this also leads to a prediction, that more than 30% of iodine released from the bundle reaches the containment as HI (~50% in Case 4), which is not consistent with measured data for FPT-0/FPT-1 (about respectively 2 and 1 %) (Ref. [6,7]).

The broad outlines of the new analyses (Ref.[11]) of the FPT-2/3 tests (Ref.[12,13]) performed with latest version of the SOPHAEROS/ASTEC v1.3 (Ref.[14]) and with a calculated fission product and structural material release kinetics by DIVA-ELSA/ASTEC, confirmed the results explained above for FPT-0/FPT-1 tests. The main results concerning the iodine retention profile in the FPT-2 circuit for two cadmium release kinetics (Figure 7) are presented in Figure 8.

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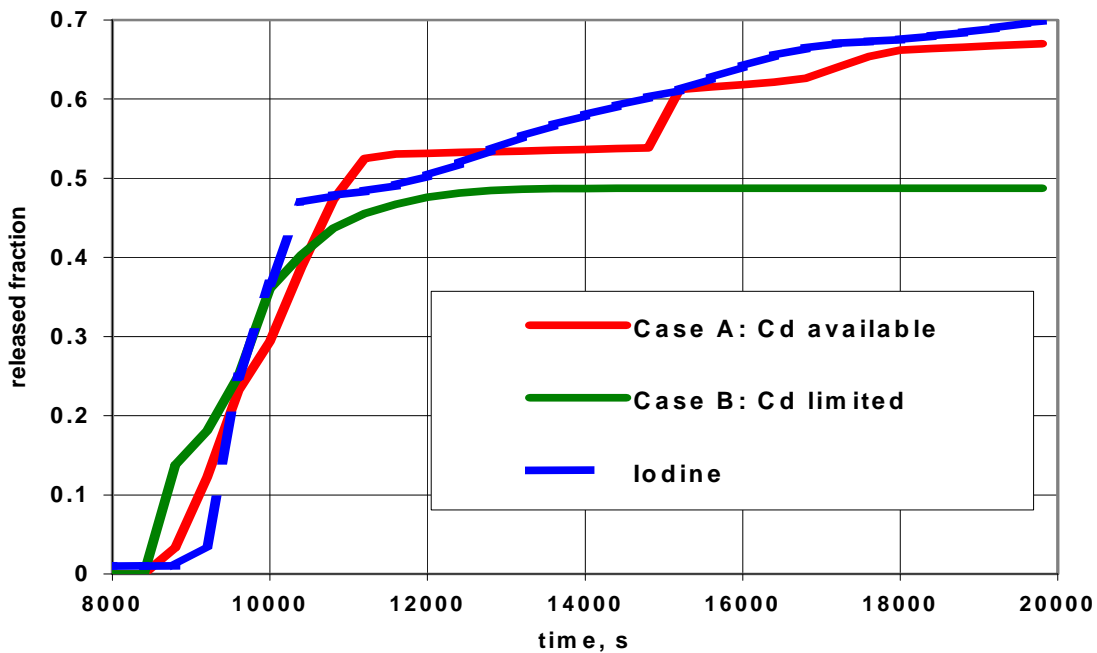


Figure 7 Cumulative fractions of initial bundle inventory released from the bundle for iodine and cadmium as calculated by ELSA/ASTEC v1.2 (Cases A and B) for FPT-2 test

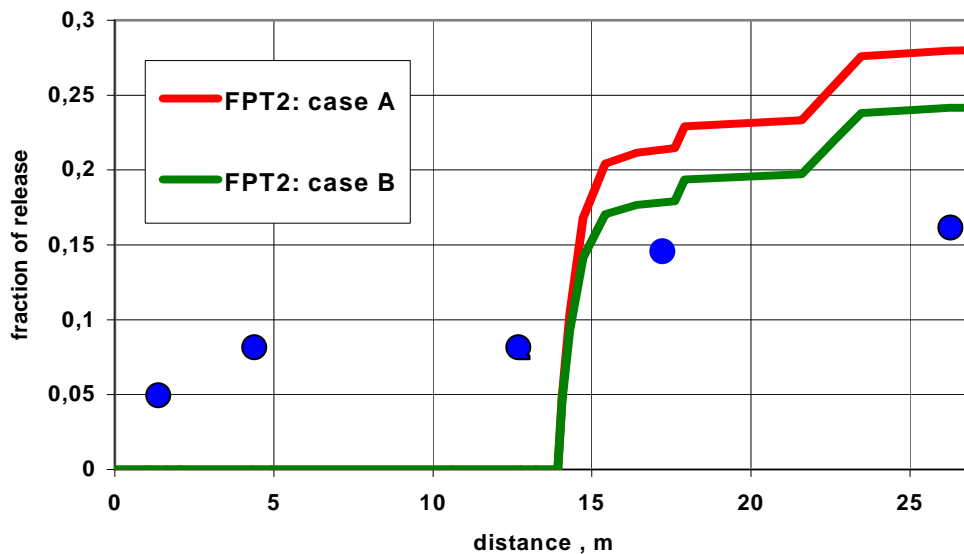


Figure 8 Calculated iodine retention profile along the circuit for FPT-2 test (blue points correspond to measurements)

Total iodine retention factor in RCS

The calculated total iodine retention in RCS is overestimated by a factor about 1.5 for FPT-0 and FPT-1 tests and 1.8 for FPT-2 , for same conditions i.e. when non-limited Cd release kinetics are assumed (Table 3). The main calculated deposition processes are

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respectively deposition of aerosols (CsI , Cs_2I_2) due to thermophoresis in SG hot leg and CdI_2 vapour condensation. In the FPT-2/3 tests, gravitational settling of aerosols in the cold leg was also calculated due to the lower steam flow rates in the primary circuit (0.5g/s) than in FPT-0/1, in agreement with experimental results indicating for FPT-2 a higher retention in this region as compared to the previous two Phebus tests.

Table 3 Comparison of the iodine retention in the circuit (SOPHAEROS/ASTEC v1.3)

	Basic Analysis	Experiment
Iodine RCS Retention Factor, [-]		
FPT-0	~0.53	> 0.3
FPT-1	~0.42	~ 0.28
FPT-2 – case A ¹⁾	~0.28	> 0.16 ²⁾
FPT-2 – case B ¹⁾	~0.24	
FPT-3	~0.19	?

¹⁾ Cases A and B correspond respectively to assumed non-limited and limited Cd release kinetics

²⁾ Higher iodine retention is suspected because of the existence of a cold spot upstream SG

The impact of iodine and caesium speciation on total iodine retention in RCS was also investigated. In particular, sensitivity analyses were performed by changing the H_2MoO_4 volatility. In FPT-1 (Ref.[15]), the total relative iodine deposition, almost entirely related to SG hot tube, decreased from 0.60 to 0.4 (or even slightly less : 0.38) when the change in H_2MoO_4 volatility is combined with the use of close to wall temperature for thermophoresis calculation in SG in which gas temperature gradient are very high. The change in the H_2MoO_4 volatility completely changes the calculated iodine chemistry in and downstream from the SG tube. While CdI_2 or HI is observed here originally, the prevailing species are CsI and RbI after. Both the shift to CsI and RbI chemistry and the proposal to use lower gas temperature corresponding to temperatures near the wall in the Talbot formula for thermophoresis (Ref.[11]) offer a way to improve the calculated retention results for FPT-1 and FPT-2 (Table 3). Note that the temperature modification influences much more CsI and RbI than CdI_2 , because, as found in the calculations, they change to aerosol completely about 1 m from the SG entrance, while CdI_2 changes to aerosol far away, in region where the gradient is much lower and thus the thermophoresis weaker. CdI_2 retention is thus mostly influenced by its vapour condensation on SG tube wall.

D.2.1.2. Volatile iodine fraction at low temperature

The volatile iodine fraction persisting at low temperature in RCS was also calculated for all the Phebus FP tests and compared to the measured fraction of volatile iodine in the containment (Table 4). The amount of calculated volatile iodine (HI) also greatly depends on the Cd release kinetics.

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Table 4 Comparison of the gaseous iodine amount at low temperature (SOPHAEROS/ASTEC v1.3)

	Basic Analysis	Experiment
Total volatile iodine (% i.b.i.) ¹⁾		
FPT-0	~2.6	≥ 2
FPT-1	~0.052	< 1
FPT-2 – case A ²⁾	~0.03	< 0.1
FPT-2 – case B ²⁾	~9	
FPT-3	~18	~ 27

¹⁾ Released from the bundle, which reaches the containment in the gaseous (as HI) and vapour form (as SnI₂, SnI₄, I₂MoO₂ or others)

²⁾ Cases A and B correspond respectively to assumed non-limited and limited Cd release kinetics

Calculation results indicate that the Cd release kinetics and CdI₂ condensation in the SG could explain the volatile iodine release observations in FPT-0 and, together with H₂MoO₄, its behaviour also in FPT-1 and FPT-2, although for these last two tests, as mentioned before, it is hardly acceptable for iodine deposition in RCS (Table 1). Furthermore, the higher measured volatile iodine release from FPT-3 circuit, where Cd was missing, is also explained. Limiting the Cd source to obtain lower iodine retention in SG (as observed) is paid by HI release to the containment in tens of percent. About 1% was calculated at the end of FPT-1 and between zero to tenths of a percent in FPT-2.

As for investigation of the total iodine retention in RCS, sensitivity studies were performed with SOPHAEROS/ASTEC for FPT-1 and FPT-2 (Ref.[9,15]) in which the H₂MoO₄ saturation pressure was decreased at low temperature (Ref.[9,15]) or it was changed to that of MoO₃ (Ref.[15]). In these cases, the iodine retention was much closer to the observed value and the Cd release kinetics impact on HI release became negligible.

Meanwhile non-equilibrium effects are currently under investigation as another potential explanation for volatile iodine persistence in the primary circuit cold leg. Indeed, in regions of the primary circuit of rapid and sharp temperature change (e.g. in the steam generator the gas temperature decreases from 700 to 150°C in about 0.5 s during the FPT-1 hydrogen release phase when the steam flow rate was about 2g/s (Ref.[21])). In these peculiar boundary conditions chemical reaction equilibrium might not be reached (e.g. CsOH + HI → CsI or Cd + HI → CdI₂) involving a limited HI destruction in the steam generator and thus an increase of HI reaching the containment.

E. CONCLUSIONS

On the way towards a better understanding of iodine chemistry in RCS in severe accident conditions, an important step is to attempt to explain the iodine behaviour in the bundle and primary circuit of PHEBUS tests. For this, the SOPHAEROS code coupling vapour and aerosol behaviour with equilibrium vapour chemistry has been used. Same models for all the tests were used to avoid “tuning” the code to one experiment. Though some gaps still exist, there has been some progress in explaining the results. All calculated Phebus tests (FPT-0 to

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FPT-3) indicated the significant fraction of gaseous hydrogen iodide HI at low temperatures and in the containment and the peculiar role of cadmium in reducing this fraction by formation of cadmium iodides, mostly CdI_2 . One would have expected a greater impact of Cs than Cd on the iodine chemistry. In FPT-0 calculations, this was not the case due to lack of caesium (trace-irradiated fuel was used in this test); whereas in FPT-1 and FPT-2 calculations, the role of caesium in iodine chemistry might have been partially inhibited because of Mo. In the FPT-3 experiment, there is almost no Cd, so the same effect of molybdic acid as in other tests might have caused the observed large fraction of volatile iodine. From the still scarce FPT-3 experimental data and calculation results, it can not yet be assessed why the CsI effect was not stronger.

Besides trying to improve further the interpretation of the analysed cases, the authors will concentrate on FPT-3 experimental result interpretation in the future. From the first results it seems that the role of boron on caesium and, as a consequence, on iodine chemistry, proposed e.g. in [18], is not very strong. The idea to explain the volatile iodine by non-equilibrium chemistry of iodine should be also pursued, though the work presented here offers explanations limited to equilibrium chemistry.

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