

Interpretation of Containment Chemistry Results from Phebus Test FPT2S Dickinson¹, N Girault², L E Herranz³ and P Raison⁴

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Summary

The Phebus-FP Project has become a fundamental reference in the area of severe accidents. Aimed at investigating key aspects of the behaviour of fission products under prototypical accident conditions, the tests have provided essential insights into iodine transport through the primary circuit and the chemistry of iodine in the containment. The current paper presents a preliminary interpretation of the iodine behaviour in the containment of test FPT2.

Modelling studies have been reasonably successful in reproducing the main aspects of the observed behaviour, although the relative importance of some phenomena varies between the different codes. Consensus has been reached on a number of points:

- The initial transient increase in gaseous iodine concentration cannot be accounted for by formation of volatile iodine in the sump;
- Radiolysis of gaseous iodine species (I_2 and CH_3I) is expected to lead to the formation of involatile species which could have an important influence on the airborne iodine behaviour;
- Unlike the earlier tests, the chemistry of iodine in the sump was not dominated by the formation of insoluble silver iodide. However, the formation of volatile species in the sump was suppressed by the high pH, high temperature conditions;
- The evaporating/condensing conditions in the chemistry phase leads to a low steady-state concentration of iodine in the containment atmosphere.

A INTRODUCTION

Phebus-FP is an international project aimed at providing integral data on the release and transport of fission products under severe accident conditions. The programme comprises a series of in-pile experiments conducted at CE Cadarache and jointly funded by IRSN/EdF, EC and a number of other national organisations. The fourth test in the Phebus-FP programme, FPT2, was performed in October 2000 (Ref. [1]). Analyses of the iodine behaviour in the containment during this test have been made using various containment chemistry codes, mainly in the framework of the Pheben 2 programme (Ref. [2]). This report describes the main results of the FPT2 test regarding iodine behaviour in the containment, and the current status of interpretation and understanding reached through analysis with the ASTEC/IODE, IMPAIR, INSPECT and MELCOR codes.

B SUMMARY OF FPT2 TEST CONDITIONS AND RESULTS

The Phebus-FP experimental circuit is shown schematically in Figure 1.

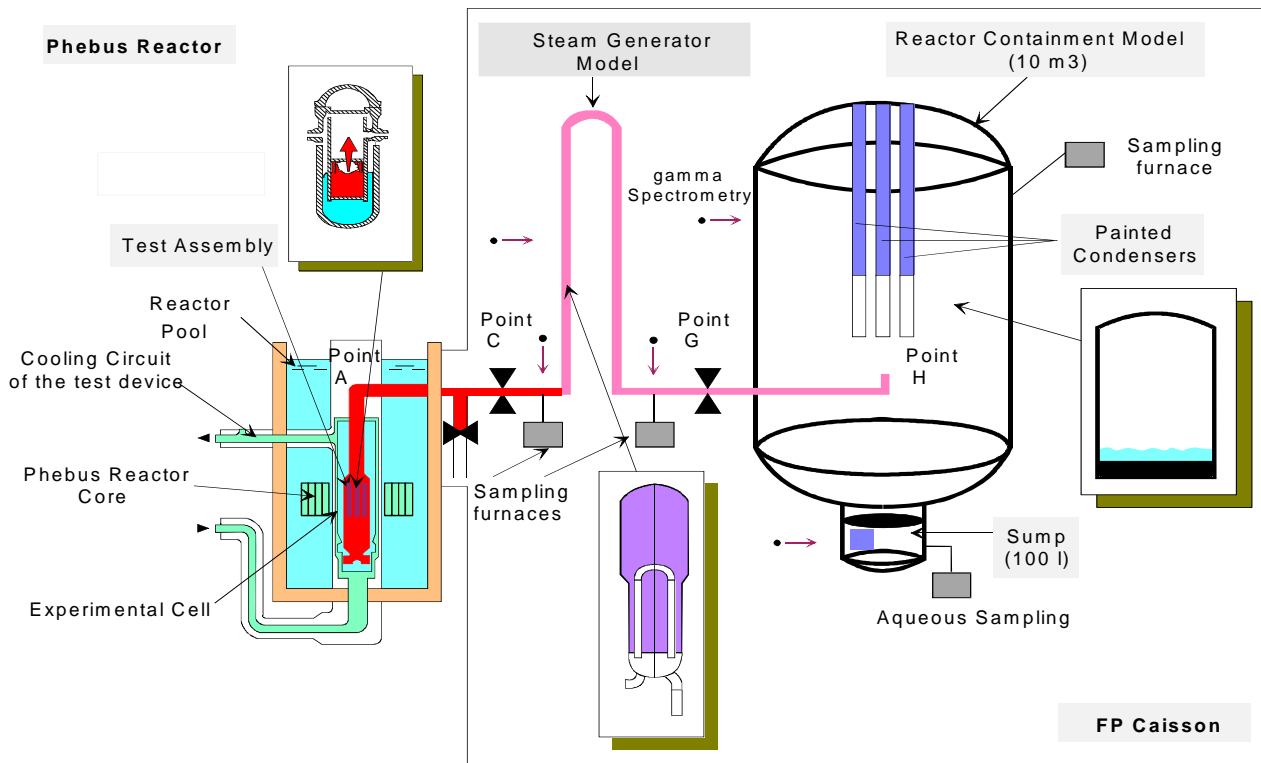


Figure 1. Schematic of the Phebus-FP Experimental Facility

The circuit comprises three main parts:

- The Test Device consisting, in FPT2 as in most of the other tests, of a metre-long bundle of 20 fuel elements and one Ag-In-Cd control rod, contained within a zirconia shroud. The iodine inventory of the fuel bundle in FPT2 was about 1.5 g.
- The Primary Circuit comprising the above-bundle pipework (“upper plenum”), an instrumented hot line held at 700°C, a steam generator tube with an outlet temperature of 150°C, and the instrumented cold leg held at 150°C. The outlet of the cold line is inside the containment vessel.
- The Containment, a 10 m³ steel vessel containing a heated aqueous sump (~100 dm³), painted condensing surfaces to control the humidity, and various instruments for measuring iodine and aerosol concentrations, as well as on-line γ -spectrometry of the sump and surfaces.

In the FPT2 test, the fuel bundle was heated to a maximum of ~2500°C and the released fission products were transported through the primary circuit to the containment in a flow of steam/H₂. The airborne concentrations of various radionuclides (including ¹³¹I) in the containment were monitored during the fuel degradation and subsequent aerosol phases. After about 48 hours, the hemispherical bottom of the containment vessel was washed by recirculating sump water to transfer deposited aerosol into the sump. Measurements of the

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airborne concentration of iodine then continued during the chemistry phase, which lasted for a further 50 hours.

In the FPT2 test, the containment sump was maintained at a weakly alkaline pH (8 –9) using a boric acid/borate buffer. The sump temperature was 90°C during the aerosol phase, and was increased to 120°C for the chemistry phase. The temperature of the containment atmosphere was maintained at 90°C throughout the test, leading to a cycle of sump evaporation and condensation. The condensate was returned to the sump via the painted condensers suspended in the vessel.

The main experimental observations with regard to iodine behaviour in the containment can be summarised as follows:

- About 55% of the iodine inventory of the fuel bundle was released and transported to the containment vessel. The large majority of the iodine measured in the containment was in aerosol form, but a small gaseous fraction was detected during the fuel degradation / fission product release transient. There was, however, no direct experimental evidence for the presence of gaseous iodine in the circuit cold leg, although specific measurement devices were employed to detect such species.
- The gaseous iodine concentration decreased rapidly by about an order of magnitude from its initial peak, and then gradually increased throughout the aerosol phase. The concentration again fell rapidly at the start of the chemistry phase, and continued to fall throughout the remainder of the test. The gaseous iodine was predominantly inorganic in nature, with organic species accounting for less than 30% of the total in all samples.
- Iodine in the sump was predominantly present in a soluble form. This contrasts with the behaviour observed in the previous tests (FPT0 and FPT1) where the iodine in the sump was mainly in an insoluble form, most probably AgI formed by reaction with silver aerosol released from the control rods. There appeared to be an increase in the amount of insoluble iodine formed during the chemistry phase, and in particular at the end of the test when the sump was cooled.
- The iodine activity measured on the vertical containment wall decreased gradually during the later part of the aerosol phase and throughout the chemistry phase. In contrast to FPT1, there was no strong decrease of the iodine activity from the painted condenser surfaces; if anything, the results suggest an increase in the activity during the second half of the aerosol phase. A small decrease in the activity of several elements, including iodine, on the condenser was observed at the start of the chemistry phase and can probably be attributed to washing by the condensate flow.

C MODELLING STUDIES

Iodine chemistry calculations have been carried out using the IODEv5.2 module of ASTEC, the empirical IMPAIR-JRC model, the mechanistic INSPECT model and the iodine module of the integral MELCOR code, which is based on the INSPECT chemistry. Although the detailed modelling varies considerably amongst the codes, the phenomena treated are generally similar and include some or all of the following:

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- Dissolution of iodine-containing aerosol in the sump to form iodide (I⁻) ions (implicitly assumed in most cases);
- Radiolytic oxidation of I⁻ to volatile iodine (I₂) in the sump;
- Reaction of I⁻ and / or I₂ with silver aerosol in the sump to form solid AgI;
- Partition of I₂ between the sump and the containment atmosphere;
- Absorption and desorption of I₂ onto painted or metal surfaces in contact with the sump water or atmosphere;
- Production of volatile organic iodide from iodine absorbed on painted surfaces and / or reaction of I₂ with organic impurities in the sump;
- Radiolytic oxidation of I₂ and / or organic iodide in the gas phase to form oxidised species.

Supplementary calculations were also carried out using the IODAIR code, which models radiolytic reactions in the gas phase. However, this was not interfaced to an aqueous iodine code so does not consider the phenomena listed above. Much of the input data required by the codes can be taken directly from the experimental measurements (e.g. flow rates of I and Ag into the containment), boundary conditions (e.g. sump temperatures, evaporation rates) or geometry (e.g. surface areas, volumes). In some cases, though, the required information is not available and estimates have to be made. The most important parameters to which this applies are:

Initial iodine speciation: previous calculations on FPT1 have shown that it is not possible to account for the peak in the gaseous iodine concentration observed early in the test on the basis of radiolytic oxidation in the sump (Ref. [3]). It is therefore common practice in modelling the Phebus tests to assume that a small fraction, usually about 1%, of the iodine entering the containment is in the form of gaseous I₂.

Silver aerosol characteristics: experimental studies of the reaction between iodine and silver aerosol suggest that oxidation of the silver surface greatly increases the rate of reaction with I⁻, which is otherwise very slow (Ref. [4]). Since the extent of any oxidation of the aerosol surface is unknown, this has to be estimated. Sensitivity studies have been made by varying this parameter between 0 and 30%. The size of the silver aerosol particles is also an important parameter since this governs the surface area and hence the rate of iodine uptake.

D MODELLING RESULTS

Although the mass balance within the containment has not yet been fully established, it is clear that most of the iodine is located in the sump or on surfaces throughout the chemistry phase, with only a very small fraction being present in the gas phase. The highest concentration of gaseous iodine, measured during the degradation phase, only accounts for about 0.5% of the final containment inventory. At the end of the chemistry phase, <0.01% of the iodine in the containment is present in the gaseous phase. This overall behaviour is generally fairly well reproduced by the models, as shown for example in Figure 2.

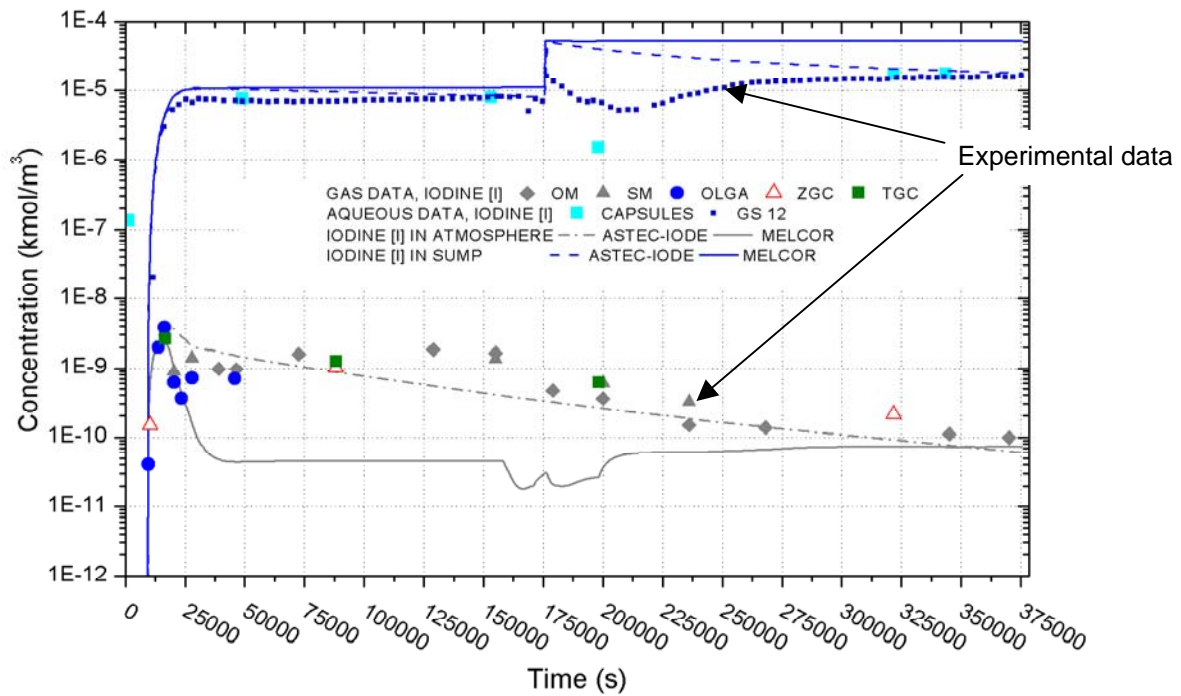


Figure 2. IODEv5.2 and MELCOR calculations of iodine mass distribution (CIEMAT)

The main phenomena determining the iodine behaviour in the atmosphere and the sump are discussed in the following sections.

D.1 Iodine in the containment atmosphere

The assumption of an early source of gaseous iodine, corresponding to about 1% of the inlet flow, is essential for the models to reproduce the iodine evolution in the gas phase. As noted above, however, it is not confirmed whether this originates from the circuit. An alternative explanation, that the early gaseous iodine peak could result from radiolytic oxidation of iodide dissolved in water on the condenser surface, has been suggested but the condenser conditions are not sufficiently well-defined for this possibility to be reliably assessed (Ref [5]).

Whatever the source of the early gaseous iodine, it is removed quite rapidly from the gas phase through a combination of surface deposition (including transport to the condensers) and radiolytic oxidation. Reactions with surfaces are generally treated as reversible, with an equilibrium gaseous concentration being established that depends on the amount of deposited iodine and the appropriate deposition and desorption rates. Although there is some uncertainty as to the values of these rates, the persistence of a significant concentration of gaseous iodine throughout the aerosol phase shows that the surfaces are not acting as a strong irreversible sink. The amount of gaseous iodine deposition on the surfaces cannot be evaluated from the test data because of the predominance of deposited aerosol. The decrease in the gaseous iodine concentration that occurs from the start of the chemistry phase can be attributed to the efficient transfer of iodine to the sump in the condensing steam (Figure 3).

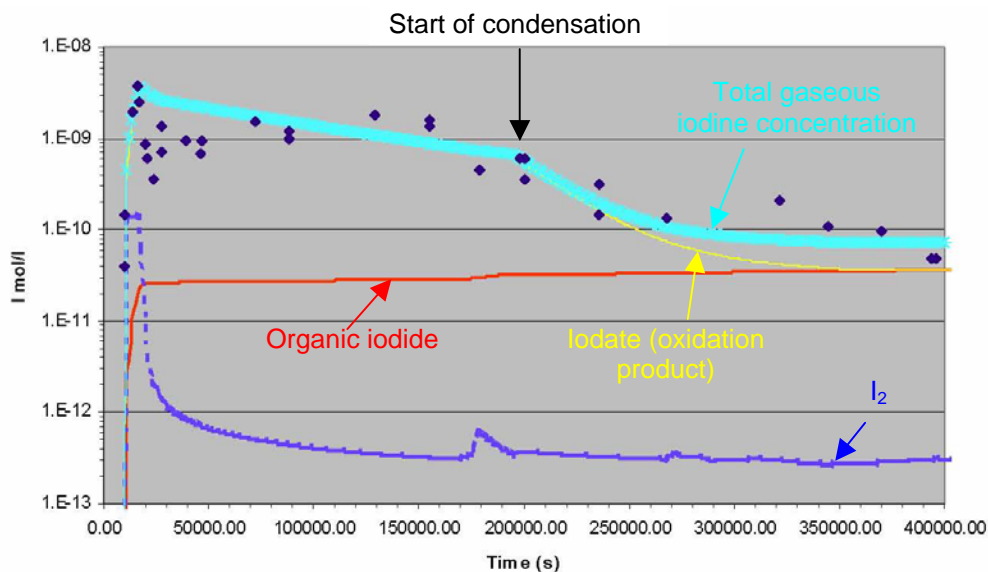


Figure 3. IODEv5.2 calculation of gaseous iodine evolution (JRC)

Gaseous iodine can be produced throughout the test from two sources: partition of I_2 from the sump and formation of volatile organic species from iodine deposited on the painted condenser surface or from organic impurities in the sump. The models suggest that the former is unimportant; the calculated gaseous iodine concentration is consequently rather insensitive to changes in modelling of the silver – iodine reactions which have a large impact on the aqueous iodine speciation (see below). There is some variation between the concentrations of organic iodides calculated by the codes, depending mainly on the assumptions made regarding the formation mechanisms, but they all calculate a rather low, steady-state concentration in the atmosphere which is in general accordance with the experimental measurements.

Another area in which the models vary significantly is in the treatment of gaseous radiolytic reactions. Until recently, the radiolytic oxidation of gaseous species, particularly I_2 , has tended to be ignored, as the form of the models existing models predicted rapid removal of iodine from the gas phase which was clearly not consistent with results of experiments such as Phebus-FP. However, work in the ICHEMM programme (Ref [6]) showed that gaseous radiolysis could be a dominant phenomenon in determining the speciation of airborne iodine, and so considerable effort has recently been put into understanding and modelling these processes. This is an ongoing process and significant uncertainties remain, particularly in understanding the reaction mechanisms at low iodine concentrations, and in modelling the formation and behaviour of the solid iodine oxide products. The results are generally encouraging; for example, Figure 4 compares the predictions of the IODAIR model, which treats the gaseous radiolytic reactions, with the INSPECT calculations. The IODAIR model calculates an increase in the gaseous iodine concentration during the aerosol phase similar to that observed in the experiment. This arises because of the build-up of gaseous products from the radiolytic destruction of methyl iodide. However, it needs to be emphasised that the modelling used here is still subject to considerable uncertainty.

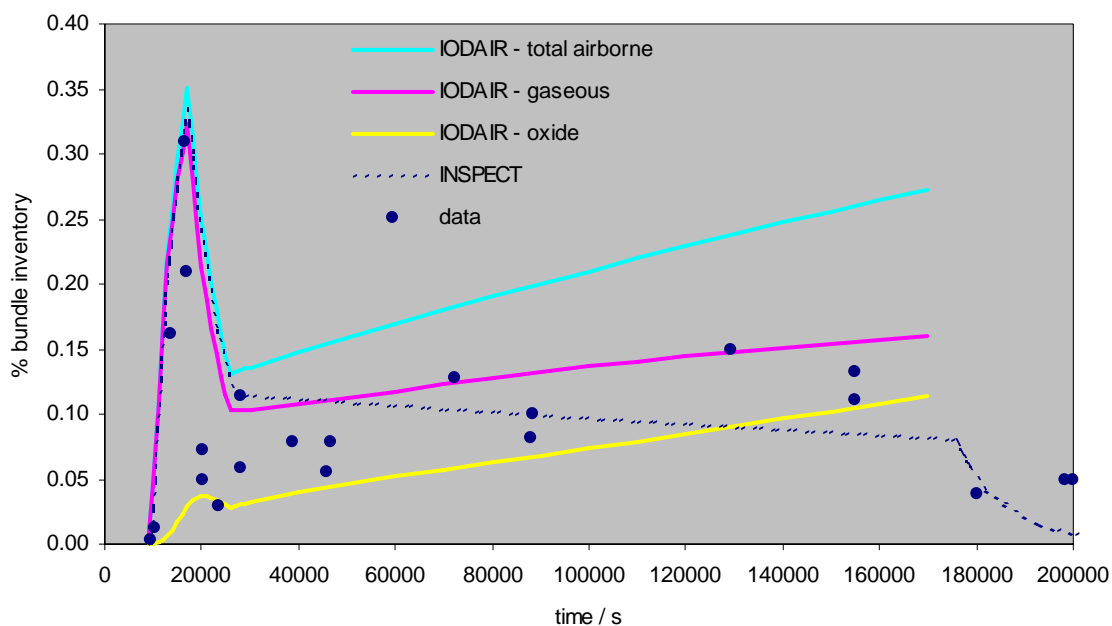


Figure 4. INSPECT and IODAIR calculation of airborne iodine speciation (WMT)

D.2 Iodine in the sump

The experimental data on iodine speciation in the sump is limited to measurements of the suspended (presumed dissolved) activity and the activity on the sump bottom, which is assumed to be AgI associated with settled aerosol (Figure 5).

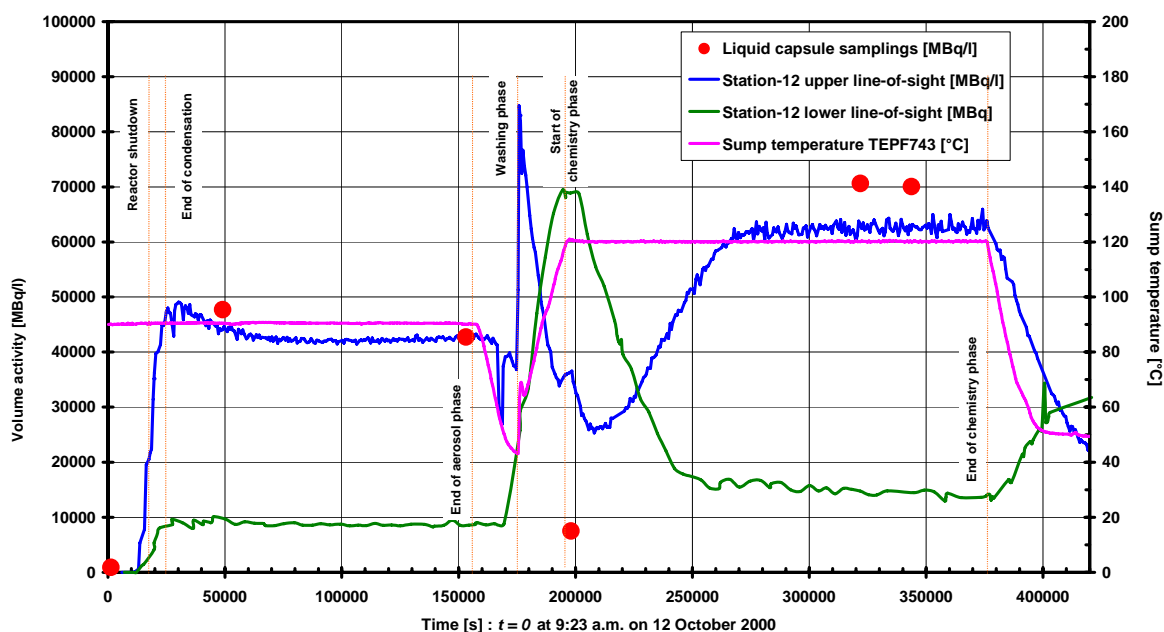


Figure 5. Iodine activity in the FPT2 sump

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These measurements indicate that iodine existed mainly in a soluble form throughout most of the test, but there appears to have been an increase in the amount of AgI present during periods when the sump temperature was lower (during washing and cooldown). There are three potential routes for AgI formation in the sump:

- i. $\text{Ag} + \frac{1}{2} \text{I}_2 \rightarrow \text{AgI}$ fast
- ii. $\text{Ag(O)} + \text{I}^- \rightarrow \text{AgI}$ fast
- iii. $\text{Ag} + \text{I}^- \rightarrow \text{AgI}$ slow

All of the models predict that the concentration of I_2 would be very low under the conditions of the FPT2 sump, since radiolytic oxidation of I^- to I_2 is favoured by low temperature and low pH. Reaction (i) is therefore negligible, and reaction (iii) is also too slow to be important. The calculated fraction of AgI in the sump therefore depends on the rate of reaction (ii), and is very sensitive to the assumed degree of silver oxidation. Figure 6 shows the speciation calculated by IODEv5.2 (IRSN) assuming that 7.5% of the silver is in oxidised form.

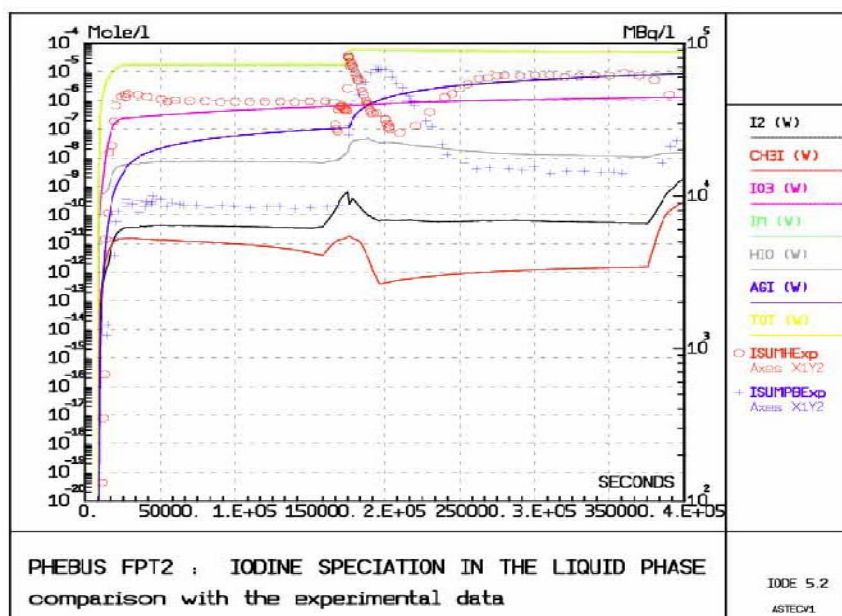


Figure 6. IODEv5.2 calculation of iodine speciation in the FPT2 sump (IRSN)

Similar results are obtained with other codes, although the extent of oxidation that gives reasonable agreement with the data varies between the codes. However, these calculations do not account for the decrease in iodine solubility observed during the washing and cooldown phases; nor can these differences be attributed to decreased AgI solubility at lower temperature. The change in solubility of iodine observed at the beginning of the chemistry phase suggests that iodine is added to the sump at least partially in an insoluble form during the washing. Silver iodide could be reduced in the sump by radiolytic reactions such as



Under more acidic conditions, radiolytic oxidation of I⁻ would generate I₂, which could react to re-form AgI by reaction (i) above. However, it has already been noted that this would not occur under the FPT2 conditions. A steady-state fraction of AgI, as observed in the test, would therefore be established by the balance between AgI decomposition and re-formation by reaction (iii). As the sump is cooled at the end of the test, radiolytic oxidation of I⁻ to form I₂ would become more favourable, and this in turn would favour more AgI formation by reaction (i).

D.3 Iodine release from containment surfaces

One aspect of the iodine behaviour in FPT2 that has not generally been considered by these modelling studies is the apparent release of iodine from deposits on the containment walls. Measurements of the wall activity suggest that almost 30% of the deposited iodine activity was re-released from the walls during the second half of the aerosol phase and the chemistry phase. Since the amount of aerosol deposited on the walls was relatively high in FPT2, this could constitute a significant additional source of gaseous iodine and could have contributed to the increase in gaseous activity measured during the aerosol phase. A possible explanation for this behaviour is that iodine was present in the aerosol in a chemical form that was stable under the reducing conditions of the circuit, but not in the oxygen-containing atmosphere in the containment. No experimental studies have been made to test this hypothesis, so this remains a purely speculative explanation.

E CONCLUSIONS

Calculations of iodine behaviour in the containment of Phebus test FPT2 have been done using a number of modelling codes, ranging from detailed mechanistic models to integral code modules. These studies have been reasonably successful in reproducing the main aspects of the observed behaviour, although the relative importance of some phenomena varies between the different codes. Consensus has been reached on a number of points:

- The initial transient increase in gaseous iodine concentration cannot be accounted for by formation of volatile iodine in the sump;
- Radiolysis of gaseous iodine species (I₂ and CH₃I) is expected to lead to the formation of involatile species which could have an important influence on the airborne iodine behaviour;
- Unlike the earlier tests, the chemistry of iodine in the sump did not appear to be dominated by the formation of insoluble silver iodide. The formation of volatile species in the sump was suppressed by the high pH, high temperature conditions. However, details of the solubility behaviour of iodine in the sump are still not understood and there is considerable uncertainty regarding formation of silver oxide, which would be important in determining AgI formation under these conditions.
- The evaporating/condensing conditions in the chemistry phase leads to a low steady-state concentration of iodine in the containment atmosphere.

Some uncertainties remain in understanding the iodine behaviour in the test; in particular, the mechanism of radiolytic oxidation of gaseous I₂ is poorly understood at low concentrations, and the identity and behaviour of the reaction products is still speculative.

F REFERENCES

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