

# Iodine Behaviour during severe Accidents

*M. Petit\**, *Y. Billarand\**, *D. Jacquemain\*\**

*N. Hanniet\*\**, *E. Belval-Haltier\*\**

IPSN/DPEA, \*\* IPSN/DRS

## 1. Introduction

In case of a severe accident with a core melt occurring in a Pressurized Water Reactor (PWR), iodine is released to the containment. The evaluation of the iodine behaviour, including its chemical forms, is necessary for the source term assessments, as iodine could be a major contributor to short term irradiation doses.

With this objective, the IPSN is conducting major experimental programs to get basic understanding of iodine behaviour under representative conditions. These include the PHEBUS PF program which has already given new insights on the physicochemical processes involving iodine, as well as a set of separate effect and intermediate scale experiments.

This paper describes the current state of understanding of iodine behaviour based on these recent experimental results. Simplified modelling allows to perform reactor applications and to determine the most important phenomena for source term quantification. This indicates the directions to be pursued, both experimentally and for severe accidents code development, in order to improve the realism of iodine source term evaluations.

## 2. Lessons learned from PHEBUS FP test results

The first test of the programme, FPT-0, using fresh fuel, was performed from December 2 to 6, 1993. The second, FPT-1, with irradiated fuel, from July 26 to 30, 1996. The PHEBUS facility is described in an other paper presented at the same conference and it is not detailed here. Figure 1 shows a schematic of the facility.

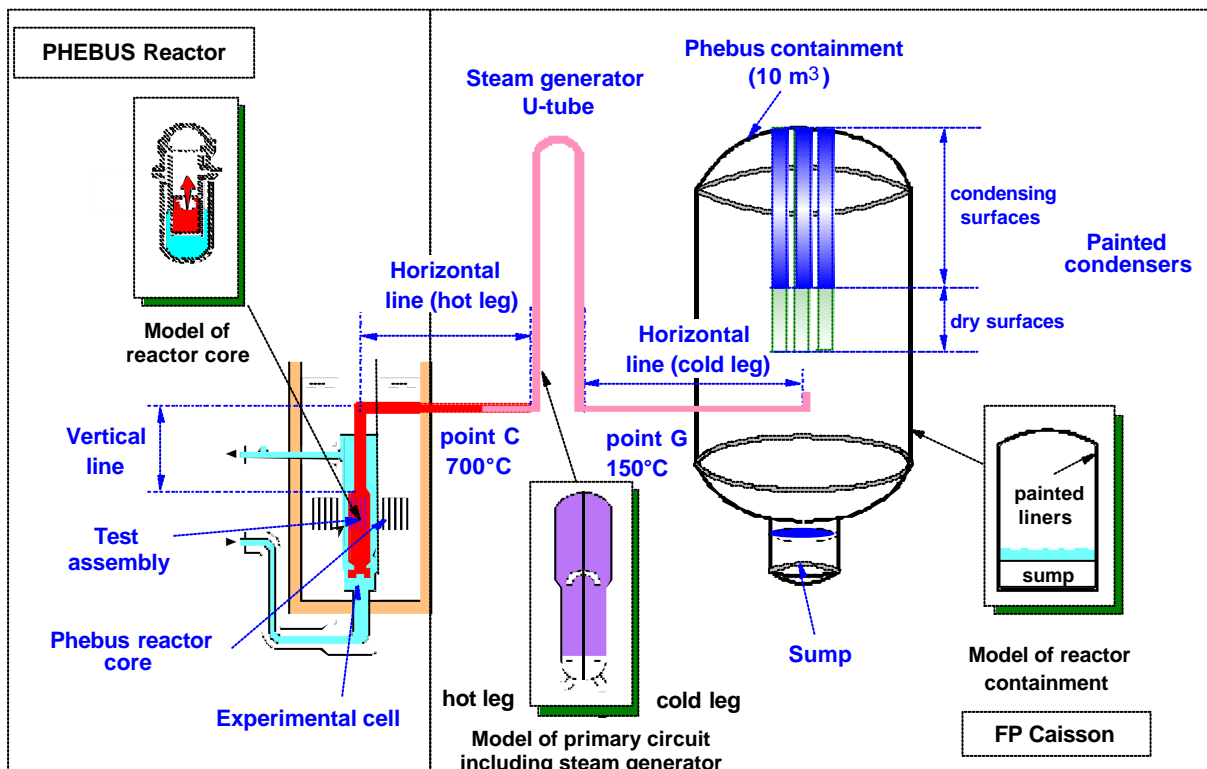


Figure 1: Schematic representation of the PHEBUS test facility for FPT-0 and FPT-1.

Both experiments were operated under similar thermal-hydraulic conditions, the main difference between them being the burn-up of the test fuel. The test scenarios were divided in experimental phases as listed in table 1.

**Table 1:** Containment boundary conditions during experimental phases of the PHEBUS tests

Phases	Duration (hours)		Containment temperatures (°C)					
			walls		condensers		Sump	
	FPT-0	FPT-1	FPT-0	FPT-1	FPT-0	FPT-1	FPT-0	FPT-1
Bundle degradation	5	5	110	110	74	90	90	90
Core shut-down - Containment isolation								
Aerosol phase	18.5	60	110	110	74 then 110	90	90	90
Preparatory phase	6	4.5	110 to 120	110 to 120	110 to 40	90 to 40	90 to 40	90 to 40
Washing	0.25	0.25	120	120	40	40	40	40
Preparatory phase	6	7	120 to 130	120 to 130	40 to 110	40 to 110	40 to 90	40 to 90
Chemistry phase	96	18	130	130	110	110	90	90
Containment depressurisation - end of experimental phases								

### Bundle degradation

In both tests, iodine was almost totally released from the fuel bundle during the degradation (about 86.5 % of the initial bundle inventory in FPT-0), probably as a gas, considering the high temperatures reached in the fuel. In the vertical line above the bundle, gaseous iodine probably reacted partially with Ag, In, Cs or Rb to form a metal iodide vapour. The existence at this location of significant unreacted gaseous iodine fractions is unexpected for reducing conditions but predicted for oxidising conditions by thermodynamic evaluations performed for PHEBUS conditions. It was estimated that, in the hot leg of the circuit (point C, 700°C), at least 20 % of the total iodine flow was present as a form which could not be condensed on the 150 °C sampling systems during the early and late Zr-oxidation phase. This form may be attributed to gaseous iodine since metal iodide compounds would have been condensed in the sampling line and in the 150°C filter as evidenced by the sampling performed during the main release phase. No similar determination could be made for FPT-0 since for this test the instrumentation in the hot leg of the circuit did not include 150°C aerosol filtration systems. However, the presence of gaseous iodine fractions in the circuit hot leg in FPT-0 cannot be excluded.

More than half of the fuel inventories of iodine successfully negotiated passage through the PHEBUS circuit to reach the model containment (63 % in FPT-0). Much of this iodine was conveyed by aerosol particles that either settled on the containment bottom or deposited on the containment surfaces (by diffusiophoresis on the painted condenser and by an unidentified mechanism on the containment walls) over a period of a few hours.

In both tests, the measured gaseous iodine fractions are at their highest level at, or following, Zircaloy-oxidation phases. In FPT-0, there was no sampling performed during the first oxidation phase. The first sampling performed about 30 minutes after this phase yielded a gaseous iodine fraction representing at least  $33 \pm 12$  % of the containment inventory at that time. This result does not exclude the possibility that temporarily, earlier after the oxidation phase, the gaseous iodine fraction could have been even higher.

In FPT-1, there were samplings performed during the two oxidation phases. The sampling performed during the first oxidation phase indicated that a few percents of the containment inventory is gaseous at that time. At this time, about 40 % of the collected gaseous iodine is not

retained on the double Zeolite filter of the apparatus, showing that a significant fraction of the gaseous iodine is not tractable by Zeolite filtration (which a priori excludes for this fraction an identification with the expected HI, I<sub>2</sub> or organic iodides). Later samplings performed with the same apparatus do not exhibit anymore this specific iodine behaviour. The « unknown » species detected early during the test probably transforms quickly into another chemical species which is then efficiently retained on Zeolite. The sampling performed during the second oxidation phase yields a gaseous iodine amount comparable to that obtained during the first oxidation phase.

After both oxidation phases in FPT-1, the gaseous iodine fraction decreases rapidly. Both decreases may be fitted mathematically by the same exponentially decaying function. A fast decrease which may be linked either to a diffusio-phoresis of gaseous iodine at the painted condensing surfaces and/or to a fast chemical transformation as mentioned earlier.

The volatile fraction of iodine originating from the primary circuit also disappeared in a few hours in FPT-0, probably due to deposition on the containment surfaces. It is however not possible to characterise precisely the gaseous iodine evolution during the bundle degradation phase in FPT-0 since only one measurement was performed during this phase.

### **Aerosol phase**

The evolution of the gaseous iodine fraction during the aerosol phase is different in the two tests. In FPT-1, the gaseous iodine fraction increases significantly immediately after containment isolation (by a factor of 2). It remains then more or less constant for about 5 hours. The increase may be attributed to a measured release of gaseous iodine from the painted condensing surfaces. The release represents about a third of the iodine which was deposited on the condensing painted surfaces at the end of the bundle degradation phase. May-pack data indicate that, at this time, most of the iodine (75 %) is found on the Zeolite stage of the device, consistent with a release of organic iodide compounds. The released iodine may have two origins : either gaseous iodine which reacted directly with the paint during the test transient or formation of iodide ions, I<sup>-</sup>, by solubilisation in the condensed steam of the soluble iodine species initially transported by the aerosol and subsequent reaction with paint. No conclusion is possible from the experimental data on this question.

In FPT-0, the gaseous iodine fraction decreased exponentially during the aerosol phase. No significant decrease of iodine activity on the painted condenser surfaces was measured. The data does not exclude however that a minor release, insignificant with respect to the total amount of iodine deposited, occurred during the long term phase.

### **Chemistry phase**

The evolution of the gaseous iodine fraction after the washing phase is different in the two tests. In FPT-1, a significant increase of the gaseous iodine fraction (by a factor close to 2) was measured. This increase may be attributed to the formation and transfer to the containment atmosphere of volatile I<sub>2</sub> formed by radiolytic oxidation of soluble I<sup>-</sup> ions. May-pack data indicate that at the washing 75 % of the iodine is trapped on the Knit-mesh stage of the apparatus, consistent with I<sub>2</sub> being the major gaseous iodine species at that time. After the washing, the I<sub>2</sub> contribution to the gaseous iodine fraction decreases regularly from 75 % down to about 25 %, probably due to a back-transfer of I<sub>2</sub> to the sump and subsequent slow reaction with Ag. The total gaseous iodine fraction remains however constant, indicating that contribution of the iodine species deposited on the Zeolite increases. This observation would indicate that a significant production of organic iodides compounds still occurs after the washing phase. However, no evolution of the iodine fraction deposited on the condensing surface of the condenser can be noted. The release at that time may be too small to be observable.

In FPT-0, no increase in the gaseous iodine concentration was observed at the washing ; the gaseous iodine fraction remained stable and represented only 0.063 ± 0.032 % of the bundle inventory. These results were consistent with an efficient trapping of the iodine by Ag and the subsequent inhibition of volatile iodine formation by sump radiolysis. May-pack data indicated that most of the iodine was trapped on the Zeolite stage of the apparatus, consistent with organic

iodides being the major gaseous iodine species at that time. This result was attributed to the release of organic iodides from the painted condenser surfaces.

For the long term evolution, the main difference between the two tests is probably determined, as mentioned earlier, by the more « soluble » behaviour of iodine noted in FPT-1. This difference in behaviour may be attributed to the large difference in between the Ag/I molar ratios determined in FPT-0 (~ 2500) and in FPT-1 (~ 50), this ratio being determinant for the kinetics of the reaction to form insoluble AgI. In short, AgI being formed quickly in FPT-0, the processes involving soluble iodide as a reactive species are strongly inhibited in this test, AgI formation being slower in FPT-1, these processes may become significant in the production of volatile iodine. These processes are :

- reaction of I ions, formed by solubilisation in condensed steam of the soluble iodine species initially transported by the aerosol, with the paint of the condenser, leading to the release of volatile organic iodide compounds,
- radiolytic oxidation of I ions present in the sump, leading to the production in the sump and transfer to the containment atmosphere of molecular iodine I<sub>2</sub>, subsequent reaction with painted condensers.

The FPT-1 data, taken as a whole, appear to be consistent with a slow Ag/I reaction process, allowing for the processes listed above to occur and determine the long term volatile iodine behaviour. FPT-0 data were consistent with a fast iodine trapping by silver, inhibiting these processes and the long term volatile iodine behaviour was essentially determined by the evolution of the gaseous iodine which was injected from the primary circuit during the bundle degradation phase. The results also show that organic iodides could very well be the major contributor to the gaseous iodine fraction at the end of both tests. These results have important applications for iodine chemistry code development and iodine source term evaluation as discussed in next sections.

To summarise, the most important PHEBUS results for iodine source term studies are :

- the existence during Zircaloy-oxidation phases of significant fractions of gaseous iodine in the model circuit, these fractions may be quite large (few tens %) in the hot leg of the circuit as indicated by FPT-1 results ;
- the low production of gaseous iodine by sump radiolysis, due to the presence of Ag coming from the control rod ;
- on the long term, organic iodides released from the painted condenser surfaces in the gas phase would dominate the volatile iodine fraction.

### **3. Simplified modelling for reactor applications**

In order to evaluate the iodine source term, a review of available models was performed. This review was of course guided by the main conclusions drawn from the PHEBUS tests results stated above. With the objective to be used for level 2 PSA source term evaluation, for which a large number of sequences have to be computed, a model based on these conclusions was elaborated. This section summarises the main characteristics of the model and provides sample applications to PHEBUS tests results and to a reactor case.

#### **Release of gaseous species in the containment**

As iodine is a very volatile fission product, it is assumed that it is totally released from the fuel. But the forms under which this release is made is of course very important and sensitive on source term evaluations. Based on the interpretation of PHEBUS results in light of reactor conditions, it is assumed that the release of iodine in the containment is 95 % under soluble aerosols and 5 % under gaseous form. Due to the lack of information on this point, the gaseous species is supposed to be I<sub>2</sub>, although it is recognised that under hydrogen containing atmospheres, other species such as HI are likely to be formed. It is stressed that these assumptions are weakly established based on the existing knowledge, and that this point would deserve more attention in the future with respect to its impact on the iodine source term.

## Radiolytic oxidation of iodide in the sump

The radiolytic oxidation of iodide has been studied in a large number of experiments during the past years. It is established that the radiolytic reactions are fast. Reference calculations were performed using the INSPECT mechanistic code which showed that, with respect to the objectives of the simplified model, molecular iodine production in the sump is rapid compared to the mass transfers.

Taking into account the previous assumption, a correlation is required to estimate the steady-state concentration of molecular iodine. This correlation is based on a model proposed by Gorbovitskaya and Tiliks and experimental results of Burns and al. It was also verified that the correlation gives results consistent with those of Lin at 25°C. The correlation is the following:

$$[I_2] = 10^{-4} \sqrt{[I^-]} \exp(3.46 - 4.5 \cdot 10^{-4} T^2) \exp(-0.016(pH^3 - 4.6^3))$$

with T being the temperature in °C and the concentrations being in mol/l. This correlation is considered to be valid for iodide concentrations between  $10^{-3}$  and  $10^{-6}$  mol/l and for a pH value between 3 and 6.

This correlation implies that the molecular iodine production strongly reduces as temperature increases and that the more diluted the solution is, the more efficient is radiolytic oxidation. These trends are consistent with the present understanding of the phenomena. The model was based on experiments at representative dose rates, which makes it applicable for reactor applications. However, it is pointed out that the model does not take into account the effect of dose rate which is its main deficiency.

## Formation of insoluble silver iodide in the sump

It is now well established that silver can play an important role in the sump because of the formation of insoluble silver iodide from either I or  $I_2$ . This role was confirmed by the PHEBUS-FPT0 experiment. Recent works, in particular in the frame of the 4<sup>th</sup> Framework Program of the European Union, have provided experimental data and modelling for the interaction of iodine with silver. This modelling has been introduced in the version 4.2 of the IODE code. It has also been established that silver iodide is very likely to be stable under radiation, although it is recognized that certain conditions have not been completely investigated and that work is still ongoing on that subject at PSI, Switzerland.

For the present work, the question to be addressed was whether or not the sump can be considered as a definitive trap for iodine. For this purpose, a parametric study was conducted using the IODE 4.2 code. Parameters investigated were the amount of silver in the sump and the percentage of oxidised silver, for both 900 MWe and 1300 MWe types of reactors which differ by the amount of silver in the control rods. It was concluded from this study that, with respect to the amount of molecular iodine released out of the containment building, the sump can be considered as an effective iodine trap for the 900 MWe but not for the 1300 MWe. Thus, sump chemistry can be disregarded for the former but not for the latter.

## Adsorption of molecular iodine on paints

The adsorption velocity in the liquid phase was based on results of adsorption experiments with paints used in French reactors obtained by Lucas and Aujollet as well as on the analysis of results obtained in the CAIMAN facility. The different results were found to be consistent with each other, and a fit of the values for the adsorption velocity  $k_{adsl}$  gave the following relation:

$$k_{adsl} = 10^{(0.0267T - 5.23)}$$

with  $k_{adsl}$  in dm/s and T the liquid temperature in °C.

The adsorption velocity in the gas phase was studied by Belval-Haltier for representative reactor conditions. It was found that both the temperature of the carrying gas and the preconditioning temperature of the paint affect the adsorption velocity. If we assimilate the preconditioning

temperature to the maximum temperature  $T_{\max}$  that the paint was exposed to, then the following relation can be established:

$$k_{\text{ads}g} = -7.68 \cdot 10^{-4} T + 1.75 \cdot 10^{-3} T_{\max} - 0.084$$

with  $k_{\text{ads}g}$ , the adsorption velocity in dm/s, and  $T$  (resp.  $T_{\max}$ ) the temperature (resp. the maximum temperature) of the gas in °C. This relation is valid in the 90-130°C temperature range only. It is also noted that the adsorption velocity can be influenced by condensation, but data are lacking for such conditions. However, it was verified on the results of one experiment conducted in the CAIMAN facility under condensing conditions that the adsorption velocity was consistent with the preceding formulation.

### Formation of organic iodide

Organic iodides are of particular importance because they are not easily trapped on filters. For these species, several mechanisms of production have been identified: homogeneous or heterogeneous reactions, in aqueous phase or gas phase. Among these mechanisms, PHEBUS-FP experiments showed that one of the most significant is the interaction of molecular iodine with paints in gas phase.

Relatively few experimental data on organic iodide production from painted surfaces in the gas are available. Furthermore, this topic is still under basic investigation and no satisfactory model is established. It is also noted that since the interaction with iodine is very likely to depend on the structure of the paint, only results obtained with the paints used in French plants, or at least those for the same type of paint (epoxy), make sense in the context of our study.

Results of small scale experiments were examined. Some results from the intermediate scale PHEBUS-RTF and CAIMAN experiments were also included in the analysis. Recent work showed that the organic iodide production is strongly dependant on surface concentration of iodine on the paint. The data were then presented in terms of conversion percentage, defined as 100 times the ratio of the number of moles of organic iodide to the number of moles of iodine on the painted surface, as a function of the surface iodine concentration as in figure 2.

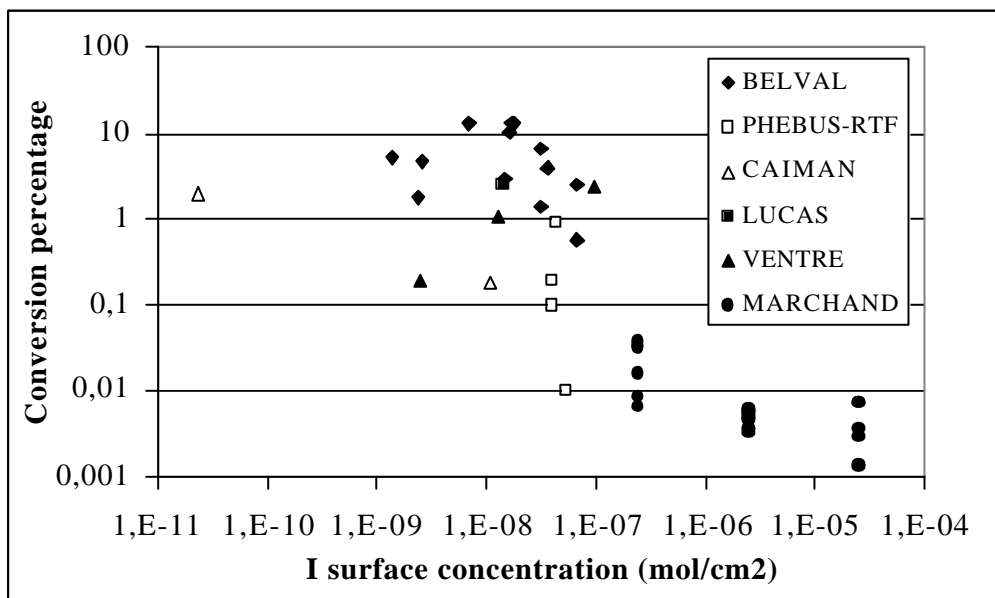


Figure 2: Conversion percentage of iodine to  $\text{ICH}_3$  as a function of surface concentration on paint for different series of experiments.

From that graph, it can be deduced that the conversion percentage is a decreasing function of the surface concentration. It is however not possible to directly derive a fit of these data which are relatively scattered. To be consistent with our overall model, we retained the assumption of a

“conservative” conversion percentage value of 10%. This production is assumed to be instantaneous.

It is recognised that the assumptions made on this point are not satisfactory and that the uncertainty on the process will directly influence the results for plant evaluations. Models for organic iodide production were however proposed recently and their possible use for reactor application must be studied.

Other routes for organic iodide production may exist. The first one is the interaction of iodine with paint in the sump. This process is not supposed to be dominant for the situations we examine because of the presence of silver in the sump which traps iodine.

Another possible production mechanism is the homogeneous interaction of methane with iodine in the containment atmosphere. Methane could be produced from the oxidation of boron carbide present in the control rods of the 1300 and 1450 MWe reactors. The degradation and oxidation of boron carbide control rods is presently not well known and this will be an objective for the upcoming PHEBUS-FPT3 test. Evaluations of the amount of CH<sub>4</sub> that can be produced show that boron carbide can be totally turned into methane in presence of excess hydrogen, which is very likely to be the case during the emission of volatile fission products. If we assume that methane and iodine concentrations in the containment are respectively of the order of 10<sup>-4</sup> and 5 · 10<sup>-8</sup> mol/l, then a literature survey showed that under representative conditions the conversion of iodine to organic iodide can be of the order of 5%. However, the reaction of iodine with methane is relatively slow and with respect to our assumptions on heterogeneous reactions in the gas, this process can be neglected.

In conclusion, we think that the “conservative” assumptions we made on organic iodide production by interaction with paint in the gas phase account also for other production mechanisms.

### Comparison to PHEBUS FP tests results

The assumptions presented above lead to a set of differential and algebraic equations which are solved using the FACSIMILE software. The resulting model was applied to the case of the PHEBUS tests. The aim was not to adapt the model to fit the experimental results, but rather to assess the complete set of assumptions for reactor applications by comparison to the most representative experimental results to date. The comparison for gaseous iodine concentration is shown in figure 3 for FPT0 and in figure 4 for FPT1.

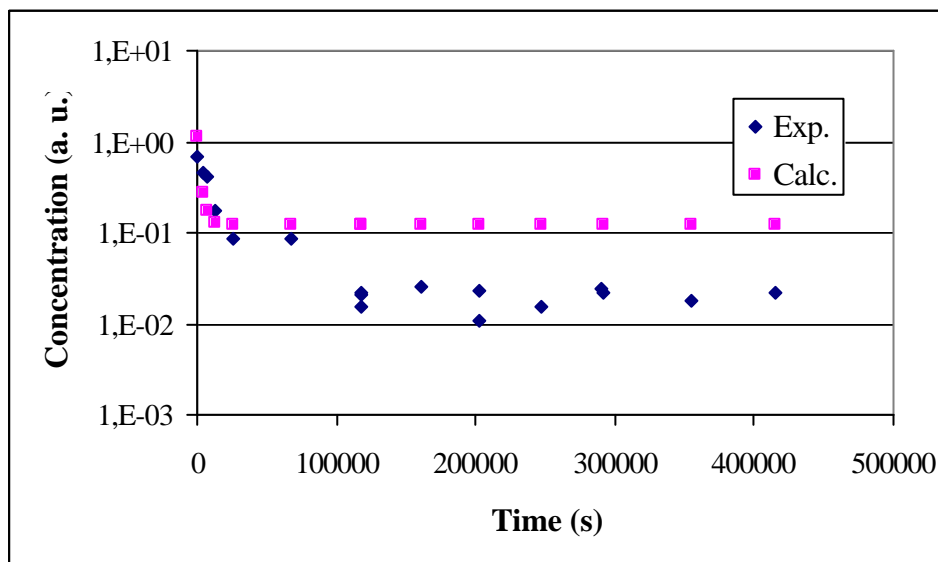


Figure 3: Comparison of the total iodine concentration in the gas phase as a function of time between FPT0 experimental results and results calculated with reactor hypotheses.

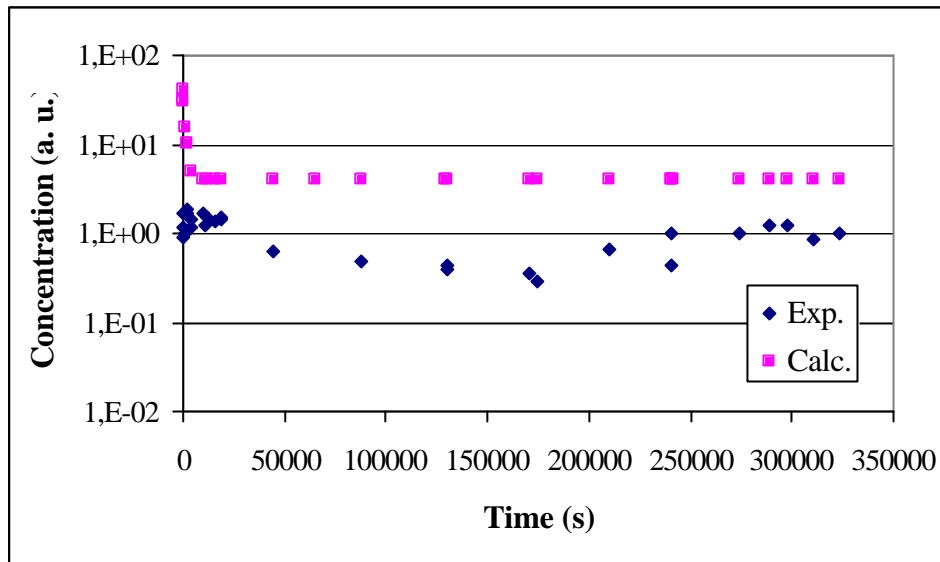


Figure 4: Comparison of the total iodine concentration in the gas phase as a function of time between FPT1 experimental results and results calculated with reactor hypotheses.

It can be seen that the model is globally “conservative” with respect to PHEBUS results, particularly in the initial phase of FPT1.

With respect to its simplicity, the model is judged to be good when compared to experimental results of global experiments and adequate for reactor applications.

### Reactor applications

This section provides a sample reactor application for both 900 MWe and 1300 MWe types of reactors. The calculated situation is that of a simplified AB sequence (all temperatures are constant along the time period), which corresponds to a large break on the primary circuit with complete loss of safety injection and containment spray. Calculation conditions are summarised in table 2. Calculated concentrations in the gas phase of both molecular iodine and organic iodides are represented in figures 5 and 6.

Table 2: Calculation conditions for the AB sequence

	900 MWe	1300 MWe
Containment volume	50000 m <sup>3</sup>	70400 m <sup>3</sup>
Sump volume	195 m <sup>3</sup>	265 m <sup>3</sup>
Sump-gas interfacial area	800 m <sup>2</sup>	1160 m <sup>2</sup>
Sump painted surfaces area	1000 m <sup>2</sup>	1200 m <sup>2</sup>
Gas painted surfaces area	24200 m <sup>2</sup>	33000 m <sup>2</sup>
Mass of silver in the sump	114 kg	38.2 kg
Core iodine inventory	11 kg	15.7 kg
pH	6.4	6.4
Liquid temperature	85°C	102°C
Gas temperature	96°C	102°C

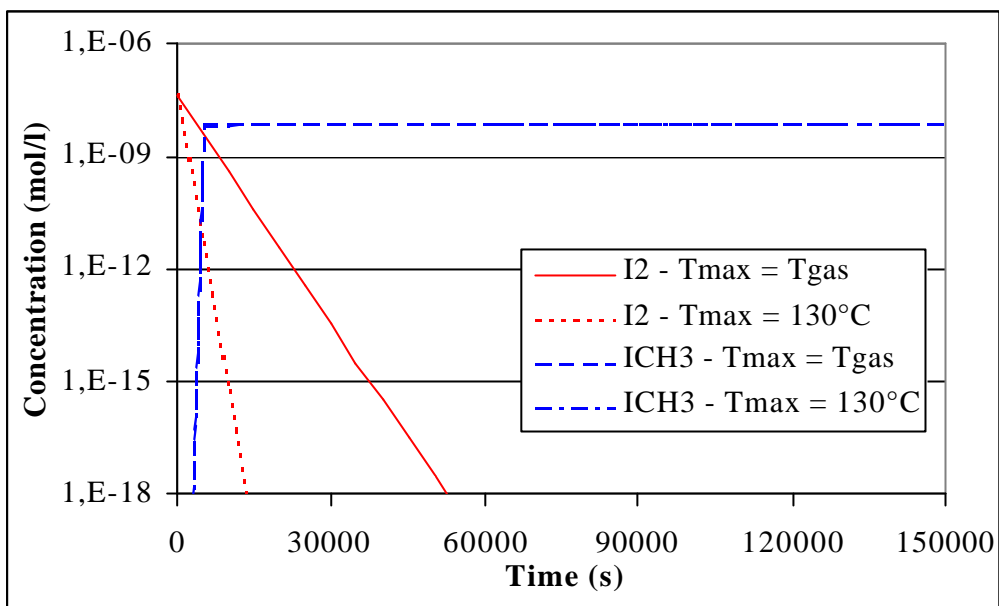


Figure 5:  $I_2$  and  $ICH_3$  concentrations in the gas phase as a function of time for the AB sequence on a 900 MWe French PWR.

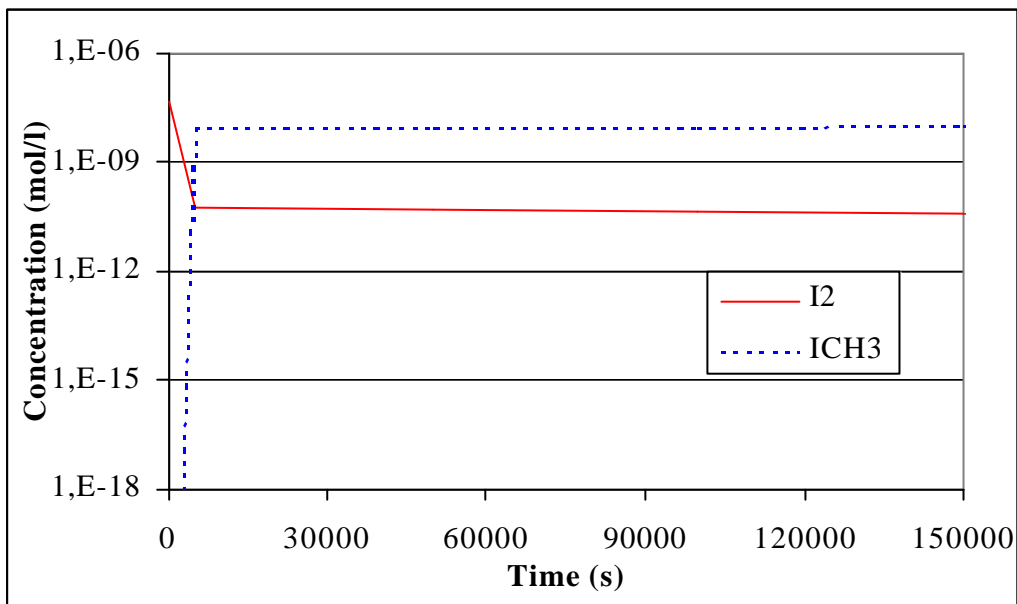


Figure 6:  $I_2$  and  $ICH_3$  concentrations in the gas phase as a function of time for the AB sequence on a 1300 MWe French PWR.

Figure 5 also shows the influence of the choice of the maximum temperature for computing the adsorption coefficient on painted surfaces. In one case, this temperature was set equal to that of the gas, in the other case to  $130^\circ C$ . It can be seen that this has a large influence on the molecular iodine concentration in the short term, but it has virtually no influence on the organic iodide concentration.

Figure 6 also shows that molecular iodine concentration reaches an equilibrium as the adsorption is balanced by the emission from the sump. This is because the amount of silver in the sump is low. This in turn induces a very small increase of the organic iodide concentration in the long term.

In any case, for the long term, the dominant form of gaseous iodine in the containment is predicted to be organic iodide.

These reactor applications confirm the conclusions that were drawn from the experimental results of the first two PHEBUS FP tests. According to the modelling, the most important phenomena for

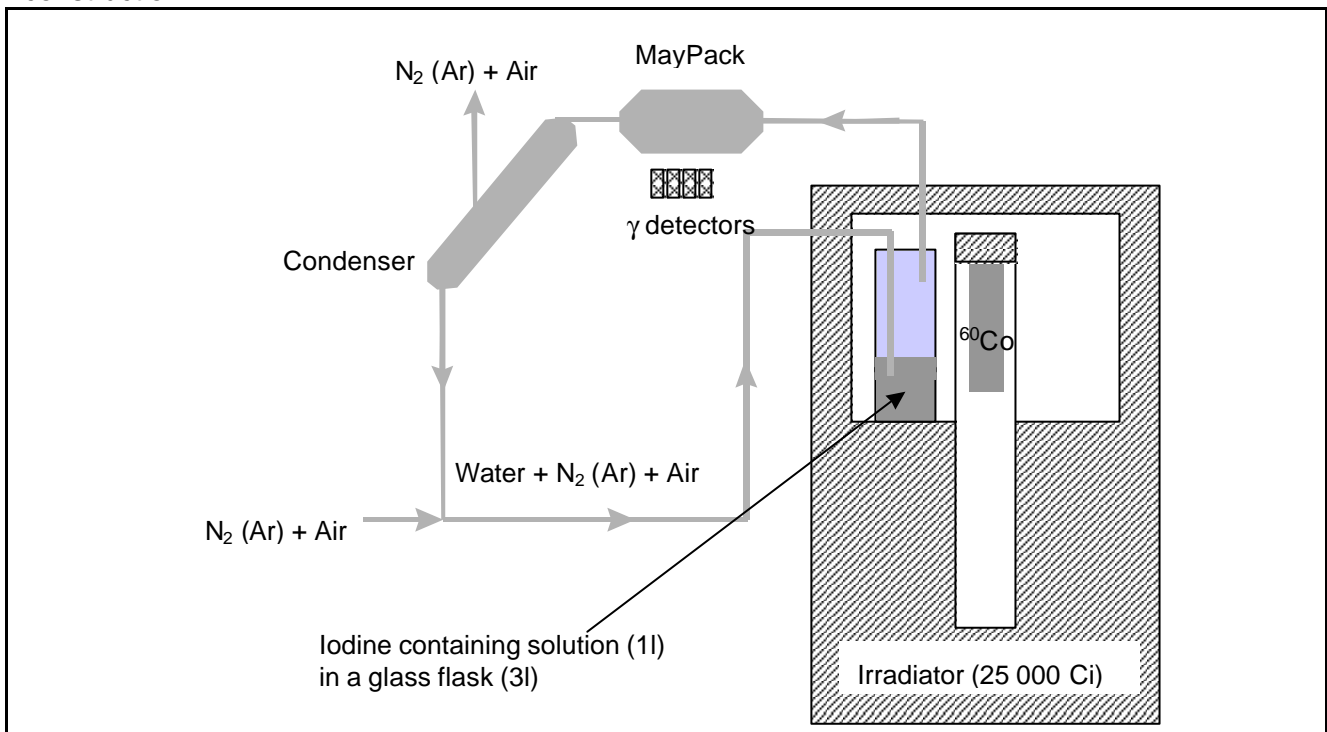
iodine source term evaluation are the initial release of gaseous iodine at the break and the production of organic iodide from interaction with paints in the gas phase. For the situations in which the amount of silver in the containment sump might not be large enough, radiolytic oxidation of iodide may also have a significant impact.

#### 4. Future directions

Reactor applications, with simplified modelling based on assumptions compatible with the PHEBUS tests results have shown the most important phenomena for iodine source term evaluations.

Concerning the release of gaseous iodine at the break, a recent review conducted by IPSN concluded that there is a need for an experimental program devoted to the chemistry of iodine at high temperature in the primary circuit. This program, called CHIP, is under preparation at Cadarache. It will eventually provide a database for modelling and validation of the SOPHAEROS code.

Concerning other aspects of iodine chemistry, the EPICUR facility, depicted in figure 7 is under construction.



**Figure 7:** Schematic of the EPICUR facility

The facility will allow to test the behaviour of iodine under representative conditions of irradiation. It will be possible to conduct experiments at elevated temperatures and in presence of painted coupons. The use of  $I^{31}$  labelled iodine together with a selective Maypack will enable the online measurement of gaseous forms produced and to discriminate between mineral and organic forms. First experimental results are expected in 2001. The first series of experiments will be devoted to the study of organic iodide production from atmospheric painted surfaces and to radiolytic oxidation at elevated temperatures, areas in which experimental data are lacking. These experimental results will be used to validate new models currently under development in the IODE code. Global validation of the IODE code will be established in particular with respect to results of global experiments conducted in the CAIMAN facility (figure 8). This intermediate scale facility, with a 300 litre containment designed to sustain pressure up to 5 bar and temperature up to 130 °C, which allows to simulate in a coupled way the physical and chemical processes relevant to the behaviour of iodine in PWR containments.

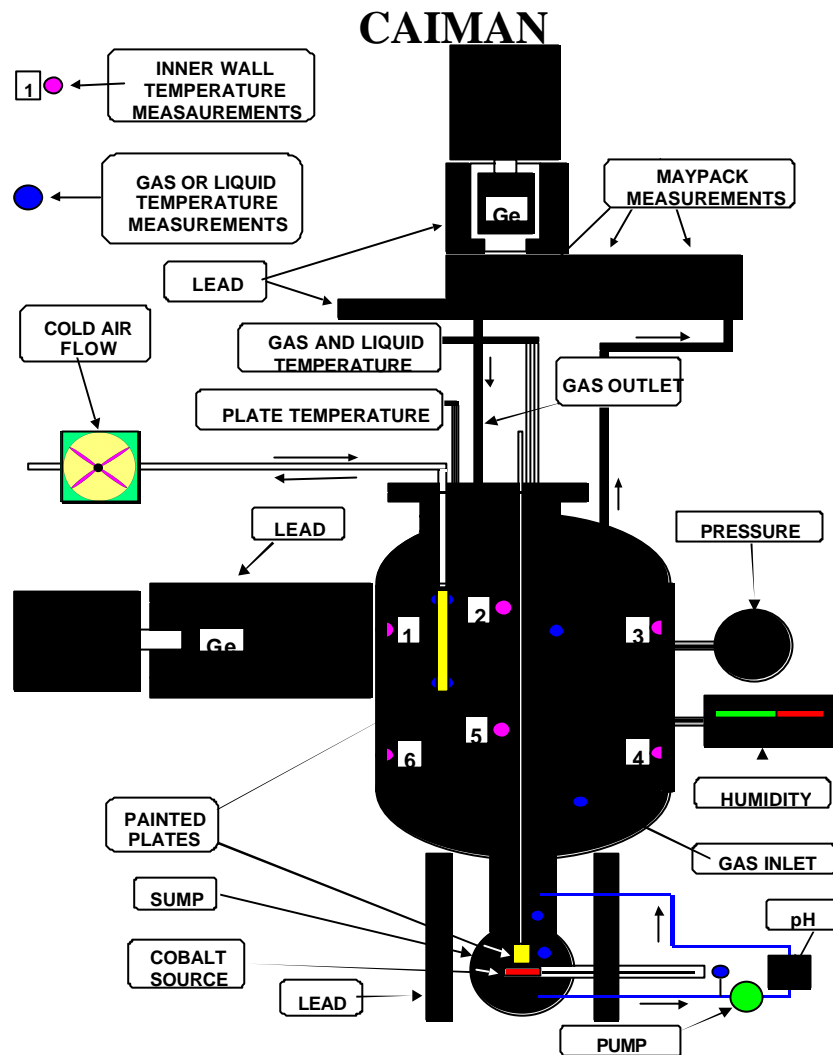


Figure 8: Schematic of the CAIMAN intermediate scale facility

## 5. Conclusions

The results relative to the behaviour of iodine in the first two PHEBUS FP experiments have revealed rather unexpected features and outlined that important processes for estimating the iodine source term in case of a severe accident in a PWR are not sufficiently understood. In particular, the release of gaseous iodine species at the break as well as organic iodide formation in the gas phase are of major importance with respect to determining the concentration of volatile forms in the reactor containment.

These results were already taken into account in simplified, fast running models for typical applications in the frame of PSA level 2 studies.

Complementary to the PHEBUS program, the IPSN develops a consistent set of small and intermediate scale experimental facilities that will eventually provide the necessary database for the validation of the SOPHAEROS and IODE codes. These codes will be used for improving the realism of iodine source term estimates.