

Simple Probabilistic Approach to Evaluate Radioiodine Behavior at Severe Accidents: Application to PHEBUS Test FPT1

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1. Introduction

The contribution of radioiodine to risk from a severe accident is recognized to be one of the highest among all the fission products. In a long term (e.g. several days), volatile species of iodine are the most important forms of iodine from the safety point of view. These volatile forms ("volatile iodine") are mainly molecular iodine, I₂, and various types of organic iodides, RI. A certain controversy exist today among the international research community about the relative importance of the processes leading to volatile iodine formation in containment [1], [2] under severe accident conditions. The amount of knowledge, coming from experiments, of the phenomenology of iodine behavior is enormous and it is embedded in specialized mechanistic or empirical codes (e.g. [12]–[16]). An exhaustive description of the processes governing the iodine behavior in containment is given in [1]. Yet, all this knowledge is still not enough to resolve some important questions. Moreover, the results of different codes -when applied to relatively simple experiments, such as RTF [5] or CAIMAN [6]- vary widely [8]. Thus, as a complement (or maybe even as an alternative in some instances) to deterministic analyses of iodine behavior, simple probabilistic approach is proposed in this work which could help to see the whole problem in a different perspective. The final goal of using this approach should be the characterization of uncertainties of the description of various processes in question. This would allow for identification of the processes which contribute most significantly to the overall uncertainty of the predictions of iodine volatility in containment. In this work we made a dedicated, small event tree to describe iodine behavior at an accident and we used that tree for a simple sensitivity study. For the evaluation of the tree, the US NRC code EVNTRE [3] was used. To test the proposed probabilistic approach we analyzed results of the integral PHEBUS FPT1 experiment [17]–[20] which comprises most of the important phenomena, including the insoluble AgI formation in the sump water.

2. Probabilistic approach to analyze containment iodine behavior

The main objective of this work was to have a simple tool to assess the relative importance of selected processes and mechanisms which govern the iodine behavior at an accident. To achieve this objective, a small event tree has been built which describes in a simplified manner the iodine behavior in containment. In the first question of the tree we are asking about the source distribution of iodine to containment (volatile iodine species versus aerosol-borne iodine —see Fig.1 with an example of the tree for FPT1). It means that the probabilistic analysis here starts with the entry of iodine to containment and that it does not look at the release from fuel and transport of iodine through RCS. In principle, it would not be too difficult to encompass the release and transport phenomena into the analysis, but that was not a goal of this work.

The containment iodine event tree has been built such as to comprise —potentially— all the important characteristics (values of parameters etc.) and processes which influence the iodine behavior. Typically, these are the initial distribution of iodine (entering the containment) among its various forms, aerosol depletion characteristics, presence and nature of organic material in containment, sump water pH, Ag source to sump, mass transfer of volatiles and sorption constants of I₂, atmosphere and sump water temperatures, dose rates in containment, etc. The most important processes are, of course, the radiochemical reactions producing volatile iodine species (I₂, RI) from non-volatile forms (I⁻) which prevail in containment originally.

Some of the most important processes or reactions governing the iodine behavior in containment are relatively slow (kinetics plays a role). It means that in analyses it does not suffice to treat those reactions as any equilibria, i.e. as fast processes, which is usually a case for the RCS iodine behavior description. This fact is embedded in the modeling by specialized containment iodine codes (deterministic modeling). However, in the probabilistic approach this poses some problems.

Probabilistic analyses of the containment iodine behavior could be done in various ways, always with simplifications of a certain degree. We can use sort of rough modeling of iodine behavior (e.g. [9]) where, for example, radiolytic oxidation of iodide in water is represented by a steady-state concentration of I₂, given known values of parameters controlling this, and other important processes are also simplified. With this, it would be possible to call the simple models from within the tree using some extra coding in the so called User Functions of the EVNTRE program. This approach seems to be the best way how to treat the problem, especially for the whole-plant analyses (PRA Level 2). Another way could be to use the results of the iodine code runs to supply some numbers to the tree separately before the tree evaluation, maybe also in connection with the simplified models. In our work, we choose the most complicated approach, probably most suitable for

the particular purpose of this work, i.e. for evaluating the iodine behavior in an (integral) experiment. This approach uses an iodine containment code [‡] (to calculate the speciation of iodine for most of the tree outcomes) which is being called directly from within the tree. This again requires a lot of extra coding to the EVNTRE User Functions. In such a way, a set of selected input values to the code run can correspond to a given path through tree via given (or calculated) values of parameters in branches of questions preceding the question from which the iodine code is being called. For example, if the path through the tree in Fig.1 goes via branches labeled "AEROSOLS", "10%AG.OX", and "noRIfatm" then the iodine code is called with the input requiring stated fraction of the total iodine being in iodide form (e.g. CsI on aerosols), requiring to use (for the reactions of AgI formation) a given part of silver in oxidized state and requiring that no reactions of RI formation in the atmosphere are to be modeled. Even the time of the start and the end of the code calculation can be supplied by this way for repeated blocks of the same (or similar) questions in the tree, dividing thus the accident sequence into 2 or more phases (possibly with different boundary conditions) for the purpose of the probabilistic analysis. There is, of course, a lot of problems with this approach, one of the biggest being that results of the tree evaluation are very much dependent on the chosen code. Also, for different codes it is necessary to have different versions of the EVNTRE User Functions (it means more coding). However, it is very easy to do any parametric study or uncertainty assessment using the same parameters (and the same values) as inputs to different codes and see the sensitivity right off.

The final outcomes of the tree evaluation are mass fractions of the volatile iodine, I2+RI, in containment atmosphere, i.e. the ratio of the volatile iodine mass in the gas phase of the containment to the total iodine mass in containment as calculated by the iodine code. These fractions are evaluated at the end of the iodine code run (at the end-time of the calculation: this time can be also specified in the tree and it may be the time where the concentration of volatiles in the gas phase is highest or anything else). For a given path through tree, the calculated fraction represents a single number which is a good indicator of the iodine volatility. Not all of the tree outcomes are necessarily calculated by the iodine code: some paths through the tree can lead to simple answers where there is no need to use a code.

[‡] French code IODE 5.1, as a part of ASTEC suite of codes, has been used

	distribution of the source to cont between I2 and aerosols	aerosols depletion, I2 init distribution, ...	organic material in cont / a lot of soluble organics in sump	sump pH	% of Ag oxidized (total amount of Ag should be OK)	temperatures, dose rates, ...	I2 sorption/desorption constants	RI formation (on [dry] surfaces) in atm	calculate I speciation with iodine code (from TSTART to TMAX)	SEQ. PROB.
	INIT_SOURCE		ORGANICS		%AG_OX		I2 SORPTION	RI_FORM_GAS	IVOLG_FRAC	
1								1.00E+00 nR1atm		
	I2ATM				0%AG_OX			1.00E+00 nR1atm		
					2%AG_OX			1.00E+00 nR1atm		
					1.00E+00 10%AG_OX			1.00E+00 nR1atm	frIGVOL01	
					0%AG_OX			1.00E+00 nR1atm		
	9.95E-01 AEROSOLS				2%AG_OX			1.00E+00 nR1atm		
					1.00E+00 10%AG_OX			1.00E+00 nR1atm	frIGVOL01	

CONTAINMENT IODINE EVENT TREE - PHEBUS FPT-1

Fig. 1 Example of the containment iodine event tree with the iodine code being directly called from within the tree (for particular purposes of the PHEBUS FPT1 evaluations, the questions in grey boxes were not asked —see discussion in text)

In principle, the outcome could be also something else than volatile iodine fraction in atmosphere, e.g. partition of iodine between water and the atmosphere, but always it ought to be one number characterizing somehow the iodine volatility (maximum or at equilibrium or whatever) [†].

Both the number of paths through the tree going to a particular outcome and the value characterizing, for instance, the fraction of volatiles in the atmosphere (for a given path through the tree) can be obtained in a single EVNTRE run. Moreover, the output files (or parts of them) from single iodine code runs can be stored and labeled. Thus, the complete results of a given iodine code run (all the iodine speciation and its time dependencies) can be traced back to the individual path through the tree.

All this was done with LAHEY FORTRAN on UNIX (PC Debian LINUX) which enables great flexibility in calling the system (and, then, any UNIX script or any program, such as ASTEC) from the EVNTRE code.

3. Application to PHEBUS FPT1 iodine behavior

As an example of the usage of the containment iodine event tree we examined the iodine behavior in PHEBUS FPT1 integral experiment. Description of PHEBUS FPT1 and all the data needed for the containment iodine behavior analysis were taken from the FPT1 Final Report [17] and from the ISP-46 Specification Report [18]. As our main task, we tried to assess the relative importance of the reactions of organic iodide (RI) formation/decomposition in containment atmosphere with respect to the total volatile iodine (RI+I2) concentration in atmosphere. By RI formation/decomposition in atmosphere we mean the heterogeneous reactions (on painted surfaces exposed to the gas phase), whose model is based on the empirical correlation proposed in [10] —cf. description of these processes, including the RI decomposition reaction, in the IODE code manual [12]. Some experts consider these processes unimportant () while others think that these processes are crucial for an explanation of the FPT1 iodine behavior. The reason for the latter opinion is based mostly on the fact that there is an abundance of silver in the FPT1 sump which should bound all the "free" iodine in water preventing thus any RI formation there. Then, the only way how to get some RI into containment atmosphere (into the gas phase) is to produce RI in the gas phase. However, there are probably other possibilities for this to happen than just the heterogeneous RI formation reactions described above. One such thing could be production of RI in water films on wet surfaces in the atmosphere by the same (or similar) mechanism by which RI is formed in the sump water —see short description of these processes in the next chapter. The impact of these processes on iodine volatility could be easily estimated in a parametric study using the event tree. Since such processes in the atmosphere are not explicitly modeled by codes they were not studied for the FPT1 experiment evaluation. Also, at least some transfer of volatile iodine from

[†] of course, there remains the question of the ratio of I2 to RI in gas phase

the sump to the atmosphere is possible depending on kinetics of the iodine uptake by silver. If this uptake is just fast, and not extremely fast, then there is a potential for some volatile iodine formation in water and subsequent transfer of that volatile iodine to the gas phase. As all containment iodine codes model the AgI formation and the models differ in different codes [7], we tried to address this issue in our sensitivity studies. The way these reactions are usually modeled is this:

Deposition of I2 on Ag in aqueous solutions is treated as a first-order process



with kinetic constant of the reaction $k = 10^{-5}$ m/s. In some codes, including IODE-ASTEC, there is modeled also another process, which is a reaction of I- with a fraction of Ag, denoted further as "Ag_ox", which had become oxidized in the course of an accident (kinetic constant of the reaction, which is first-order relative to iodide, is similar to the first reaction). As the concentrations of I- in the sump at relevant stages of a severe accident are generally much higher (several orders of magnitude) than the I2 concentrations, the reaction with Ag_ox is likely to be much faster than the first reaction. A thorough discussion is given in [2].

The evaluations of the tree by the EVNTRE code for FPT1 were being done in the so called "sampling" mode which enables processing of multiple sets of inputs (e.g. set of selected input values to the iodine code). This facility of the EVNTRE code permits Monte Carlo sampling to be used to generate mapping from input to output [3].

The iodine event tree for FPT1

The most important questions (events) in the tree are depicted in the graph in Fig. 1. The questions framed in grey boxes were not asked for the particular purpose of the PHEBUS FPT1 evaluation. These were typically the questions asking about the sump water pH and dose rates and temperatures in the containment. The sump water pH remained constant at approximately 5 all the time during the experiment (pH was controlled and measured) and the small changes to this value would not influence the iodine volatility pronouncedly. The same is true about the temperatures and dose rates (which are also known quantities). In contrast, the numbers used in the simulation for the I2 sorption description (sorption/desorption constants), and also interfacial mass transfer coefficients for I2 and RI (CH3I in IODE), are very uncertain and could have a great impact on iodine volatility. Therefore they were included into the sensitivity study (the I2 sorption/desorption processes and the interfacial mass transfer of I2 and RI are treated with standard models described elsewhere —cf. for example [12] and [11]). Also, the kinetic constants of the basic reactions in water (I- radiolytic oxidation to I2, and I2 reduction), as given in IODE 5.1, were not studied. These reactions are modeled in a similar way in all iodine codes and even if they could be a source of discrepancies in containment analyses, it is out of the scope of this work to study that. We must suppose that these basic models are correct in the code we are using, i.e. in the IODE 5.1.

All this is done for the purposes of a simple sensitivity study. If we are to make any uncertainty assessment (which will be the next step to this work) it would be necessary to begin with a sort of screening sensitivity analysis. This is designed to determine the relative significance of every single input parameter by a defined (and scrutable) statistical technique [4].

All default values to the IODE runs were used in simulations, typically values of kinetic constants of all reactions. The only gas phase reactions used were the reactions of heterogeneous RI formation. The RI formation in water was modeled using the Taylor-Liger model [12]. This represents homogeneous formation of RI by reactions of I2 with dissolved organic materials in sump (e.g. thinners of paints) and is similar to models in other containment iodine codes [15]. As a template for the input to IODE 5.1, the FPT1 validation data were used which had been distributed with the ASTEC suite of codes (official distribution). The definition of the iodine source to containment (flow rates of aerosols and gaseous iodine) was taken from [18] and from ISP-46 calculations of FPT1 iodine behavior [19], [20]. In total, approximately 0.7g of iodine got to PHEBUS FPT1 containment during the test. Only about 0.5% of that source represents iodine in volatile form. The source of Ag is taken to be 42times higher than the source of iodine during each phase of the test —cf. [19].

Results of the sensitivity study

As the base case evaluation (it does not necessarily mean the most realistic) of the tree we choose the case where there was no oxidized silver in the sump. Sorption/desorption constants of I2 for adsorption in gas phase on painted surfaces were taken from the validation FPT1 input deck ($K_{ADS}^{(PDRY)} = 1 \cdot 10^{-4}$ m/s, $K_{DESO}^{(PDRY)} = 4.5 \cdot 10^{-6}$ sec⁻¹) and on stainless steel it was $K_{ADS}^{(SDRY)} = 1 \cdot 10^{-5}$ m/s, $K_{DESO}^{(SDRY)} = 1 \cdot 10^{-7}$ sec⁻¹. The overall (composite) interfacial mass transfer coefficient K (cf [11]), for both I2 and CH3I, was taken to be $5 \cdot 10^{-5}$ m/s. In IODE, there must be input —for both volatile species, I2 and CH3I— also a value of $K' = P \cdot K$, where P is the volume partition coefficient of a species (constant for a given temperature) [12]. This number was calculated for known temperatures, being roughly ten times higher than K for I2 and about equal to K for CH3I.

Evaluations of the tree (in the sampling mode of EVNTRE runs) was done simultaneously both with and without modeling of the RI gas phase formation. In figures 2 and 3, these two cases have always the same symbols and are distinguished by filled (RI formation/destruction reactions switched on) versus unfilled (reactions off) inner space of the symbol. It can be seen that in our analyses switching the RI gas phase formation model on or off does not have a pronounced effect on changes in iodine volatility. One of the possible explanations (if our analyses are not completely wrong, of course) could be that the only source available for the RI formation in the current model, i.e. the ad-

sorbed I₂, is two small (for given boundary conditions in PHEBUS FPT1 test, such as dose rates in containment etc). The available I₂ is probably not enough of iodine to see any big effect on iodine volatility from these reactions, taking into account reasonable values of sorption constants and other kinetic limitations. If the model allowed for an extra source of iodine for the RI formation, such as iodine wall deposits from aerosols, the result could be different —cf. FPT1 iodine calculations for ISP-46 by Krausmann [19].

Much more pronounced effect on iodine volatility, at least in this work, seems to have the way in which the AgI formation is formulated. If we use just the reaction of Ag with I₂ (corresponds to 0%Ag_{ox} in IODE) we will see the calculated fractions of volatile iodine in atmosphere above $2 \cdot 10^{-3}$ (at the end of experiment). In such a way, the AgI formation is modeled, for instance, in IMOD and LIRIC codes [7]. If we use, in addition, the reaction of I- with oxidized Ag (2%Ag_{ox} or 10%Ag_{ox}) its impact is huge, at least for the base case (BASE01 in Fig.2). Similar behavior was observed with the IODE code in the parametric calculations for ISP-41 Follow-up exercise [7]. This result gives support to the expected picture: complete blockage of the "free" iodine in the sump water in case of 10%AG_OX but, as there is not any other strong type of mechanism of volatile iodine formation, the corresponding volatile fractions in atmosphere are low when compared to experimental values. A value of 100m²/kg for the IODE input parameter SPAG (specific surface area of silver) has been used in accordance with the FPT1 validation data. In preliminary calculations, changes to this number did not seem to have much impact on calculated results.

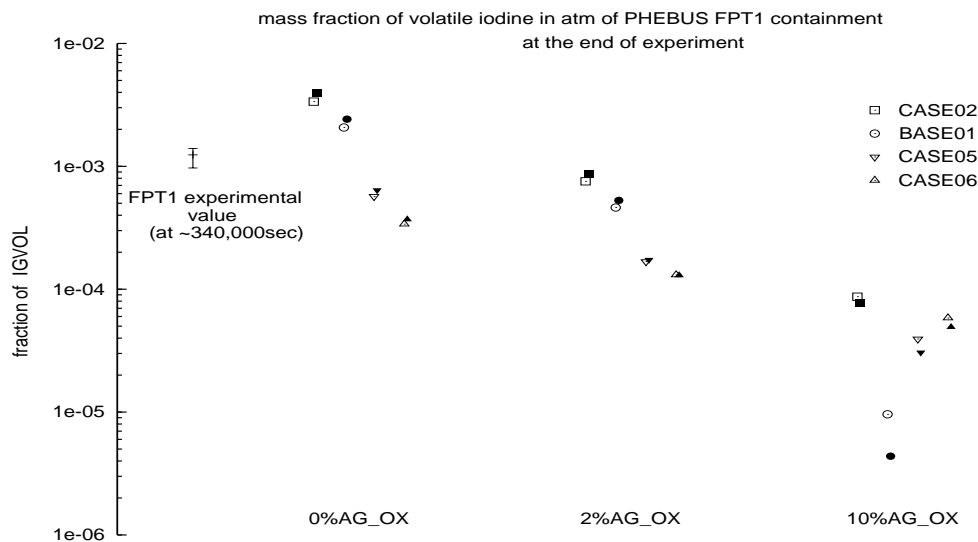


Fig. 2 Results of the sensitivity study —see description in text
Calculated values of IGVOL for the end of PHEBUS FPT1 experiment
(IGVOL is the ratio of the amount of volatile iodine forms in the atmosphere to the total amount of iodine in containment); experimental value was taken from [17] (Fig 5.4-18)

Sensitivity calculations in Fig.2 have been performed with changing values of the overall mass transfer coefficient, K , of I₂ and RI (CH₃I) for the interfacial transfer between water and the atmosphere. The calculations are denoted by labels CASE02 for $K = 10^{-4}$ m/s (this represents very rapid transfer of volatiles between water and the atmosphere), CASE05 for $K = 10^{-5}$ m/s, and CASE06 for $K = 5 \cdot 10^{-6}$ m/s. The effect on iodine volatility is maybe not so high as the effect of silver reactions. It should be noted, however, that the studied changes to the AgI formation definition, as modeled in IODE, are relatively dramatic.

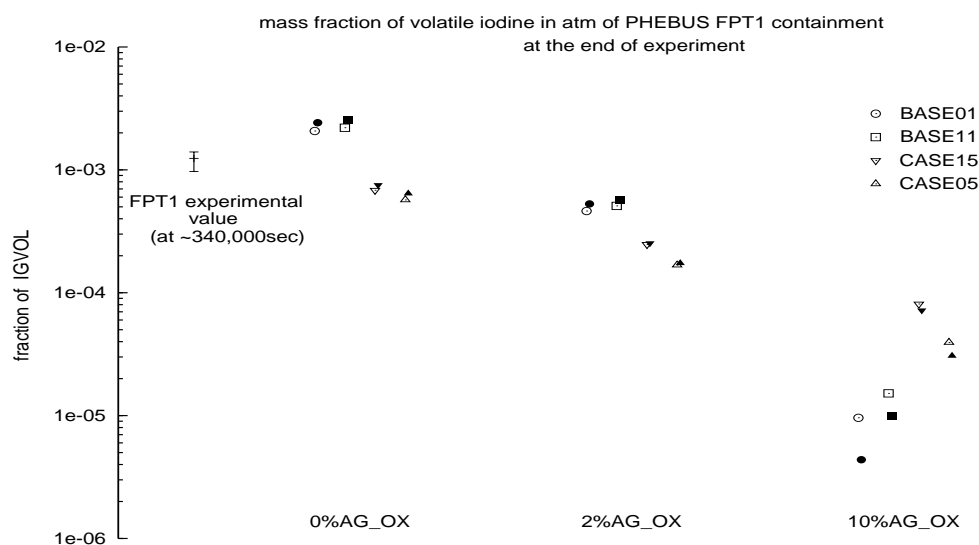


Fig. 3 Results of the sensitivity study —see description in text

Calculated values of IGVOL for the end of PHEBUS FPT1 experiment

(IGVOL is the ratio of the amount of volatile iodine forms in the atmosphere to the total amount of iodine in containment); experimental value was taken from [17] (Fig 5.4-18)

In Fig.3 there is shown a sensitivity of the calculated volatile iodine fractions to a change in the I₂ desorption constant for the deposition on stainless steel exposed to the gas phase. The number was changed, for BASE_CASE (BASE01) and for CASE05, to be one order of magnitude higher: from 10^{-7} sec⁻¹ to 10^{-6} sec⁻¹ (BASE11 and CASE15) in order to have more I₂ ready for reactions in atmosphere. The effect was more pronounced only for the 10%AG_OX case (which was expected) —compare CASE05 and CASE15. The total volatile iodine fraction remained still relatively low when compared to the experimental value.

4. Conclusions

A simple probabilistic method for evaluation of the containment speciation and transport of radioiodine at an accident is proposed. The incentive for this work was, generally, the poor agreement of deterministic analyses of iodine behavior performed with different codes and models, as demonstrated e.g. by the calculations for the ISP-41 Follow-up exercise [8]. The iodine behavior in containment has been described in this work with the help of a small event tree which was being processed by the EVNTRE code. The ambition was to have such event tree which would comprise all the important characteristics (values of parameters etc) and processes affecting the speciation and transport of iodine in containment. The approach with the containment iodine event tree was applied to iodine behavior analysis for the integral PHEBUS FPT1 experiment. The event tree was used for a simple sensitivity study, with direct call from within the tree (from EVNTRE) to a containment iodine code (to calculate the speciation of iodine in PHEBUS containment). The final goal of the presented approach, however, will be thorough analyses of the uncertainties linked with processes which govern the iodine behavior at an accident. Using of the iodine codes in this task need not be necessarily useful in all instances. Simplified models of the processes in question could be used instead. Such models also have a potential to facilitate complex applications of the probabilistic approach, such as iodine behavior description for the purposes of the whole-plant PRA analyses.

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