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**NUCLEAR ENERGY AGENCY**
**COMMITTEE ON THE SAFETY OF NUCLEAR INSTALLATIONS**

**STATE OF THE ART REPORT ON IODINE CHEMISTRY**

*Working Group on Analysis and Management of Accidents (WGAMA)*

*Members of the Writing Group:*

*B. Clément (IRSN), Coordinator*
*L. Cantrel (IRSN)*
*G. Ducros (CEA)*
*F. Funke (FRAMATOME-ANP)*
*L. Herranz (CIEMAT)*
*A. Rydl (NRI)*
*G. Weber (GRS)*
*C. Wren (UWO, formerly AECL)*

For further information regarding this document please contact Carlo.Vitanza@OECD.org

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# EXECUTIVE SUMMARY

From the beginning of nuclear power plant developments, it has been realised that a severe accident in which the normal core cooling is lost could lead to fuel elements melting and fission product release beyond the plant limits. Nuclear power plants are designed with engineering systems and associated operational procedures that provide an in-depth defence against such accidents. A good understanding of iodine behaviour is required for the analysis of severe accident consequences because Iodine is a major contributor to the potential source term to the environment. Qualified tools for the calculation of the iodine source term are also needed to perform meaningful risk analyses and make decisions in the field of accident management, mitigation measures and emergency procedures;

For a long time, the Nuclear Energy Agency of the OECD has recognised the importance of iodine behaviour and has organised Workshops and International Standard problems on the subject. In the meantime, experimental and modelling efforts have been pursued, aiming at the improvement of the knowledge and the predictive capability of calculation tools. This status paper reviews the insights gained and evaluates the progress made during the last ten years in an attempt to shedding light on the current status of the understanding of iodine behaviour.

## Iodine release from fuel

At the beginning of 80's, the knowledge about iodine release from fuel was primarily derived from analytical experiments where fuel samples were heated at temperatures not exceeding 1800°C. In these conditions, the release of iodine ranged from 20 to 50%. During the 90's, experiments have been performed up to or near fuel melting, resulting in a near total release. This is now reflected in models used in calculation codes for iodine release from fuel.

## Iodine transport in the RCS

According to the studies performed after the TMI2 accident, it was generally considered that iodine would be mostly transported in the RCS as caesium iodide, and suggested it could be partly emitted in volatile form in the containment. The Phebus-FP results in the 90's showed that caesium iodide is not the only likely species, especially for those reactors using silver-indium-cadmium control rods.

The early presence of gaseous iodine in the containment model of Phebus experiments led to the hypothesis that a fraction of the iodine was emitted into the containment in a gaseous form. It is suspected that this is due to non-equilibrium chemical reactions. Preliminary kinetic release models have been proposed but modelling efforts suffer from a lack of data. A new experimental programme has been launched to try solving the issue.

## Iodine behaviour in the containment – thermal-hydraulics and aerosol physics

Most of the iodine enters the containment building as metal-iodides that are incorporated into agglomerated aerosol particles containing other fission product and structural material. The airborne concentration of these iodine-bearing particles is governed by aerosol physics, the main depletion mechanisms being gravitational settling, diffusiophoresis and thermophoresis. These processes depend on thermal-hydraulics in the containment building, for instance steam condensation. Many of the numerical

codes allow calculating the deposition of iodine-bearing particles on various surfaces, dry or wet, and their transfer to the sump water. More recently, tighter coupling between thermal-hydraulics, aerosol and iodine chemistry models has been achieved and could be validated on the THAI large-scale multi-compartment experiments.

**Iodine behaviour in the containment – liquid phase chemistry**

Most of metal-iodides, with the exception of silver iodide, are soluble and will be readily dissolved in the sump water, to form iodide ions. The large amount of fission products released into the aqueous phase will yield an important dose rate in the water, resulting in water radiolysis products such as $\cdot$OH, O2-radicals etc. Iodide ions will be oxidised thermally and radiolytically to form volatile $I_2$. A large number of reactions such as hydrolysis are involved and a large number of species are formed. The formation of $I_2$ depends on a number of parameters, the most important being the pH – should the PH be alkaline as the result of engineering features, the rate of production of volatile $I_2$ will be very low. The sump water also contains organics released by materials such as paints. The organic radicals will react with iodine to produce volatile and non volatile organic iodides. It should be noticed that in all cases, both formation and destruction reactions do exist.

All the above processes have been extensively studied in the last fifteen years both theoretically and experimentally (mostly by means of laboratory experiments done at well defined conditions and using gamma radiation), and are reasonably well understood. One of the important mechanisms that is still being discussed regards the formation of organic iodides in the aqueous phase and the effect of the type and energy of radiation.

More recently, it has been realised in the first two Phebus tests that silver, if in excess as compared to iodine in the sump water, seems to efficiently suppress the iodine volatility, although the chemical and physical form of the silver reacting with iodine is not well characterized.

Two different complementary approaches are used in iodine behaviour numerical tools to describe iodine chemistry in the liquid phase. On the one hand, mechanistic codes such as LIRIC or INSPECT, model a very large number of reaction and species, being thus very useful for detailed studies. On the other hand, so-called semi-empirical codes, such as IODE, IMOD or IMPAIR, model the main iodine species with a limited set of reactions. The second kind of models is generally used in the integral severe accident codes, e.g. ASTEC.

The ISP 41 exercise on iodine behaviour codes showed significant differences between iodine models in the predicted overall production rate of volatile $I_2$ in the aqueous phase, with a tendency to overestimate at low pH and underestimate at high pH. The latter point is not so important in a safety perspective, as the production of volatile $I_2$ is very low in alkaline conditions. It should also be noticed that uncertainties on boundary conditions, such as pH evolution if uncontrolled and release rates of organics have an impact on the prediction by chemistry models.

Validation efforts for iodine behaviour models should be continued using the existing database and expanded to include forthcoming experiments such as EPICUR.

**Iodine behaviour in the containment - gas phase chemistry**

Volatile iodine will be present in the containment's atmosphere through two routes: from the RCS and from the sump water. To determine the kinetics of the second route, a good knowledge of mass transfer phenomena is essential.

Volatile iodine will be adsorbed at and desorbed from surfaces above the sump area. From a safety perspective, painted surfaces are among the most important especially for those plants with small sump volumes but with very large containment painted surface areas; their action on iodine behaviour is two-fold: they act as a sink for $I_2$ and as a source for volatile organic iodine. Radiation plays a strongly enhancing role, as it induces fast radiochemical reactions between iodine and the paints or paint components. The same approach is used by all the iodine codes to adsorption on and desorption from surfaces. The input parameters (adsorption velocity and desorption rate) depend on the nature of the surfaces and thermal-hydraulic conditions. The ISP exercises have evidenced a large spread in the values depending on the users.

Air radiolysis products such as ozone and nitrogen oxides would react with $I_2$ to form iodine oxides and nitroxides, leading primarily to non-volatile species. These effects were ignored in many codes due to the lack of experimental data. Experiments have more recently been performed that measured and allowed the development of models to simulate the decrease of $I_2$ concentration in an irradiated atmosphere as the result of these reactions. However, only high iodine concentrations of iodine were studied, and the validity of the extrapolation at low concentrations is not guaranteed. It is expected that the results from the current PARIS project will allow the development and the extension of current models. More recently, radiolytic destruction of gaseous methyl-iodide was studied, in conditions relevant to reactor situations. A mechanistic model was developed to help interpreting the experiments and understanding the main reactions. An empirical model was also developed and incorporated in some codes.

Gaseous iodine removal by spray was studied in large-scale facilities in the 60's and 70's, yielding fractional removal rates by the observation of exponential decay of gaseous iodine concentration. In the 90's, more detailed experiments were realised, allowing the development of models that take into account iodine chemistry within the droplets and mass transfer from the gas to the droplets.

**Iodine behaviour in the containment- exchanges between sump and atmosphere**

At the interface between the sump water and the atmosphere, the concentration ratio between concentrations of volatile species in both media obeys the Henry's law. The mass transfer phenomena between the two phases are governed by diffusion and mainly natural convection induced by thermal gradients. This is, in general, described by a two-film model in iodine codes, using user specified parameters. A difficulty arises, however, when extrapolating results from small-scale experiments to reactor scale. Recently, improvements have been made using the coupling between thermal-hydraulic and iodine codes and general correlations from literature. It was also confirmed that the two-film model is not valid in evaporating conditions. Specific experiments were performed to obtain data under evaporating conditions and a new model for mass transfer under these conditions was proposed.

**Iodine source term to the environment**

The phenomenological understanding of iodine behaviour and the iodine behaviour models allow for the prediction of the time-dependent evolution of aerosol and gaseous iodine concentration in the atmosphere of the containment. Several controlled and uncontrolled pathways exist for activity release to the environment (we do not consider here early containment failure). The first one is the uncontrolled path which is associated with the natural leaks of containment in accident situations. The retention in the leakage paths is not well known and generally not credited for in the safety studies aiming at giving a conservative value. The second one is a controlled release and is associated with containment venting through filters in case of overpressure, for those reactors using such a procedure. Certain venting procedures involve filters having a very high retention for aerosols, a low one for $I_2$ and a negligible one for organic iodides. The third uncontrolled release path is associated to basemat penetration by molten

corium/concrete interaction. The filtering medium is then the soil and the assumption that retention is the same as for filtered venting is often made.

A fourth pathway is associated with containment by-pass sequences. The risk-dominant sequence involves a pathway involving the secondary side of a PWR steam generator (SG) containing one or more ruptured tubes (SGTR).The severe accident may be initiated by the SGTR or the pathway is initiated due to the severe accident. Concerning severe accident SGTRs, some of the current safety studies consider a small retention in the SG secondary side. Knowledge about retention of aerosols has been enhanced by the results of the EU's 5. Framework Project SGTR and will be further improved by the ongoing ARTIST project carried out at PSI Switzerland. There is however a lack of data on iodine behaviour that has not been specifically addressed.

**Main conclusions**

The large effort achieved so far, both in the experimental and modelling fields, has resulted in an improved understanding of iodine behaviour in severe accident conditions, which in turn appears in the current models already incorporated in the codes used for safety studies. The main iodine species and the dominant routes for their formation have been identified.

The evolution of gaseous iodine in the atmosphere of the containment, which has the main bearing on the risk-perspective, is mainly governed by:

- the fraction of iodine injected as a gaseous form from the RCS into the containment,

- the radiolytically induced formation of volatile iodine species in the sump water, and their release into the containment atmosphere by mass transfer,

- the adsorption and desorption of $I_2$ on painted and non-painted containment surfaces including the potential formation of organic iodides by paint-iodine reactions,

- the interactions of volatile iodine with air radiolysis products and the fate of the resulting oxidation products.

These phenomena are modelled in codes with various degrees of sophistication. Mechanistic codes are generally used for detailed studies and thorough understanding, while empirical ones are generally incorporated in system-level codes. The models and codes have been validated against separate-effect tests, intermediate-scale and integral experiments. They depend on input parameters that are either user-defined or provided by other models such as those dealing with thermal-hydraulics or aerosol physics.

The degree of confidence we can put in the predictive capability of model and codes depend on the adequacy of the underlying knowledge of phenomena and on their validation status.

A number of experimental programs currently undergoing or in planning stage address a number of issues which need further knowledge:

- high temperature  gas phase chemistry with an objective to characterise the iodine speciation as well as the formation of volatile iodine in the primary circuit; this is the objective of the newly launched CHIP programme,

- the desorption rate of organic iodide from painted surfaces; this is addressed in the ongoing EPICUR programme,

- effect of certain radiation induced reactions and impurities ($NO_2^-$, $NO_3^-$, $Cl^-$, $H_2O_2$) on the iodine in the aqueous phase (addressed in an experimental program currently conducted at PSI)

- the interactions of iodide ions with painted surfaces after steam condensation,

- the effect of impurities on oxidation and reduction of iodine species in liquid phase,

- the iodine behaviour in the secondary side of steam generator,

- the interactions of volatile iodine with air radiolysis products, especially the nature and fate of oxidation products.

Concerning the validation, the effort is being and must be further pursued, especially for:

- the homogeneous formation of organic iodide in liquid phase,

- the organic iodide formation by reaction with submerged paints.

A number of boundary conditions are required as input for iodine chemistry calculations, and some of them are not predicted with sufficient accuracy. This is particularly the case for the influence on pH of the amount and nature of materials released into the containment. Particular emphasis should be placed on the silver oxidation state when arriving into the sump, conditions leading to further silver oxidation in the sump as well as the transient behaviour of the silver particles in the sump (homogenously mixed distribution versus settlement) its further evolution. The current PARIS programme is expected to provide information on the last item.

The iodine chemistry codes also suffer from the fact that the values of some crucial parameters are user-defined and not internally calculated. This is due to the fact that the available data are not yet generic enough to cover a variety of situations leading to the establishing universal models. Improvements have been made in certain codes by using the coupling between thermal-hydraulic and iodine chemistry calculations for mass transfer coefficients. This is not the case for adsorption velocities and desorption rates of volatile iodine to/from various different surfaces. It would be valuable that a commonly agreed set of values for these parameters be agreed upon, depending on prevailing conditions, in order to provide a clear guidance for code users.

Finally, it would be desirable that a common understanding is reached on the ultimate goal in terms of predictive capability, e.g. on whether code predictions of gaseous iodine concentration within an order of magnitude could be acceptable or not. This may be dependent on the level of concentration, i.e., lower accuracy for low concentration, as well as on the nature (conservative or best-estimate) of the safety studies. It may also be reactor-dependent.

# 1. INTRODUCTION

An accident in which the normal core cooling is lost could lead to fuel elements melting and fission product release beyond the plant limits. Nuclear power plants are designed with engineering systems and associated operational procedures which provide an in-depth defence against such accidents. Iodine is a major contributor to the potential source term to the environment, thus a good understanding of its behaviour and validated calculation tools are required to perform meaningful risk analyses and make decisions in the field of accident management, mitigation measures and emergency procedures;

The Committee on the Safety of the Nuclear Installations (CSNI) of the OECD Nuclear Energy Agency has recognised the importance of the subject for a long time and four workshops on "the chemistry of iodine in reactor accidents" between 1974 and 1996 [1, 2, 3, 4] and a workshop on "iodine aspects of severe accident management" in 1999 [5] were organised. In 2000, a thorough review entitled "insights into the control of the release of iodine, caesium, strontium and other fission products in the containment by severe accident management was published [6]. More recently, two International Standard problems ISP 41 [7,8, 9] and ISP 46 [10], dealing with iodine chemistry have been successfully completed. In the meantime, experimental and modelling efforts have been pursued, aiming at the improvement of the knowledge and the predictive capability of numerical tools. This status paper reviews the insights gained and evaluates the progress made during the last ten years in an attempt to shed light on the present situation.

A number of experimental programmes, involving separate-effect and integral tests have been carried out during the last decade, providing new and valuable results that have improved our understanding of iodine phenomena. A modelling effort has also been pursued in order to encapsulate the acquired knowledge in the calculation tools prepared for predicting the iodine behaviour under severe accident conditions. In view of the progress made, the Working Group on Analysis and Management of Accidents (GAMA) considered the necessity of producing a status paper on iodine chemistry, with the following objectives:

− to review insights gained and evaluate the progress made during the last 10 years on the understanding of phenomena governing iodine chemistry and release in the case of a reactor severe accident,

− to evaluate the current status of iodine chemistry knowledge and tools used for source term prediction in connection with accident management and emergency planning, under various reactor conditions, to identify the remaining weaknesses, discuss the reactor safety relevance of these issues and make recommendations as necessary.

This paper aims at shedding light on the present situation, helping end-users and decision makers to adequately address questions related (i) to iodine behaviour under severe accident conditions (ii) to essential programmes of work in this area.

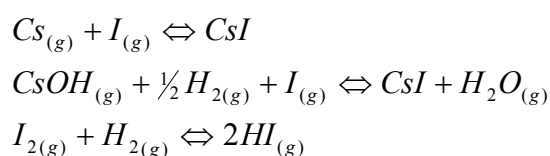## 2. OVERALL DESCRIPTION OF IODINE BEHAVIOUR IN SEVERE ACCIDENTS

At the beginning of the 60's, the reactor site criteria of most present nuclear reactors were set. Given iodine potential radiological impact due to the $I^{131}$ isotope, its significant fission yield and its fast and almost complete volatilisation at high temperature, some assumptions were made concerning its behaviour under accident conditions [11]. These are:

- Half of the iodine core inventory is instantaneously available in the containment

- Half of the in-containment iodine is deposited onto surfaces rapidly.

- Most of the iodine entering the containment (91%) was supposed to be in the form of volatile molecular iodine ($I_2$) and the rest were almost equally distributed in particulate form (5%) and organic species (4%).

Since the accident of Three Mile Island a vast amount of research dealt with severe accident source terms. The main outcome was summarised by Soffer et al. [12] in 1995. As far as iodine is concerned, the NUREG-1465 report stated that:

- Around 60-70% of iodine core inventory would enter the containment.

- Iodine source to the containment would last 4-5 hours.

- Most of iodine arriving at the containment (95%) would be in particulate form as caesium iodide (CsI) and the remaining 5% would consist of vapour species (a mixture of atomic iodine (I) and hydrogen iodide (HI)).

This iodine scenario resulted from numerous studies based on thermodynamic considerations where the following reactions played a major role:

$$Cs_{(g)} + I_{(g)} \Leftrightarrow CsI$$
$$CsOH_{(g)} + \tfrac{1}{2} H_{2(g)} + I_{(g)} \Leftrightarrow CsI + H_2O_{(g)}$$
$$I_{2(g)} + H_{2(g)} \Leftrightarrow 2HI_{(g)}$$

Identification of the presence of CsI in the effluent lines of TREAT [13] and PBF tests on reactor fuels degrading in steam has been reported [14]. Nonetheless, other possible chemical forms of iodine were identified at that time and, in the light of new research results obtained during last decade some criticism has been raised with respect to studies merely based on thermodynamics.

Recent experimental investigations in the VERCORS and Phébus-FP programmes [15,16] have confirmed that iodine is highly volatile and would be released almost completely during the first phases of a severe accident. Its release from the fuel in gaseous form [17,18], probably as atomic iodine [19], and the chemistry determining its speciation and the transport through the primary circuit piping are known to be determined by the thermo-hydraulic conditions, the composition of the carrier gas (steam and hydrogen) and the potential chemical reactions with other elements emitted from the core.

As said above, thermo-chemical studies predict formation of very stable alkaline halides, such as CsI or rubidium iodide (RbI), but no experimental confirmation is yet available. Recent studies [20] suggest

that kinetic considerations could result in other potential iodine species, like silver iodide (AgI), indium iodide (InI) and cadmium iodide ($CdI_2$). Regardless of these potential iodine compounds as the temperature decreases in the Reactor Coolant System (RCS), reactions of metal iodide vapours with aerosols originating from structural and control materials and/or other fission products as well as vapour condensation on their surfaces would result in iodine-bearing particles. A substantial fraction of all the released iodine from the fuel could eventually reach the containment (60-70% of the initial core iodine inventory). The data from experiments FPT0 and FPT1 of the PHEBUS-FP programme [16] indicated that a significant fraction of iodine (from to 2 to 4% of bundle inventory) reached the containment in vapour form; theoretical studies [21] postulate HI and to a less extent $CdI_2$ as candidate vapour compounds.

Assuming most iodine enters containment in the form of suspended aerosols containing metal iodide, once in the containment the largest fraction of iodine would mainly settle and also deposit by diffusiophoresis under aerosol laws of physics and, in the short term, the in-containment gaseous iodine inventory can be accepted as dominated by gaseous iodine released from the RCS.

Iodine chemistry within the containment has been thoroughly described by Wren et al. [22] and Krausmann [23]. A simple sketch is displayed in Figure 1.



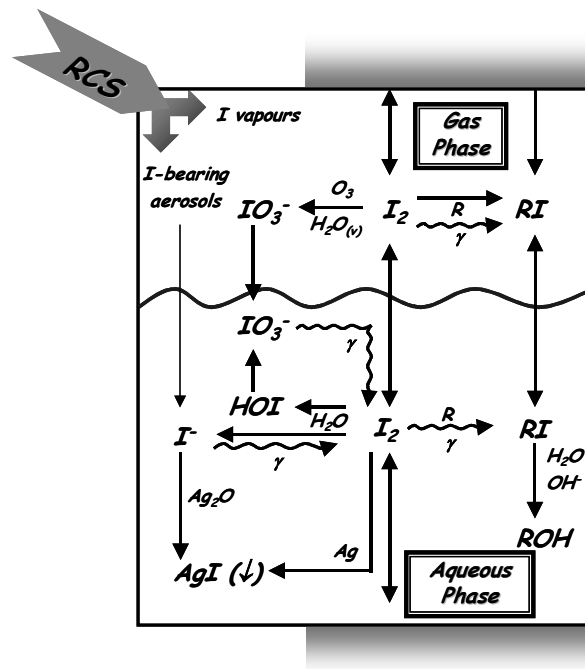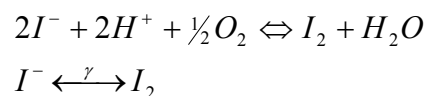**Figure 1. Simplified diagram of iodine transformations within the containment**

Iodine embedded in soluble aerosols would dissolve in water ponds and would release iodide ions ($I^-$). These $I^-$ anions could become slowly or rapidly oxidised to $I_2$ by thermal and by radiolytic reactions respectively:

$$2I^- + 2H^+ + \tfrac{1}{2}O_2 \Leftrightarrow I_2 + H_2O$$

$$I^- \xleftarrow{\gamma} I_2$$

The extent of $I_2$ production would depend upon sump conditions, like pH (acidic conditions being favourable), dose rate and temperature. As a result of $I_2$ volatility, an $I_2$ fraction could return to the containment atmosphere. In addition, the iodine inventory in the sump (i.e., $I_2$ and/or $I^-$) could react with dissolved or suspended organic impurities in water or with immersed painted surfaces to form organic iodides (RI). Some of the produced organic iodides are very volatile and could increase the gaseous iodine inventory in the containment atmosphere:

$$I_2 + 2CH_3R \Leftrightarrow 2CH_3I + 2R$$

$$(I^-, I_2) + S_{pa\,int} \xleftarrow{\gamma} RI$$
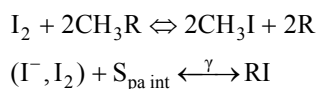
Conversely, hydrolytic as well as radiolytic reactions would destroy RI. Therefore, the aqueous chemistry of iodine could result in volatile iodine species that would eventually result in a gas source to the containment atmosphere. Other further oxidised iodine species such as iodate, $IO_3^-$ might also appear in aqueous pools as a consequence of $I_2$ hydrolysis and subsequent decomposition of hypoiodous acid (HOI):

$$I_2 + H_2O \Leftrightarrow I^- + HOI + H^+$$

$$3HOI \Leftrightarrow IO_3^- + 2I^- + 3H^+$$
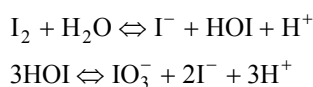
However, iodate could be reduced to $I_2$ thermally via the Dushman reaction as well as in the presence of radiation fields respectively.

$$2IO_3^- \xleftarrow{\gamma} I_2 + 3O_2$$
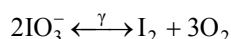
Finally, another major element that could significantly affect iodine chemical behaviour in the sump is silver (Ag). Ag is known to readily react with $I_2$ and $I^-$ either in metallic or oxidised form to yield a precipitate that would behave like a sink of iodine in the sump:

$$2Ag + I_2 \Leftrightarrow 2AgI (\downarrow)$$

$$Ag_2O + 2I^- + 2H^+ \Leftrightarrow 2AgI(\downarrow) + H_2O$$
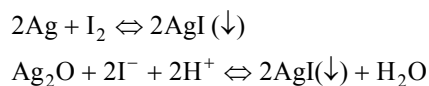
The second reaction is very effective and eliminates the formation of volatile iodine; however, its effectiveness depends on the availability of the silver oxide. Silver, due to its very low vapour pressure, constitutes the seed as the vaporised fuel or other structural material, e.g. Sn, for the formation of aerosol particles in the reactor pressure vessel and further in the hot leg. Therefore, under accident conditions, the following main items determine the availability of non-oxidised and oxidised silver and hence effectiveness of the two reaction sets shown above: a) amount of pure silver released into the containment, which is not fully covered by layers of other fission products and structural materials, b) its level of oxidation before the pure silver particles enter into the sump, c) extent of possible further silver surface oxidation in the sump if pure silver particles exist, and finally d) whether such bare or oxidized silver particles stay homogenously distributed throughout but not settled in the sump water. Furthermore, in-situ β-irradiation experiments [24, 25] demonstrated that AgI colloids formed from the reaction nr. 2 decompose depending on the prevailing conditions.

Physical and chemical phenomena could remove gaseous $I_2$ from the containment atmosphere. Sorption (/desorption) occurring on the surfaces of the containment walls and the airborne aerosol particles would eventually result in a decrease in the $I_2$ concentration. Steam condensation could additionally enhance the diffusion of iodine on such surfaces. Furthermore oxidising agents, like ozone ($O_3$), or presence of gaseous organic compounds can transform $I_2$ into other chemical species (as introduced above for the aqueous phase).

$$2\,I_2 + O_3 \xleftarrow{H_2O} 4IO_3^-$$
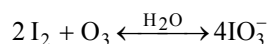
# 3. IODINE PHENOMENA

## 3.1. IODINE RELEASE FROM FUEL AND BEHAVIOUR IN THE RCS

### 3.1.1. Iodine inventory and activity

The amount of iodine created inside the fuel during power plant operation is relatively small with regard to other FPs: on the 2000 kg of FPs within a PWR 900 core at its equilibrium, the total iodine mass represents only 12 kg, about ten times less than caesium for instance. On the other hand, due to its numerous short half-life isotopes, total iodine activity is one of the most important among other FPs over the first few tens hours from the core shutdown, around ten times more than caesium. The main short half life isotopes are $^{131}$I (8 days), $^{132}$I (2.3 hours, but "effective half life" of 3.3 days imposed by its parent $^{132}$Te), $^{133}$I (20.8 hours), $^{134}$I (0.9 hour) and $^{135}$I (6,6 hours).

### 3.1.2. Iodine release from fuel

*Status of knowledge early 80's and main improvements since*

At the beginning of the 1980 decade, the knowledge of iodine release from fuel was essentially due to some analytical experiments, in which short fuel samples were heated between 1500°C and 2400°C. Those included: SASCHA [26], performed in Germany on fuels with implanted FP substitutes, HI performed in USA on real irradiated fuels, HEVA [27] performed in France on irradiated and re-irradiated fuels[1]. Under these conditions iodine release ranged between 20% and 50% with a steady state fuel sample during the entire test. It is only in the early 90's, with experiments that examined more severe conditions (higher temperature including or not fuel melting) that higher, nearly 100% iodine releases have been quantified. Examples of these experiments are the VI program performed in USA (particularly from VI-3 test at 2300°C), VERCORS [15] program performed in France (particularly form VERCORS 3 test performed at 2300°C), VEGA [27a] programme performed in Japan (particularly VEGA-6 test performed at 2500C), PHEBUS [17] experiments, etc.

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[1] The spent or fresh fuel segments before subjected to high temperature were re-/irradiated at low power in a MTR reactor allowing re-/creation of short half-life fission product nuclides without any release during the in pile phase for the use of on-line gamma spectrometry later. On-line gamma spectrometry employed during the heating phase conducted in an hot cell facilitated an accurate measurement of the released important fission product nuclides Other tests (SASCHA, HI …) employed off-line chemical analysis and hence provided less accurate data in comparison with that produced by the HEVA program.
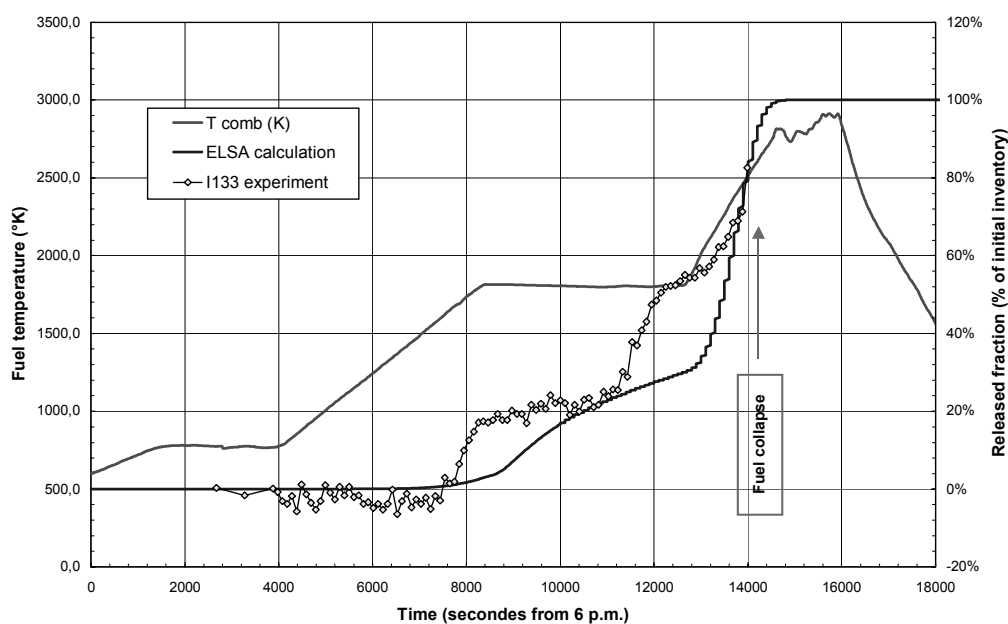
**Figure 2: Iodine release in VERCORS HT1 test**

Today iodine release from fuel for the case of severe accident up to fuel melting temperature can be considered to be quantitative with a very small uncertainty. This release occurs primarily (80-90%) when the fuel is intact and for a limited part (10-20%) during fuel relocation and melting as illustrated in Figure 2 (VERCORS HT1 test [15]).

*Modelling aspects*

Concerning FP release modelling, it is clear now that codes predict a correct value for total iodine release at high temperature. Nevertheless improvements could still be obtained concerning release kinetics at intermediate temperature (see figure 2) where calculation underestimates iodine kinetics. This trend is observed in the correlation models like ELSA as well as in more mechanistic models like those implemented in MFPR code. A better description of the iodine fraction located in the pellet-clad gap and in intragranular position within the fuel, at the end of the LWR base irradiation, could probably improve the present models.

### 3.1.3 Transport through the primary circuit

In the earlier safety studies conducted 10 years ago, it was usually assumed that most of iodine released during an accident would reach the containment as CsI aerosol. The rationale for the formation of CsI as the bulk iodine species is that caesium and iodine are released simultaneously with about the same kinetics. Since the amount of caesium released is about 10 times larger than that of iodine the formation of CsI is favoured in a pure steam environment without other constituents of core degradation. Once CsI aerosol particles are released into the containment it was assumed that the bulk of CsI particles settle to the sump. CsI is a soluble compound, therefore CsI aerosol particles instantaneously dissociate into $Cs^+$ cation and $I^-$ anion in the sump.

The understanding of iodine transport was mainly based on experimental results from TREAT and PBF experiments [13, 14] and on the work performed by Elrick and Sallach (see e.g. [28]) further extended by data coming from the FALCON programme [29]. In addition to the behaviour of the Cs-I-O-H system, the influence of boric acid and interactions between vapours and surfaces were studied. In particular, the

role of boron was highlighted, as the formation of caesium borate could inhibit the formation of caesium iodide and thus promote the formation of more volatile forms of iodine. The JAERI (now JAEA) WIND project also confirmed the influence of boric acid through tests where it reacted with CsI at high temperature (>600K) to produce more volatile iodine forms [27b, 27c].

All transport codes, like VICTORIA or SOPHAEROS for example, model the aerosol physics and predict chemical composition by using equilibrium calculations. Only few attempts [30, 20] have been made to examine the influence of kinetic reactions on chemical speciation. The preliminary conclusions of these attempts seem to indicate that the kinetics could play an important role on iodine distribution within the RCS.

Before PHEBUS-FP results were available, CsI was predicted to be the large dominant form of iodine vapours or aerosols in the primary circuit. The silver indium cadmium control rod degradation and hence the release of silver were not modelled.

Certain fission products and structural materials can modify directly or indirectly the iodine chemical speciation in the primary circuit. Integral experiments involving real fuel, control rod and structural materials under prototypical severe accident conditions have provided results, although very complicated to interpret, most useful to understand the context in this respect. Therefore, the main experimental results available from TMI-2 accident occurred 1979 in USA and from the severe accident integral test programme Phebus FP [17] will be introduced below briefly but not the ones from numerous separate effect small or large scale experiments.

### Experimental results

### Three Mile Island accident (TMI-2)

According to the studies carried out on the TMI-2 accident [31], it was suggested that iodine could be emitted partly in volatile form into the containment. Due to the stuck open pressuriser power operated relief valve, the released fission products in gaseous and particulate forms were transported through the reactor coolant system and flowed through the pressuriser [32] and released out into the containment. Since the pressuriser was full of water certain amount of soluble fission products must have been retained in the pressuriser water by pool scrubbing. Since HI and CsI are very soluble iodine species, it was not possible to attribute the main iodine species as CsI or a mixture of CsI and HI before the particles/gas entered into the pressuriser. Similarly it was also not possible to know the form and the speciation of iodine released into the containment Evaluations concluded that the main iodine species in the containment atmosphere was the organic iodides.

### PHEBUS-PF Programme

The PHEBUS FP programme is a major international programme co-operation investigating main phenomena occurring during a severe accident in a PWR. The PHEBUS tests aimed at simulating a large-break loss-of-coolant accident with a rupture located in the cold leg of the primary circuit. PHEBUS results [33,34,35] were important for the transport aspects for the three main reasons:

 − Firstly, they highlighted the fact that CsI is not the only iodine species but other species can be generated. Phebus results highlighted the importance of modelling the silver indium cadmium control rod degradation and hence their release as well as accurate prediction of aerosol composition leading to the determination of amount of pure silver particles.

- Secondly, and more importantly, a substantially high fraction of iodine was observed in the containment atmosphere right at the beginning of the two first Phebus tests (Table 1) that cannot be explained only by the production and release of volatile species from the liquid phase. Three explanations are envisioned; a) the volatile iodine was formed from an early production mechanism in the containment atmosphere, b) iodine in gaseous form was released directly from the RCS at a temperature as low as 150 $^{\circ}$C, and c) a possible combination of both possibilities. Without understanding the iodine speciation at the prototypical hot and cold leg conditions it is worth noticing that for the safety studies it is currently not possible to make an accurate prediction of possible early gaseous iodine concentration in the containment atmosphere if the likely explanation 'b' might have caused the observed situation.

- It has also been observed in the FPT2 test that the hot-leg iodine deposits were significantly re-vaporised after the steam starvation phase when oxidising conditions were again present. This phenomenon is important to understand and modelled for the potential delayed releases.

The PHEBUS FPT0, FPT1, FPT2 results are consistent with one another, and the main results are displayed in Table 1. The iodine detected in the hot leg is mainly in gas or vapour form. For example, in FPT1 test, depending on the progression of degradation and release from the fuel, the condensed iodine fraction collected on the 700°C filters ranged between 7% of the total iodine during the first oxidation phase to 13% during the late oxidation phase. This is due to the fact that the vapour pressure of various iodine species is still high enough at this temperature avoiding a significant vapour condensation on the existing aerosol seeds. This trend is similar for other tests. The most probable vapours are CsI, RbI, AgI, $InI_x$ or $CdI_2$. Specific instrumentation devices called TGTs (Thermal Gradient Tube) were set on the cold leg of the circuit in order to identify the chemical composition of the aerosols. Measurements were performed for FPT0 and FT2 tests but at the moment the iodine aerosols produced appear like a complex mixture of different species. Roughly, 20-30% of iodine flowing through the RCS is deposited in the first part of the steam generator mainly due to thermo-phoretic effects imposed by a sudden drop of the SG wall temperature from 700$^{\circ}$C to 150$^{\circ}$C.

Based on mass balance considerations, it can be estimated that a significantly high gaseous iodine fraction is present in the cold leg of the circuit (150°C) although the gas capsules used did not provide evidence supporting this conclusion.

In addition, apart from thermodynamic calculations [36], currently no experimental data is available to assess the impact of boron carbide ($B_4C$) on the iodine speciation and its transport within the RCS. Decomposition products of $B_4C$ could easily modify the iodine speciation within the RCS and containment atmosphere especially under radiation. The FPT3 test might produce information on this issue.

Finally, an ambitious experimental programme has just been launched at IRSN, called CHIP [37] (Chemistry Iodine within Primary circuit), in order to measure chemical speciation in relevant conditions of a RCS.

| location | Inventory | FPT0 | FPT1 | FPT2 |
|---|---|---|---|---|
| Fuel | fuel (g)<br>release (%) | 0.036<br>87 ± 13 | 1.12<br>84± 16 | 1.54<br>87± 4 |
| Point C (700°C) | percentage under gas or vapour form | ~ 90 | ~ 90 | ~ 90 |
| Point G (150°C) | percentage under gas or vapour form | < 2 | < 2 | < 2 |
| G.V | condensed percentage (/initial bundle inventory) | 24 ± 4 | 19.2 ± 3.6 | Data not open |
| TGT | Condensation temperature range | 430°C - 220°C | | 660-560°C<br>560-480°C<br>250-180°C<br>570-540°C |
| Point G | Gaseous percentage at 13508 s (CAPF723) | > 1,9 | | |
| | Gaseous percentage at 15233 s (CAPF704) | < 11 | | |
| | Gaseous percentage at 18138 s (CAPF724) | > 1,3 | | |
| Containment | Percentage of iodine (/ bundle inventory) | 63 ± 13 | 64 ± 13 | Consistent with previous tests |
| | Gaseous percentage (/ at the iodine inventory in the Containment) | 33 (13608 s) | 4.05 (11370 s)<br>0.19 (14300 s)<br>0.45 (15870 s)<br>0.12 (17400 s) | Data not open but consistent with FPT-1results |

**Table 1 : Experimental data about iodine transport and release for PHEBUS tests**

## 3.2. IODINE BEHAVIOUR IN THE CONTAINMENT - THERMAL-HYDRAULICS AND AEROSOL PHYSICS

### 3.2.1 Interactions of Iodine Chemistry with Thermal Hydraulics and Aerosol Physics

*Interaction processes*

In a severe accident the iodine source term is not only governed by its chemistry but it depends also on the thermal hydraulic conditions and aerosol processes taking place in the interaction processes are driven by:

−   Thermal hydraulic boundary conditions,

−   Aerosol behaviour of particulate iodine species,

−   Inter-compartmental iodine transport,

−   Iodine feedback on thermal hydraulics and aerosol physics.

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The main interaction processes are schematically shown in Figure 3. Temperature and other controlling thermal-hydraulic parameters govern the transfer of iodine between the aqueous and gas phase and to the surfaces. Several homogeneous and heterogeneous reactions have a significant dependence on the gas and water temperatures (s. chapters 3.2.2 and 3.2.3). The $I_2$ adsorption on surfaces additionally depends on the gas flow velocity along the walls. Under wet conditions the wall condensation rate drives the $I_2$ diffusion towards the surfaces. Other important boundary conditions for many reactions are indirectly dependent on the thermal hydraulics and aerosol behaviour. A crucial parameter directly affecting most of the reactions is and the local and bulk dose rate in the sump and atmosphere. The local dose rate depends on the fission product concentrations in the containment atmosphere, on the walls and in the sump. Since Phebus tests may suggest a strong influence of excess silver on the suppression of the iodine volatility, conditions expressed in Section 2 for silver to become effective should be known for a proper modelling.

The aerosol behaviour of the particulate iodine species (a great fraction of about initial 6 to 15 kg iodine inventory is bound to the particles in a containment of a PWR of 350 to 1300 MWe range) is mainly governed by the behaviour of the airborne aerosol mass (> 200 kg) containing other fission products and structural materials subjected to aerosol physics. Large amount of aerosols generated by the molten corium and concrete interactions (MCCI) (several 100 kgs) will further enhance the settlement rate of already existing airborne particles due to agglomeration. Another process for depletion of gaseous iodine involving airborne particles is a two-step depletion process; the first step is the adsorption of gaseous iodine species, i.e., $I_2$, HI, on airborne aerosol particles and the second step is the removal of iodine bearing aerosol particles together with the others from the air space by aerosol deposition and settling.

Atmospheric flows distribute the gaseous iodine as well as iodine bound to particles in the containment and transport the iodine to the adjacent buildings. Depending on the accident scenario and the containment geometry the iodine distribution in the atmosphere and the water pools may be rather inhomogeneous, e.g. in a stratified containment atmosphere differences of several orders of magnitude in the $I_2$-concentration are observed in the recent ThAI tests conducted in Germany.

Concentrations of reactants are the key controlling parameters in all iodine reactions. Therefore accurate estimation of local concentrations of the iodine species is important for iodine analyses especially if the iodine source term to the environment is very sensitive to the iodine concentration at the location of the containment leak.

Iodine isotopes, I-131, I-132 and I-132 produce a large amount of decay heat (roughly 50 % of the total decay heat) mostly by beta-irradiation. Depending on the location of high mass concentration of iodine bearing aerosols several effects of the decay heat can take place. Additional high local heat source to the structures, which might cause a substantial temperature increase of such structures leading to failure (steam generator tube rupture, surge line, hot/cold leg breaks); high local heat source to the containment atmosphere by the iodine bearing particles which might possibly modify the local humidity and surface temperature of particles and hence volume and wall condensation rates, which, in turn effectively alter the aerosol growth by hygroscopicity, and the steam condensation rates. Further feasible effect of local heat source in the containment atmosphere could be initiation or modification of natural convective flows within the containment atmosphere when the airborne aerosol particle concentration is substantially high enough. If iodine bearing aerosol particles deposited in large quantities in water pools, depending on the amount of heat source added by the iodine containing aerosol mass, pools could experience substantial evaporation and even reach boiling. Substantial steaming could alter the containment pressure. Other issue which is not yet considered is the possible effect of large local dose rates as a result of β- and α-emissions. Since higher dose rate (higher linear energy transfer (LET)) can be achieved by these radiation types than that achieved by the secondary electrons from gamma photons as used in the experimental investigations, certain surface reactions (e.g. paint – iodine reactions leading to formation of organic iodides) and

radiolytical stability of normally stable iodine species (tests conducted for the radiolytic stability of AgI under in-situ β-irradiation demonstrates such interesting effects) are prone to reconsiderations.
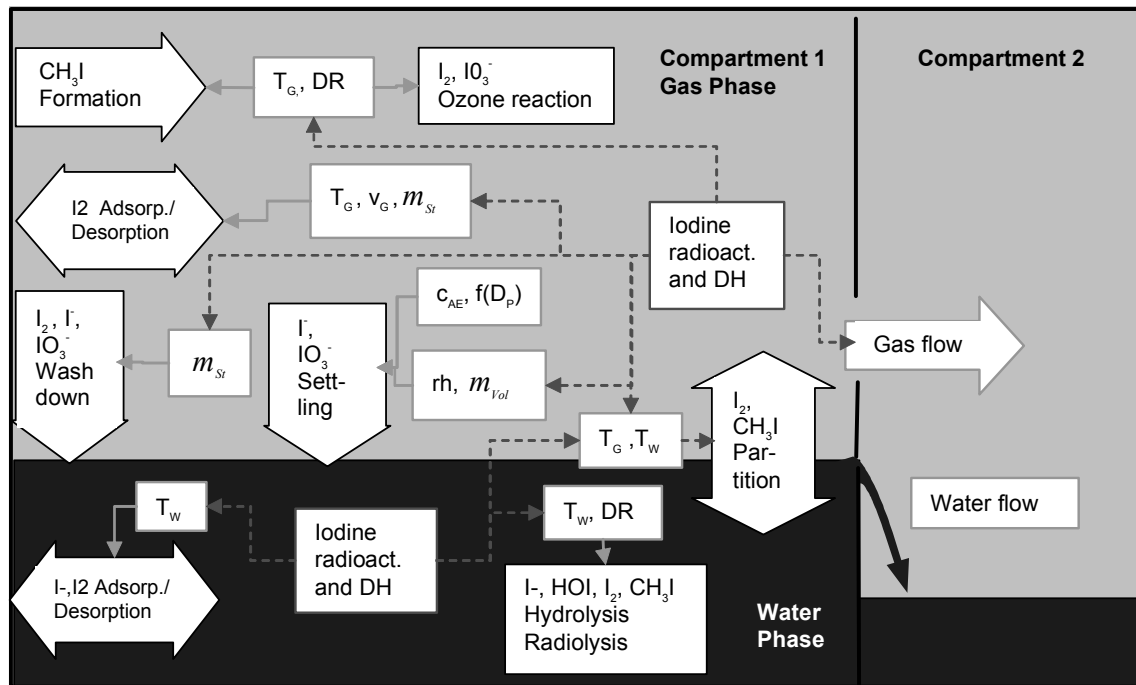


**Figure 3: All feasible main interrelation and feedback processes between iodine chemistry, thermal hydraulics and aerosol physics in a LWR containment. The envisioned impacts on iodine behaviour are marked green, the feedbacks from iodine are marked red. Legend: $T_G$ and $T_W$ gas and water temperatures, rh relative humidity, DR dose rate, $\dot{m}_{St}, \dot{m}_{Vol}$ wall and volume condensation rates, $v_G$ gas velocity along the wall, $c_{AE}$ aerosol concentration, $f(D_P)$ particle size distribution, DH decay heat**

All these interaction processes have to be considered to the extent it is possible for a comprehensive and higher quality iodine source term analysis. Deemed accuracy of the analysis is of course not only dependent on how accurate the iodine models are but on the uncertainties in the rest of the thermal-hydraulics and aerosol behaviour affecting the iodine behaviour.

*Progress and status*

Traditionally iodine chemistry models have been designed as stand-alone models applicable in a single control volume enclosing one gas and one water space allowing the transfer of volatile species in between, principally replicating the experimental apparatus with water pool and air space above. Thermal-hydraulic and aerosol boundary conditions have been delivered by separate calculations. The transfer of iodine species between various compartments of containment was not considered.

An important step was the development of the multi-compartment version IMPAIR-3 which allows for the first time to calculate the iodine transport between a chain of compartments [38]. With modifications for an arbitrary arrangement of compartments IMPAIR-3 was incorporated in the multi-compartment containment code FIPLOC [39]. This implementation offered a new quality of multi-compartment iodine calculations for containments. The accuracy of the iodine source term evaluation was significantly increased. FIPLOC is one of the precursor codes of COCOSYS [40].

At present iodine modules are integrated in several accident codes (Table 2) [41,42,43,44,38] All these multi-compartment codes make use of the lumped-parameter technique. By use of a suitable nodalisation the boundary conditions for the iodine problem, the iodine transport and certain interactions eluted above are described. An INSPECT type of iodine chemistry model for water pools is integrated in the semi-mechanistic and fast-running code MELCOR [45]. ASTEC contains semi-empirical code IODE. The feed back due to the high decay heat of iodine and to the possible high local dose as eluted previously have not been considered in these codes.

**Table 2: Accident codes with an integrated containment iodine model**

| Accident code | Integrated Iodine Model (Containment) |
|---|---|
| ASTEC | IODE |
| COCOSYS | AIM |
| MAAP | Iodine model |
| MELCOR | steady-state version of the INSPECT reaction chemistry |
| IMPACT/SAMPSON | Iodine model |
| ART | based on IMPAIR; tight coupling |

The aforementioned boundary conditions for the iodine problem can be provided in general with the necessary accuracy in each compartment. Exceptions are some thermal hydraulic parameters (relative humidity, volume condensation rate) which sometimes can not be calculated for aerosol problems accurately enough [46].

Presently only a few safety studies with multi-compartment iodine code applications exist. One reason is the incomplete validation of iodine multi-compartment features. One early calculation was performed for a German PWR with the core melt scenario at low pressure according to the German Risk Study, Phase B, showing pronounced multi-compartment effects [47].

Validation of the integral iodine models on intermediate-scale tests is only possible to a certain extent. For the validation of multi-compartment effects, large-scale tests with all important volatile iodine species (e.g., $I_2$, Ch3I, etc) are necessary. As an example, $I_2$ can easily re-suspend from surfaces and water pools at favourable conditions. Its physical behaviour differs principally from those of the un-reactive gases $CH_3I$ and HMWI, and the aerosols CsI and $IO_3^-$.

Most integral severe accident codes in Table 2 have been validated for un-reactive non-condensable gases, and for aerosols. Some aerosol tests were made with hygroscopic CsI aerosols, e.g. the KAEVER tests. A good overview on the status of the containment codes in Table 2 is given by the International Standard Problems ISP-37 on the VANAM M3 test [48] and by ISP-44 on five KAEVER tests [46] and on the international benchmark on the thermal hydraulic F2 experiment [49].

In several intermediate scale tests the effects of temperature, wall condensation and gas flow conditions were measured. RTF and CAIMAN test series were performed in vessels of about 300 l which are rather small for containment volumes of several thousand $m^3$ from the thermal hydraulic point of view. The International Standard problem ISP-41 Follow up/Phase 2 [50] was performed on selected RTF and CAIMAN tests. In the PHEBUS FP tests FPT0 and FPT1 the thermal hydraulic and aerosol behaviour in the 10 $m^3$ vessel and its impact on iodine behaviour was measured [51]. In the PHEBUS FP tests the vessel atmosphere was well mixed and the decay heat release was too small to have any effects. Because of their

small size and the well mixed conditions these experiments are not suited to validate the multi-compartment modelling.

At present multi-compartment iodine tests are performed in the 60 m³-vessel of the ThAI-facility [52]. The $I_2$-distribution by atmospheric flows is measured in a 5-compartments geometry with a sump under accident-typical conditions. First experimental ThAI-results show large $I_2$-concentration differences in a stratified atmosphere, on the surfaces and in the sump. In the previous nine separate-effect tests the adsorption and desorption of $I_2$ under various thermal hydraulic conditions in a single-compartment geometry were measured. The series will be continued with specific tests on re-entrainment from a boiling sump. In the past 15 years, no other large scale iodine tests have been performed.

*Conclusions*

Through the integration of aerosol models in multi-compartment severe accident codes an essential step towards providing accurate boundary conditions for iodine behaviour analyses was achieved. . Further steps for higher quality safety analysis could be achieved by considering the feedback from iodine chemistry as well as the decay heat generated by the decays of the iodine nuclides to thermal-hydraulics and pipe-work structural behaviour. Concerning certain iodine chemistry models improvements are still needed for some sub-models requiring the coupling with the thermal-hydraulics, e.g. an improved modelling of iodine adsorption and desorption considering variable thermal hydraulic conditions.

For validation of the coupled thermal hydraulic-aerosol-iodine codes the data from numerous intermediate scale tests are of limited value. For the validation and assessment of multi-compartment features, large-scale iodine tests in subdivided containments or multi-compartments of containments under prototypical accident conditions are necessary. In particular, the complex $I_2$ behaviour in multi-compartment geometries has to be investigated. Such tests are currently being performed in the German ThAI facility.

## 3.3. IODINE BEHAVIOUR IN THE LIQUID PHASE OF THE CONTAINMENT

Aqueous iodine reactions are the main *source* of gaseous iodine in containment together with the initial release from the RCS (see Section 3.1). Because the relatively large concentrations of both iodine and radiolytically-produced reactive species, the aqueous phase provides optimum conditions for the conversion of non-volatile iodine species to volatile iodine species[2], where volatile iodine species include molecular iodine ($I_2$) and organic iodides (collectively represented as RI), and non-volatile iodine species include $I^-$, HOI, $I_3^-$, $IO_3^-$, etc. The volatile species formed in the aqueous phase could then be transferred to the gas phase at prevailing conditions. Thus, the rates of volatile $I_2$ and RI production/destruction in the aqueous phase are crucial parameters in determining gaseous iodine concentration.

The main aqueous phenomena that would influence the volatile iodine production in containment under accident conditions are schematically shown in Figure 4. Iodine deposition on immersed surfaces

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[2] The reasons for this are that containment sump water would collect the majority of iodine (unless the relative sump area is small) soon after it is released into containment, and that containment sump water, compared to air or structural surface, would provide the most chemically reactive environment due to the presence of radiation in containment following an accident. Any reaction medium, water, air/gas, aerosols or solids will absorb ionizing radiation and form reactive species. However, aqueous phases (or bulk water) would contain the highest concentrations (amounts per unit volume) of these reactive species. The reason for this is that the denser the medium, the more radiation would be absorbed and, hence, the more reactive species are initially formed. However, the reactive species formed in solids are not very mobile and as a result they tend to recombine with each other or the medium rather than to react with other species present in the medium at relatively low concentrations (e.g., iodine in our case).

(structural surfaces and possibly colloids) is also included in the discussion in this section. The importance of these processes on the gaseous iodine production, parameters affecting these processes, progresses made over the last ten years, the current status of understanding, and the areas for improvement are discussed.
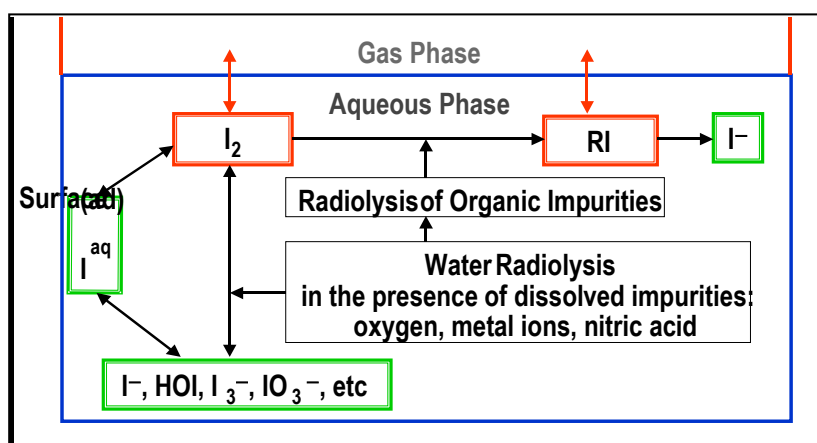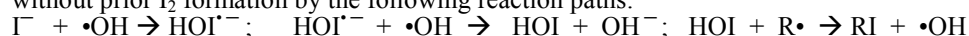


**Figure 4: Main Aqueous Phenomena**

*Conversion of Non-Volatile Iodine Species to $I_2$*

The production of $I_2$ from non-volatile iodine species in the aqueous phase is a fundamental process responsible for gaseous iodine production. In addition, the formation of the other volatile iodine species, RI, requires in general $I_2$, though other routes from iodides have been considered, regardless whether it occurs in the aqueous or gas phase, or on surface (see Section 3.2.2.3)[3]. Once in the gas phase, organic iodides, being more unreactive towards surfaces than $I_2$, could persist longer and become the dominant iodine species in the gas phase. Therefore, the rate of the $I_2$ production in the aqueous phase is crucial for determining the gaseous concentrations of organic iodide as well as $I_2$

For conservative considerations it may be assumed that the majority of iodine released into containment could be present in the sump water volume. Under these conditions it is expected that the iodine concentrations would be less than $10^{-4}$ mol·dm$^{-3}$ (or 0.1 ppm)[4] which can be regarded to be very low. This low concentration of iodine and the presence of radiation in post-accident containment mean that the conversion between $I_2$ and non-volatile iodine species would occur mainly via reactions with chemically reactive water radiolysis products such as $\bullet OH$, $\bullet O_2^-$, $H_2O_2$, $e_{aq}^-$, etc., and not as a result of direct absorption of radiation by iodine species. The reactions of iodine species with the water radiolysis products are very fast. Thus, the only thermal iodine reactions of importance are the fast iodine equilibrium reactions.

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[3]   This statement is probably not unconditional. Mechanistically organic iodide can also be formed from iodide without prior $I_2$ formation by the following reaction paths:
$I^- + \bullet OH \rightarrow HOI^{\bullet -}$;   $HOI^{\bullet -} + \bullet OH \rightarrow HOI + OH^-$;   $HOI + R\bullet \rightarrow RI + \bullet OH$
The above reaction path is probably also favoured at the low iodine concentrations suggested below ($10^{-6}$ M). Presumably the reaction of iodine atoms (I•) with organic radicals (R•) would also form organic iodide.

[4]   It was estimated for a typical PWR reactor that even if all of the iodine inventory in fuel were released, the total iodine concentration in containment sump water would be less than $10^{-4}$ mol·dm$^{-3}$.

The key reactions that would determine the conversion rate of non-volatile iodine species to $I_2$ include (a) the reactions of inorganic iodine species with water radiolysis products, and (b) hydrolysis ($I_2 + H_2O = HOI + I^- + H^+$) and other thermal equilibrium of iodine species)[5].
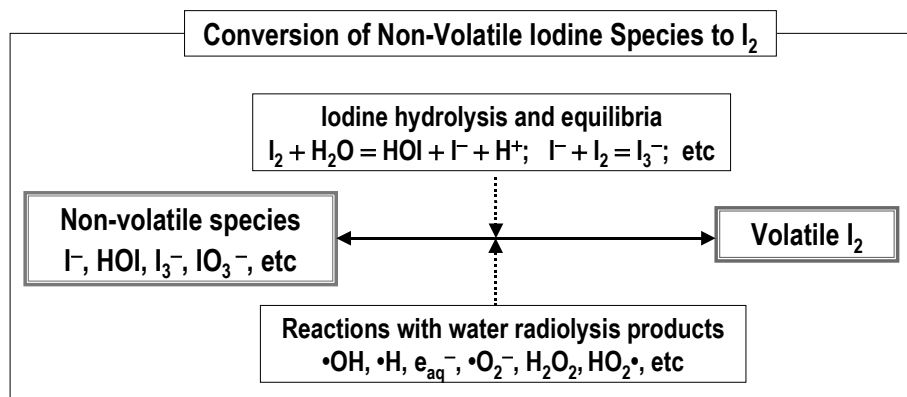


**Figure 5: Inorganic Iodine Reactions Responsible for the Conversion of Non-Volatile Iodine Species to $I_2$**

The conversion process involves tens of elementary reactions, with the net rate of the conversion being a function of the rates of these individual reactions. These individual rates depend on the reactant concentrations and reaction conditions, such as temperature, pH, radiation dose rate, etc. Although it is not necessary to include all these reactions explicitly, any iodine model that will be used to predict iodine volatility under accident conditions should adequately reflect the effect of dependencies of the individual rates on the reaction parameters to the net rate of the aqueous $I_2$ production in the model.

Most of these elementary inorganic reactions were studied in 1980s. Their reaction mechanisms and rate laws (the rate constant and the order of dependence on reactant concentrations) have been reasonably well established, except perhaps at high temperatures ($> 80^o$C) (see a recent review on the rate constants and equilibrium constants [53]. One important study in this area over the last ten years is the reduction of $I_2$ by hydrogen peroxide ($H_2O_2$) [54]. Hydrogen peroxide is formed from water radiolysis and its reaction with $I_2$ is one of the key reduction reactions which convert $I_2$ back to non-volatile iodide, $I^-$ [55]. The study by Ball et.al. [54] has examined the reaction over wider ranges of pH, temperature, and types of buffer than previous studies, and has been able to explain many of the discrepancies reported in the earlier literature. The uncertainties in the rate constants and their dependence on pH and temperature were significantly reduced as a result of this study. Recent PSI investigations provided additional insights on the hydrogen peroxide – iodine reactions in acidic solutions. In addition, most radiolysis experiments to date were performed using small to moderate doses (a few kGy). The recent results at PSI under non-sparging conditions, using much higher but typical anticipated sump doses (~ 200 kGy or more) have shown that $I_2$ is the major fraction from boric acid – iodide solutions. A state-of-the-art mechanistic code is likely to predict $I_2$ fractions, which are, in contrast, much less. Catalysed hydrogen peroxide – iodide reaction could be responsible for the observed large $I_2$ fractions.

One of the inorganic elementary reactions that may require better data is the temperature dependence of the equilibrium constant of the iodine hydrolysis[6]. The hydrolysis of $I_2$ is another key $I_2$ reduction paths

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5    Note that the $I_2$ concentration in the aqueous phase also depends on its reaction rate with organic radicals forming RI and its transfer rate from the aqueous to the gas phase. These are described in Section 3.2.2.3 and 3.2.x, respectively.

6    A recent examination of the equilibrium constant reported in the literature indicates that the original analysis of the data inadvertently could have led to a wrong temperature dependence of the literature value [Private communication, Ball and Mitchell, 2001].

back to non-volatile species, and its contribution to the overall $I_2$ reduction becomes more important at higher temperatures [53,55]. It is also one of the key reactions responsible for the pH dependence of iodine volatility, particularly at high pH values. Most of iodine models do not reproduce well the temperature dependence of the gaseous iodine concentrations observed in the intermediate scale tests performed in the RTF (Radioiodine Test Facility) and CAIMAN [56]. The uncertainties in the hydrolysis equilibrium at high temperatures may be one of the factors contributing to the discrepancy, and should be examined more carefully, even if experimental data are available in the literature.

The most significant progress made over the last decade in the area of the interconversion between the inorganic iodine species is perhaps the recognition of the importance of the radiolytic reactions on iodine volatility, owing to the intermediate scale tests performed in the RTF and CAIMAN and subsequently highlighted by various scale laboratory experiments. Before the effect of radiation on iodine behaviour was fully realised, the prediction of iodine volatility under accident conditions was mainly based on the thermodynamic properties of the iodine species at equilibrium. Equilibrium calculations show that non-volatile $I^-$ and $IO_3^-$ are the predominant species for most of the redox potential and pH ranges, whereas $I_2$ (and also HOI) dominate only under highly acidic and oxidising conditions [57]. These early studies also assumed that HOI was highly volatile [58], but the projections of HOI stability and volatility are no longer considered to be valid [59].

The effect of radiation on volatile iodine production from non-volatile iodine species at low concentrations had been difficult to measure. The relative importance of radiolytic reactions on iodine volatility thus became fully recognised only after the results from the RTF (and later CAIMAN) became available in the last decade. The gas phase iodine concentrations and iodine speciation observed in the intermediate-scale tests were very different from those predicted from the equilibrium thermodynamic calculations. Under the radiation conditions expected in a reactor accident, equilibrium is not reached and iodine behaviour is dominated by the reaction of iodine species with water radiolysis products that are being produced continuously. Because of the continuous production of species, the kinetics of key chemical reactions is central to determining iodine behaviour in containment. All iodine codes now have taken into account the impact of these radiolytic reactions on the $I_2$ production to a varying degree of details[7].

The progress in our understanding of the radiation-induced interconversion process represents a significant technical achievement. However, there still remained some uncertainties in the overall conversion rate from non-volatile species to $I_2$, mainly due to our insufficient knowledge on water radiolysis behaviour in less pristine containment environment where various dissolved impurities could significantly influence the behaviour. These aspects are discussed next.

*Water Radiolysis in the Presence of Dissolved Impurities*

The main reactions that drive the conversion of non-volatile iodine species to $I_2$ (and also RI) are the reactions with water radiolysis products. These reactive species are continually formed by the radiolysis of water but also undergo various reactions with each other, iodine and other impurities dissolved in water (Figure 6). For determining iodine behaviour, the impurities to be considered are those that would have more impact on water radiolysis than iodine. These impurities may include, among others, dissolved oxygen, nitrate/nitrite ($NO_3^-/NO_2^-$) produced by air radiolysis, trace metal ions such as $Fe^{2+}/Fe^{3+}$ dissolved from steel surfaces, chloride ions coming from the pyrolysis/radiolysis of polyvinyl material from cables

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[7]    Semi-empirical codes such as IMOD, IODE, IMPAIR and AIM have incorporated the effect of the iodine reactions with water radiolysis products in the overall rates of the oxidation ($I^-$ to $I_2$) and reduction ($I_2$ to $I^-$) of iodine, whereas comprehensive mechanistic codes, such as LIRIC, INSPECT and MELCORE-I, contain a full water radiolysis reaction set consisting of as many as 50 reactions (see Section 3.2.2.2).

and organic impurities (RH) from painted surfaces and polymers. Most of fission products released into containment would be relatively inert toward the water radiolysis products because of their high redox potentials.
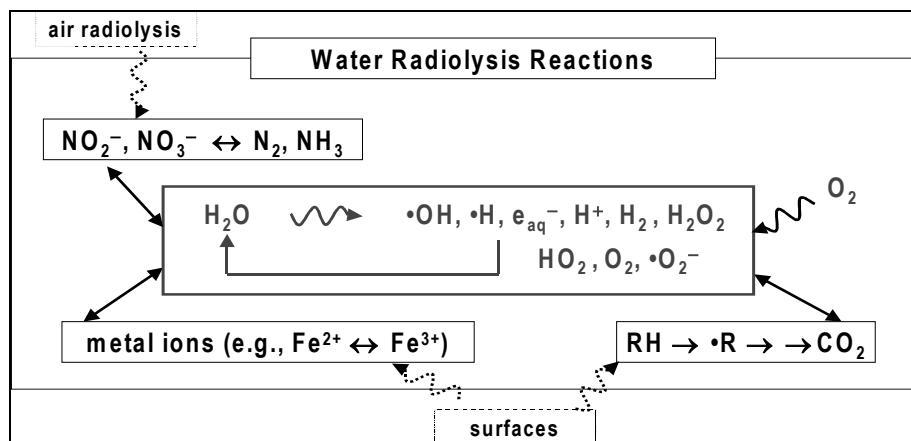


**Figure 6: Water Radiolysis Reactions in the Presence of Dissolved Impurities**

Even in the absence of any impurities, the radiolysis of water is a complex process. Upon absorption of ionising radiation, water decomposes and produces chemically reactive species; $\cdot OH$, $\cdot H$, $H^+$, $e_{aq}^-$, $H_2$, and $H_2O_2$, which would react with each other to reform water, during which additional species such as $HO_2$, $O_2$ and $\cdot O_2^-$ are also formed. The primary yields of the products from the decomposition of water and about 40-50 elementary reactions of the radiolysis products have been established reasonably well for the temperature range ($0 - 150^{\circ}C$) expected in post-accident containment [60].

Although the individual reactions of the water radiolysis products have been reasonably well known, their overall behaviour as a function of containment conditions has not been established unequivocally. The reason for this difficulty is that the reactions of water radiolysis products are synergistic. Nevertheless, a considerable progress has been made over the last ten years in our understanding of the interaction between iodine species and the water radiolysis products in the absence of other impurities. As mentioned earlier, all iodine codes now have taken into account the effect of water radiolysis on the $I_2$ production in the aqueous phase to a varying degree of details, considerably improving our capability in determining iodine behaviour, compared to the earlier assumption based on thermodynamic equilibrium calculations.

There has been, however, very limited investigation on the role of other impurities which can affect the concentration of water radiolysis products. This produces considerable uncertainties in assessing the net effect of water radiolysis products on iodine behaviour in containment sump water. If the concentration of iodine species are in large excess in comparison with those of the impurities iodine species react readily with the water radiolysis products, and hence the effect of the other dissolved species on water radiolysis can be ignored. However, it is anticipated that the iodine concentration in containment water would be at an impurity level (see Section 3.2.2.1) and various other impurities could play a major role in competing for the water radiolysis products:

a.  *Dissolved oxygen* reacts with hydrated electron, $e_{aq}^-$, very effectively and lowers its concentration, which would result in lowering $\cdot OH$ and $\cdot H$ while increasing $H_2O_2$, $H_2$ and $O_2^-$. These changes could have a significant impact on the $I_2$ production rate discussed above

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b. *Metal ions*, even at a trace level, can significantly affect water radiolysis product concentrations by catalytic consumption [61] and could considerbaly affect iodine volatility[8] [2,4].

c. Effect of *slicium oxides* on the iodine behaviuour is a subject of investigations of the current Russion ISTC project EVAN tecnically and financially supported by the European union.

d. *Nitrate/nitrite ions*, formed by the radiolysis of humid air [62] (see Section 3.2.3), could alter the pH of the water and react with water radiolysis products. They consume the reducing species, $e_{aq}^-$ and •H, to form compounds that are successively lower in oxygen content and more reduced than their precursors. (The outcome of a recent PSI programme on the effect of nitrate and nitrate ions on iodine volatility is to be made available shortly within an international programme).

e. *Chloride ions*, formed mostly by cable pyrolysis. HCl generated could strongly lower the sump pH and also provides chloride ions well in excess of iodide. Chlorine ions could also react with water radiolysis products producing chlorine radicals. Recent PSI results also dhow an increase in the iodine volatility under weakly alkaline conditions.

f. *Organic impurities (RH)* dissolved in water would react with water radiolysis products to form organic radicals (•R), which either react with $I_2$ to form organic iodides (RI), or react with dissolved oxygen and decompose eventually to $CO_2$ [63].

The importance of the effects of most of these impurities on water radiolysis product concentrations, and hence, on the net conversion rate from non-volatile species to $I_2$, has been realised only recently. Nevertheless, there have been considerable progresses in our understanding over the last five years, particularly of the effects of dissolved oxygen and organic impurities [53,55,63]. However, the effects of trace metal ions and nitrate/nitrite ions have been recognised only recently and our current understanding of these processes is limited and requires further studies. Similarly the effect of $CO/CO_2$, which is also formed from concrete – corium interactions or from boron carbide oxidation, on the iodine sump chemistry is not well known and hence also requires further study. Hence the effect of $H_2CO_3$ on sump pH as modelled in the LIRIC 3.2 code [52] deserves experimental confirmation as well as study of its radiolytic effects. The effects of impurities on the water radiolysis product behaviour under representative post-accident containment conditions are being addressed under the AECL-UWO (University of Western Ontario) collaborative research projects, with an objective to provide manageable models that can quantitatively describe the effects on iodine volatility. It should also been recognised that elements such as copper, zinc or aluminium (see e.g. [64]) may have an impact on iodine volatility.

*Formation and Destruction of Volatile Organic Iodides (RI)*

The post-accident analysis of the Three Mile Island 2 event showed organic iodides were the dominant gaseous iodine species detected in the containment atmosphere [65]. Organic iodides have chemical and physical properties that differ from $I_2$, making the aqueous/gas phase partitioning of these species also different. Furthermore, some organic iodides do not absorb in solutions or onto surfaces as readily as $I_2$, making them more difficult to remove from atmospheres by engineered systems such as filters and scrubbers. Therefore, since the TMI-2 post-accident analysis, efforts to predict the rate of formation of organic iodides has been one of the main tasks of international iodine community.

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[8]    The potential impact of the trace metal ions on iodine behaviour via its interaction with water radiolysis products has been explored by model sensitivity analysis using the Sellers reaction set with LIRIC . This study indicate that the presence of these metal impurities at a trace level ($10^{-5}$ mol·dm$^{-3}$) can increase iodine volatility by over an order of magnitude at pH values greater than 6.

In the radiation environment expected in post-accident containment, organic iodide formation in the liquid phase is mainly due to the reaction of $I_2$ with organic radicals (•R) produced from the reactions of dissolved organic impurities with water radiolysis products. Organic iodides can also decompose radiolytically to non-volatile iodide $I^-$ and organic radicals, or hydrolyse to form non-volatile $I^-$ and a corresponding alcohol (ROH) [66] (Figure 7). To determine the concentration of organic iodides and its contribution to the gas phase iodine concentration, the rates of these reactions should be known as a function of containment conditions.
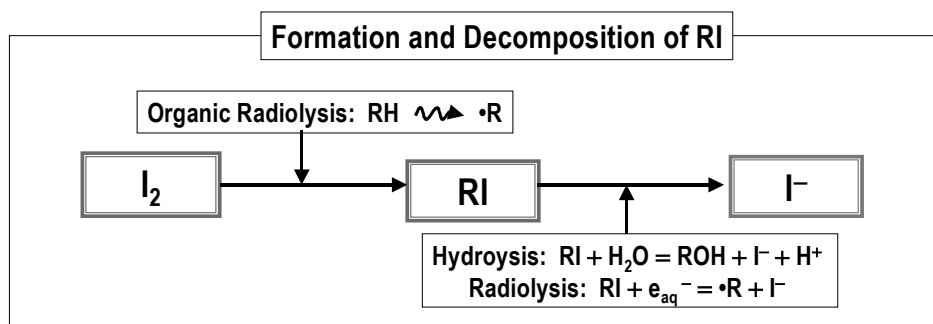


**Figure 7: Organic Iodide Formation and Decomposition**

The rate constants of the reactions of $I_2$ with •R and RI with $e_{aq}^-$ are reasonably well established and do not vary much from one organic compound to another: being radical reactions, their rate constants are nearly diffusion controlled. However, the hydrolysis rate constant depends strongly on the type of RI and temperature and pH. The aqueous-gas phase partition coefficient also varies considerably with the type of RI and temperature. Therefore, the type of organic iodide is also important even if organic iodides with low volatilities would not end up in the gas phase as much as $CH_3I$.

The rate of the RI formation depends also on the concentrations of $I_2$ and •R. Therefore, the uncertainties in the prediction of $I_2$ and •R concentrations (see Section 3.2.2.1 and 3.2.2.4, respectively) would also propagate into the uncertainties in prediction of the RI concentration.

One of the most significant progresses over the last ten years has been the establishment of the aqueous organic iodide production[9] as one of the main source for gaseous organic iodides in containment. Previously, the main mechanism for organic iodide production was thought to be the reaction of $I_2$ with methyl radical (•$CH_3$) formed from methane ($CH_4$), either in the aqueous or gas phase. The low solubility of methane in water and the low concentrations of $I_2$ and •$CH_3$ in the gas phase could not explain the high organic iodide fraction observed in the intermediate scale tests or the TMI-2 analysis [65]. Reactions between iodine species with organic compounds attached to paint or organic polymer surfaces were also examined. Although significant organic iodide formation in or on the polymer matrix is possible, once formed, these organic iodides are unlikely to be released from the polymer matrix. Furthermore, analysis of the bond energies [67] for C-C, C-H, and C-I bonds, and comparison with the radiation chemistry of chlorinated polymers [68], indicate that irradiation or thermal activation of iodinated polymers would preferentially release iodine atoms and not organic iodides. Therefore, the surface reactions could not be responsible for the large fraction of organic iodides in the gas phase.

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[9]  The aqueous reactions also include those occurring in water-saturated pores and channels inside a paint matrix, or in a water film on the paint exterior. The production of organic iodides in containment via these processes can then be treated as a combination of the homogeneous organic iodide formation in the pores or the water film, transport of organic iodides from the pores into the bulk aqueous phase and then partitioning of organic iodides with the gas phase.

These early studies on organic iodide formation focused mainly on methyl iodide ($CH_3I$) because it is the simplest organic iodide compound with high volatility. Hence, the potential presence of other organic iodides in containment under accident conditions was not fully addressed in early studies, although some other longer chain alkyl iodides, such as propyl and butyl iodides, were detected at very low levels [69]. Furthermore, there was simple expectation that volatile $CH_3I$ would be produced from reactions with methyl groups of any organics present.

Studies performed in the RTF as well as bench-scale studies over the last two decades under the AECL and COG [70] subsequently have shown that, even when cured and dried for a long time, painted surfaces could release substantial amount (~ 100 ppm) of soluble organic compounds into water, and that these organic compounds could be one of the main sources of organic iodide formation (see Section 3.2.2.4). Many of the organic impurities released from paints are oxygenated compounds, and their radiolytic decomposition products into air-saturated water would be more oxygenated as the decomposition progresses. The organic radicals formed during the radiolytic decomposition would react with $I_2$ to form a wide variety of organic iodides, and a large fraction would be oxygenated organic iodides that are more soluble in water (less volatile) than $CH_3I$[10]. Because $CH_3I$ has one of the highest volatilities and other organic compounds including iodides would eventually decompose to smaller compounds in the presence of radiation, $CH_3I$ would become the dominant species in the gas phase. However, the majority of organic iodides formed in the aqueous phase initially would be more soluble (less volatile) organic iodides and understanding their behaviour is important in determining the $CH_3I$ concentration in the gas phase.

After the realisation of the importance of other organic iodides, considerable efforts have been made to build database on the aqueous-gas phase partition coefficient and the hydrolysis rate constant through the AECL and COG Reactor Safety Containment behaviour Research Projects [71]. These values vary considerably from one organic iodide to another. Consequently, the main difficulty in adequately assessing the net production of organic iodides in containment would arise from the large number of different types of organic impurities and organic iodides that could be present in containment. Inclusion of the reactions of every potential organic iodide in modelling iodine behaviour is not practical. Therefore, one of the key remaining issues is to develop a practical but accurate way to determine the overall impact of the aqueous organic iodide production on the gaseous organic iodide concentration. One way to manage the variety of possible organic iodides is to consider them as members of a smaller number of groups. One of the strategies recently suggested is to group organic iodides together, based on their hydrolysis rates and partition coefficients [71]. This strategy then also requires assigning appropriate organic iodide production ratio to these groups. This strategy should be validated and the uncertainty it brings to the iodine volatility prediction should be examined.

*Source and Radiolytic Decomposition of Dissolved Organic Impurities*

Organic impurities dissolved in containment water would react with water radiolysis products to form organic radicals (•R), which either react with $I_2$ to form organic iodides (RI), or react with dissolved oxygen and decompose eventually to $CO_2$ [63]. Therefore, they could affect iodine volatility in three ways: (1) by affecting water radiolysis behaviour and hence the $I_2$ production rate, (2) by forming organic iodides, and (3) by changing pH through formation of organic acids and $CO_2$. Because of these multiple effects, the behaviour of organic impurities, their concentration and type, must be well understood in order to be able to determine iodine volatility. This section thus examines the source of organic impurities in containment water and their radiolytic decomposition reactions.

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[10]     The aqueous to gas phase partition coefficient of organic iodides varies considerably, ranging from 1.5 for butyl iodide and 4.8 for methyl iodide to 490,000 for iodoethanoic acid at 25$^{\circ}$C .

*Source of Dissolved Organic Impurities:* As mentioned above, a considerable progress has been made in identifying the source of dissolved organic impurities over the last ten years. While there may be other sources of organic material that can contribute[11], the leaching of organic solvents trapped in painted surfaces into containment water is expected to be one of the major sources of dissolved organic impurities. The solvents and thinners used in paints are generally small molecules that have an intermediate volatility suitable for paint application (e.g., methylethylketone (MEK), methylisobutylketone (MIBK), toluene, xylene, ethylbenzene, methanol, ethanol and acetone). These compounds, particularly those with hydroxyl and ketone groups, are also reasonably soluble in water. Relatively large concentrations of these compounds were observed in the RTF and bench-scale studies when water was in contact with aged painted surfaces ( ~ 100 ppm MIBK at a painted surface to water volume ratio of 0.2 cm$^3$ [72]).

In addition to the total amount of organic impurities that could be released into water, the rate of the release is an important factor. The rates of release of these organic paint solvents into water have been measured as a function of temperature, paint type, paint thickness and aging [72,73]. These studies have shown that the organic solvent dissolution is mainly determined by the diffusion of water through the pores in the paint matrix and, hence, relatively independent of paint or organic solvent types. This simple dependence of the organic solvent release kinetics makes modelling of the organic solvent release into water manageable.

*Organic Radiolysis:* Once released into water these organic compounds undergo reactions with water radiolysis products, and form organic radicals (•R). Organic radical could react with another radical (or other RH) to reform an organic compound, or react with dissolved oxygen to form a smaller but more oxygenated organic compound such as organic acid (RCOOH) and eventually $CO_2$, or react with $I_2$ to form organic iodide (Figure 8).

The radiolytic decomposition of an organic compound could involve hundreds of elementary reactions. As many as 130 reactions, in addition to about 40 water radiolysis reactions, have been used to describe the radiolytic decomposition of a relatively simple compound containing only four carbon atoms, MEK [63]. The number of reactions required to comprehensively address all possible reactions of intermediate species increases with the number of carbon atoms in the initial compound. However, detailed understanding of kinetics of all the intermediate steps, except the initial step for forming •R, may not be required in determining iodine behaviour because the introduction of organic impurities into containment water would much slower than the radiolytic decomposition []. Under these conditions, the overall rates of forming the final decomposition products (RI and $CO_2$) would be limited by the production of •R from the reaction of organic compounds and water radiolysis products (mainly •OH) and the relative ratio of the concentrations of the reactants ($O_2$ and $I_2$).

The remaining uncertainty for determining the impact of organic radiolysis on iodine behaviour is the type of •R formed from the starting organic compound and its decomposition products. Again the difficulty arises from the large number of different types, and a strategy to handle the large number in a practical, but meaningful way should be developed. The simplification of the organic radiolysis model, which can quantitatively determine its impact on water radiolysis product behaviour and on organic iodide production, is continually being addressed under the AECL and UWO collaborative research projects.

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[11]   Organic polymer chains that form insulation material or the binder in paints (paint matrix) are very difficult to break into water-soluble organic species, even in the presence of radiation. In fact, irradiation tends to increase cross-linkage of organic polymers. However, the organic solvents used in paint application remain trapped inside the paint matrix which then are released by water diffusion when wet.
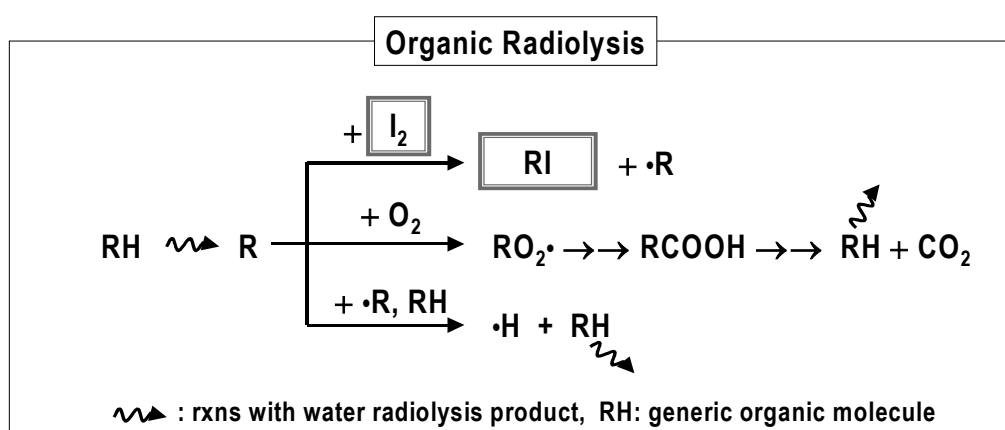
**Figure 8: Radiolytic Decomposition Paths of Dissolved Organic Impurities**

*Deposition of Iodine on Immersed Surfaces*

There are a variety of surfaces present in a containment building, including steels, aluminium, organic-based painted surfaces, bare concrete, zinc-primed surfaces and plastics. There would be also colloids or solid particles of fission products or reactor materials released during a severe accident. For iodine deposition on immersed surfaces, zinc-primed surface and silver/silver oxides are of interest, where the latter could be released from the melting of a control rod used in some PWR reactors.

Zinc primer coating is often used to protect carbon steel from corrosion, and is applied as an undercoating for a variety of epoxy and vinyl containment paints. In some applications it is the final coating on containment surfaces and would therefore be exposed to iodine directly in the event of an accident[12]. Of all of the containment surfaces zinc-primer has the strongest affinity for iodine in the aqueous phase. An RTF test performed with zinc-primed surface showed that about 80% of iodine inventory eventually deposited on the immersed surface at the end of the test.

Reaction and adsorption of iodine on zinc primer surfaces is a complex function of solution pH, oxygen content of the water, and iodine speciation [74]. At neutral and acidic pH values, zinc primer simply reduces $I_2$ to $I^-$, whereas in basic solution, zinc primer surfaces are oxidized to $ZnO$, $Zn(OH_2)$, and $Zn_4CO_3(OH)_6$ [74]. Oxidation of the zinc surface is accompanied by incorporation of iodide into the oxide/hydroxide layers. The details of the kinetics of these processes have not yet been established.

As a result of control rod melting, a significant release of silver into the containment vessel was observed in the PHEBUS FP0 and FP1 tests. This had a significant impact on iodine volatility observed in the containment vessel. Since then, there have been various studies on the mechanism and kinetics of the reaction of silver and iodine and of the decomposition of silver iodide in the aqueous phase in the presence of radiation [24,25]. These studies have significantly improved our understanding of the radiolytic reactions of silver and iodine. These studies have established that silver iodide can be formed by the reactions of Ag with $I_2$, $Ag_2O$ and $I_2$, and $Ag_2O$ with $I^-$. However, it was not possible in these studies to isolate individual reactions and study the kinetics of one reaction path independently from the others, because $I_2$ is always in (pseudo-) equilibrium with $I^-$.

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[12] It is estimated that in Bruce generating station, up to 132,000 $m^2$ of exposed zinc primer surfaces exists in containment.

Other issues regarding the silver iodine interaction are the extent of silver oxidation under post-accident containment conditions and the stability of AgI in the presence β-radiation (presumably due to the kinetic energy of the β particles (electrons) from radioactive iodine). Silver is likely to be released as Ag aerosols rather than silver oxide aerosols from the PHTS (Pressurised Heat Transport System). Once released into highly oxidising containment atmosphere (radiation and air), Ag could be oxidised in the gas phase before the aerosols settle and enter the bulk water phase and/or continue to be oxidised in the aqueous phase while undergoing the reactions with iodine. The stability of AgI in the presence in situ-β- and external γ-irradiation has been experimentally shown in a dedicated PSI experimental programme [24, 25]. The routes for the radiolytic decomposition and conditions for the generation of volatile iodine were studied in the referred programme. Very low to substantial decomposition in terms of production of volatile and non-volatile species was measured under in-situ β-irradiations. The tests indicated clearly the conditions affecting the volatile iodine production as a result of radiolytic decomposition under β-irradiation, e.g., AgI colloidal concentration, level of excess iodide, colloidal stability, other conditions favouring or suppressing the generation and transfer of volatile iodine. Many experiments on the effect of γ-radiation on silver iodide covered silver wool surface [75] or silver iodide colloids [25] have shown no AgI decomposition. However, it was suggested that the small decomposition observed in the AEA test [75] using silver iodide coated silver wool could be the result of the decomposition by dissolution. Therefore, there still remains a large uncertainty in quantifying the impact of silver on iodine volatility.

Rosenberg found that initial deposition velocities for $I_2$ on submerged (wet) epoxy-type paints were more than two orders of magnitude greater than those for vinyl paints at 25ºC, and that the temperature dependence of sorption behaviour was very different depending upon the paint type. These findings are consistent with RTF experiments, where it was observed that Amerlock epoxy paint absorbed significant quantities of $I_2$ and $I^-$ in the aqueous phase, but the vinyl paint retained very little iodine. A literature survey has revealed that there is very little data available for iodine adsorption on aluminium, carbon steel, galvanized steel and concrete surfaces (either exposed to the gas or aqueous phase). In order to reduce the uncertainty in the capability for predicting iodine volatility under accident conditions, studies on the adsorption/desorption of iodine on a wide variety of containment surfaces to establish the mechanisms and rate constants within acceptable uncertainties are being carried out under the AECL-UWO collaborative project.

## 3.4. IODINE BEHAVIOUR IN THE GAS PHASE OF THE CONTAINMENT

### 3.4.1 Introduction

Even a modest iodine inventory in the containment atmosphere could lead to extensive release over time if leakage is significant. Formation and persistence of gaseous iodine species in the containment can lead to additional release to the environment via leakage, venting or failure. It is therefore important to understand and quantify the processes controlling the gaseous iodine concentration in the containment [76]. The claim should be to develop the iodine model such that it predicts the iodine inventory in the gas phase of containment within one order of magnitude.

### 3.4.2 Main Phenomena

Iodine species in the gas phase can be grouped into:

−   Volatile iodine: molecular iodine, organic iodides

−   Iodine in aerosol form: metal iodides, iodine in oxidised forms

- We concentrate here on the *volatile* iodine. The EURSAFE PIRT (**P**henomena **I**dentification and **R**anking **T**ables) provided those phenomena that were assessed to be important for source term [77]. The selected phenomena for future studies on the iodine behaviour in the gas phase were:

- adsorption / re-suspension at / from surfaces.

- homogeneous conversion from non-volatile iodine species into volatile iodine species and reverse, especially the heterogeneous formation of organic iodide and its destruction.

- effect of steam condensation.

- Additionally, the on-going analysis of the PHEBUS-FP test results highlights the importance of a good understanding of the radiolytic oxidation of iodine, both in the inorganic and the organic form [78].

- Other important effects on the iodine behaviour in the gas phase will be discussed in other sections of this report:

- release from reactor coolant system (refer to Ch. 3.1).

- re-suspension from sump, transfer to sump through the gas/sump interface, transfer to sump through spray droplets (refer to Ch. 3.2.4).

ACE/RTF tests [79], PHEBUS/RTF tests PHEBUS FP tests [80], COG-RTF and CAIMAN tests all end up with steady-state concentrations of the volatile iodine in constant boundary conditions within hours or days: this is the combined result of the effect of sources and sinks of fast processes.

The following section describes the status of understanding of selected phenomena ten years ago, the recent progress and defines future research needs.

### 3.4.3 Adsorption at surfaces and desorption from surfaces

Iodine is a notoriously "sticky" molecule, and iodide is also known to easily react with certain metals. Many surfaces in containment could absorb iodine and have a significant impact on iodine volatility. There are a variety of surfaces present in a containment building, including organic-based painted surfaces, stainless steel, aluminium, bare concrete, zinc primed surfaces and plastics. During an accident, these surfaces could be in contact with the containment atmosphere in non-condensing conditions (dry surfaces) and condensing conditions (wet surfaces). The importance of dry or wet surfaces in the containment atmosphere will depend on the accident scenario and on the considered compartment of containment.

*Dry surfaces*

Most of the work on iodine/surface interactions has concentrated on organic painted surfaces. Organic paints in the containment possess a two-fold action, they act as an iodine sink but they also act as a source of volatile organic iodide. The latter process is discussed in the next section. Steel surfaces, due to the generally much lower surface areas, are of less significance for source term and therefore not explicitly treated in this report. However, it should be noted that the correct analysis of validation data from many small-scale and integral iodine experiments (many of which contained predominantly steel surfaces) relies upon adequate representation of iodine deposition and re-suspension from these surfaces.

Kinetics of adsorption and desorption at painted surfaces were not well known 10 years ago: paint type, ageing, radiation and temperature were considered as important parameters but still to be investigated. Results from the ACEX project confirmed the large scattering of reaction rates [81] for both adsorption onto the surface and re-suspension from the surface. The ACEX work also included the often cited, very good and extended bench-scale studies by Rosenberg [82].

A part of the uncertainties is associated with experimental artefacts, e.g. on the problem with providing painted coupons loaded with iodine in a proto-typical way in laboratory-scale tests. Another significant influence stems from the mass transfer from the bulk gas phase through the boundary layer and to the surface. This entrains the necessity to measure adsorption/desorption rates in realistic thermal-hydraulic boundary conditions which is difficult to impossible in lab-scale tests.

The status of knowledge on iodine deposition and desorption was recently assessed in [83]. Large-scale and laboratory-scale tests were carried out, and usually simple first order kinetics was deduced. The reality with paints and steel surfaces is much more complex [82, 84]. For example, the $I_2$ –stainless steel interaction is complicated by the formation of iron oxy-iodide scales [84] and the iodine sorption rate is sensitive to the oxygen content of the gas phase. This leads to uncertainties in applying the data to conditions outside the studied range. An additional and more important gap is that the chemical nature of the sorbed iodine on most surfaces and the rate at which it is desorbed have not been established. This leads to uncertainty in assessing the speciation of sorbed iodine, the potential for its revolatilisation, and the ease of decontamination of surfaces. Finally, surface deposition as a function of temperature and relative humidity (including condensing conditions) has not been established rigorously.

The current ThAI project aims at measuring adsorption/desorption of molecular iodine at/from surfaces and the impact of iodine mass transfer from the bulk gas phase through the boundary layer at the surface, considering especially the parameters "humidity" and "steam condensation". Application of derived models to the reactor case should then directly be possible since realistic thermal-hydraulic boundary conditions are installed in the 60 m$^3$ ThAI test vessel [85]. Steel surfaces are up to now used but painted surfaces are also envisaged for the future.

In addition, a literature survey has revealed that there is very little data available for iodine adsorption on aluminium, carbon steel, galvanised steel and concrete surfaces. In order to reduce uncertainties in the capability for predicting iodine volatility under accident conditions, studies on the adsorption/desorption on a wide variety of containment surfaces are being carried out under the AECL-UWO collaborative project.

*Effect of steam condensation*

Condensing steam washes off deposits from the surface and transports them down onto floors or sumps of lower compartments. This mechanism is an efficient way to remove iodine from the gas phase, because (i) the transfer rate from the gas to the wall surface is increased and (ii) the re-suspension of iodine from the surface back into the gas phase is reduced due to the transfer into a sump. So far, models in iodine codes assume the complete and instantaneous wash-off of deposited iodine from the surface. This assumption is probably not correct, and this open question therefore means an important uncertainty in the iodine distribution in containment.

Data to model the removal of iodine from the gas phase in condensing conditions and the iodine wash-off following deposition in dry conditions are scarce. ACEX work on modelling the effect of falling water films on iodine distribution on containment states the need of experimental data [81]. The measurement of such data is on-going in the current ThAI project [85] using I-123-tracered molecular iodine in a 60 m$^3$ vessel and in accident-relevant thermal-hydraulic boundary conditions.

*Heterogeneous formation of organic iodide*

There has been a debate about the major source of organic iodide in containment within the past decade [83]. The two mechanisms "homogeneous formation of organic iodide, resulting from radiolytic processes within the sump and followed by interfacial mass transfer to the gas phase" and "heterogeneous formation of organic iodide from painted surfaces in the gas phase loaded with iodine" were opposed to each other.

Given the large surface areas in PWR's, significant amounts of iodine deposit onto the painted surfaces and react with the organic components to produce organic iodides whose volatile forms can be released back into the gas phase. Radiation plays a strongly enhancing role, as it induces fast radiochemical reactions between the iodine and the paint. This heterogeneous production of organic iodide is highlighted here.

Speciation of organic iodide

Previous models often considered the release of organic iodide from painted surfaces in the form of methyl iodide, since this is a very volatile representative of the organic iodides. However, this assumption tends to overestimate the volatility of organic iodide, because lower volatile organic iodides would reduce the overall release of organic iodide. The release of significant fractions or even dominant fractions of other organic iodides different from methyl iodide was indeed shown e.g. at IPSN and AECL (e.g. [86,87], [79]).

Production rates of organic iodide

The Organic Iodine Chemistry Project (OIC) as part of the 4th EU Framework Programme studied the formation of volatile organic iodide from pre-loaded painted surfaces exposed to a gas phase [88]. Radiation dose as an experimental parameter is clearly more efficient in producing volatile organic iodide than temperature. Data of this project and of previous similar experiments were used to develop simple empirical models on the production of organic iodide from a variety of different paint types from several countries. These models reproduce the experimental database within one order of magnitude, considering the paint itself as a "black box". Unfortunately, this uncertainty already exhausts to a large extent the total uncertainty acceptable for predicting the total iodine inventory in the gas phase of a containment.

Future work

The EPICUR programme (**E**xperimental **P**rogramme on **I**odine **C**hemistry **U**nder **R**adiation) will be performed by IRSN to extend the database on the formation of organic iodides at painted surfaces exposed to gas or water spaces, in high radiation fields and at high temperatures, and considering particularly thermal-hydraulic conditions assumed for French PWR's. This project will also study the radiolytic oxidation of iodides dissolved in aqueous solutions, the radiolysis of air and the interaction of the air radiolysis products with molecular iodine and the silver - iodine interactions.

*Homogeneous reactions in the irradiated atmosphere*

Radiolytic oxidation of inorganic iodine

In the presence of radiation, gaseous $I_2$ could react with the radiolysis products of humid air to form solid non volatile iodine oxides (e.g. $I_2O_5$, $I_4O_9$) and other non-volatile iodate ($IO_3^-$) and periodate ($IO_4^-$) ions [89].

$$N_2, O_2, H_2O \text{ in air} \xrightarrow{\bullet OH, HO_2\bullet,} \bullet O, O_3, e^-, \text{ etc}$$

$$I_2 + \bullet OH, HO_2\bullet, \bullet O, O_3, e^-, \text{etc} \rightarrow I_xO_y, HIO_3, HIO_4 \text{ in humid air}$$

$$\rightarrow H^+ + IO_3^- \text{ or } IO_4^- \text{ in water}$$
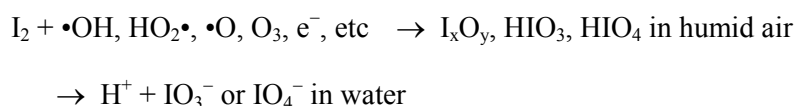
In principal this means the conversion of a volatile iodine species into a non-volatile one. In containment atmospheres, any surfaces of walls, aerosols or water droplets will take up the iodine oxides. So far this process has mostly been ignored in iodine codes, especially due to the insufficient experimental knowledge on the associated processes.
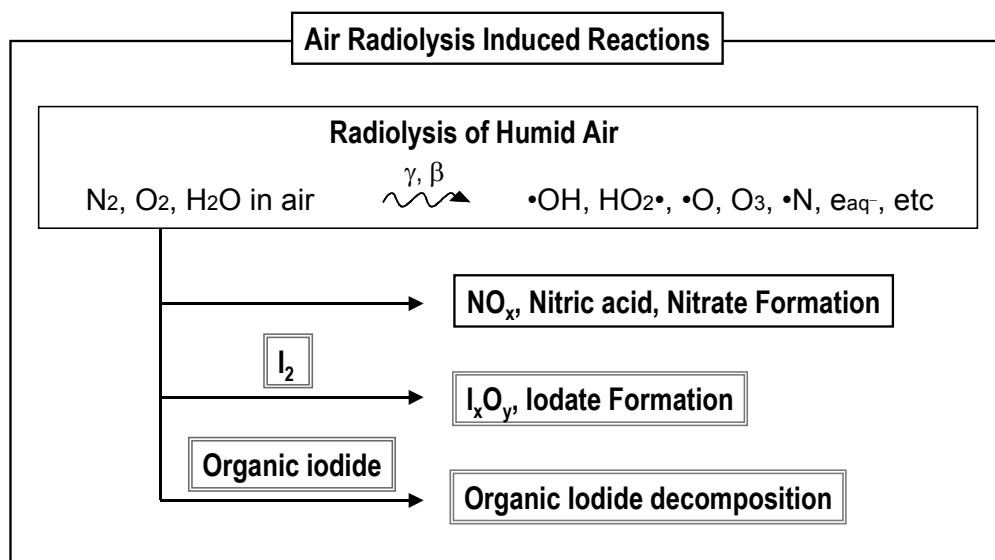


**Figure 9 Air radiolysis Induced Reactions**

Lab-scale tests were performed to measure the decrease of volatile $I_2$ in irradiated atmosphere of air or air/steam mixtures up to 130°C [90]. Iodine oxides were observed in non-condensing conditions, and found as expected as iodate upon dissolution in water. The higher the dose the greater was the rate of $I_2$ decrease. No significant effect of steam was identified, within the uncertainty of the results which were strongly scattered. Decreasing the initial iodine concentration and decreasing the temperature resulted in an acceleration of the $I_2$ destruction. The experimental results were explained on the basis of the sum of several individual steps, the formation and destruction of an $I_2$-oxidising species ("ozone") and the reaction between $I_2$ and ozone according to [89].

However, only high $I_2$ concentrations were studied, and the kinetics of radiolytic oxidation at lower concentrations typical for severe accidents could be different. Little is known about the speciation of air radiolysis products, instead only the "integral oxidising capacity" of air radiolysis was measured so far.

The current PARIS project (Project on Air Radiolysis, Iodine and Surfaces, 2003-2004, [91]) was initiated by IRSN to extend the knowledge on the radiolytic reactions in the gas phase, through experimental work on the 1-liter-scale, performed by Framatome ANP. The four project phases comprise the (i) kinetics of air radiolysis, (ii) surface effects on air radiolysis products, (iii) interactions of $I_2$ with air radiolysis products and (iv) surface effects and kinetics of air radiolysis products formation on $I_2$ concentration evolution. The main boundary conditions for the experiments are a high steam content, optionally the addition of hydrogen, high temperatures and dose rates, extremely low but accident-relevant $I_2$ concentrations and presence of surfaces typical for containment such as painted surfaces, steel and silver. The chemical analyses included air radiolysis products, iodine speciation and volatility and surface

deposition. Development and extension of the current mechanistic model will be performed after finalizing the experimental work.

*Radiolytic destruction of organic iodide*

A previous experimental study of radiolytic destruction of methyl iodide showed that the destruction rate is proportional to the radiation dose at 15°C in air without steam, and the empirical model developed from the experiments expressed the rate of methyl iodide decrease as proportional to the dose [92].

New experimental measurements on the rate of the radiolytic destruction of gaseous methyl iodide were performed by AEAT within the ICHEMM Project as part of the 5th EU Framework Programme [93]. A range of conditions relevant to reactor containments (temperature, dose rate, humidity, atmosphere, etc.) was considered. A speciation of the reaction products was not performed. The measured decomposition rates and dependency on dose were consistent with the previous data at ambient temperature. Increasing the temperature was found to only weakly accelerate the radiolytic destruction rate. Ethyl iodide was destroyed with the same rate as methyl iodide. The bulk gas phase composition is a decisive parameter only when switching to pure nitrogen atmospheres, which can be relevant to BWR's. An empirical model of methyl iodide destruction suitable for use in containment iodine chemistry codes was developed.

Furthermore, AEAT developed a mechanistic model in the ICHEMM frame to assist in interpreting the experiments and the understanding of the main reactions [93]. This model was also shown to give good agreement with the previous data on the radiolytic oxidation of gaseous $I_2$ in [90].

*Removal of iodine with spray systems*

Status 10 years ago

Spray systems are installed in many containments to reduce the pressure in accident scenarios. At the same time they wash out aerosols and volatile iodine.

The effect of spray systems on volatile iodine (and partly other aerosols) was studied in large-scale facilities in the 1960's and 70's. For example, large-scale tests were performed in the Nuclear Safety Pilot Plant at Oak Ridge ($3.8 \, m^3$, [94]), the Containment Systems Experiments (CSE) vessel of Battelle Memorial Institute ($850 \, m^3$, [95], the PSICO-10 vessel at Pisa ($95 \, m^3$, [96]), and the JAERI model containment ($708 \, m^3$,[97,98]). BWR and PWR conditions were reflected in the experiments, both in the chemical conditions of the spray volumes and for the thermal-hydraulic conditions of the falling drops.

More detailed experiments at a smaller scale and more detailed were performed in the 90s in the CARAIDAS facility of IRSN at Saclay to determine the collection efficiency of aerosols and iodine absorption by drops under representative conditions, with measurements of the droplet size evolution during their fall.

Fractional removal rates were determined from the frequently observed exponential decays of volatile iodine concentrations, particularly for elemental iodine. The removal rate is represented in the simple models parameters such as the absorption efficiency (depending on the chemical reactions within the spray droplets and mass transfer at the gas/liquid interface), the partition coefficient between droplet and atmosphere, and the residence time of the droplets in the atmosphere (defined by the ratio of the volumetric spray rate and the total spray volume), see. e.g [99]. Inherent in this removal rate are other significant parameters as droplet size and the falling velocity of droplets, and thermodynamic conditions such as temperatures of droplets and atmospheres, as well as steam concentration.

The removal of aerosols by sprays depends more on thermal-hydraulics than on chemistry, aside from the effects of solubility and deliquescence of particles. On the other hand, chemistry plays a significant role in the removal of volatile iodine. In this case aqueous iodine chemistry similar to sump iodine chemistry must to be considered to be acting at the same time as mass iodine transfer at the liquid/gas interface of the falling droplet. Fast chemical reactions on the scale of seconds (e.g. iodine hydrolysis) are important. Reactive additives to the spray such as sodium thiosulphate lead to fast conversion of absorbed $I_2$ into non-volatile iodine species increase the removal rate. Additionally, a high pH of spray solutions, favouring iodine hydrolysis, increases the removal of volatile iodine.

*Recent improvements*

Existing models on $I_2$ removal are often strongly related to the experiment from which they were derived. More recently developed models, such as the one implemented in the ASTEC code, take benefit of the more detailed results of the CARAIDAS experiments. The model is based on mass transfer in the gas phase, transfer at the interface, mass transfer in the liquid phase and chemical reactions in the liquid phase. It is validated on CARAIDAS and CSE experiments and reflects well the fact that spray is rather ineffective in the removal of $CH_3I$.

The **GIRS** tests [100] were performed at CIEMAT to quantify the effect of pH, temperature and droplet sizes on the $I_2$ removal.

The removal of organic iodine (studied: methyl iodide) is much less efficient as compared to $I_2$ removal, because the chemical conversion reactions within the droplets are generally slower than with $I_2$. Due to the relatively indifferent behaviour, much less attention has been paid on the experimental study of methyl iodide removal by sprays.

*Future work*

Future experimental work should concentrate on quantifying the removal of organic iodine forms. The existing experimental database is very small, although TMI-2 and Phebus FP have clearly shown that organic iodine is the pre-dominant gaseous iodine species in the long-term containment atmosphere, and any severe accident measure to reduce iodine source term to the environment needs to consider this iodine speciation.

The current ThAI project with a 60 m$^3$ test vessel for iodine tests includes a work package to perform spray tests. The facility offers the opportunity to study the interaction between spray chemistry and thermal-hydraulic conditions.

### 3.4.4 Open questions

The radiolytic destruction of iodine (molecular iodine as well as methyl iodide) results with iodine being present as an iodine oxide, which is partially identified as iodate upon dissolution in water. As pure substances, iodine oxides exist as solid phases, with negligible partial pressures. Once formed as molecules in the gas phase, they would deposit onto surfaces, aerosols or water droplets, or agglomerate in case of high concentrations. It is however unknown, how and how fast the volatility of iodine is changed upon conversion from $I_2$ or methyl iodide into iodine oxide particularly in the extremely low accident-relevant concentration range. So far, the application of the existing model on radiolytic destruction of iodine assumes an instantaneous conversion from the volatile state of the oxidized iodine into a into a non-volatile aerosol state.

The validity of this simplifying model will also be studied in the current ThAI project, i.e. the impact of ozone on the inventory of iodine in the gas phase of a large 60 m$^3$ vessel and in accident-relevant

thermal-hydraulic boundary conditions [85]. The data shall validate the current empirical model on the radiolysis of inorganic iodine in COCOSYS.

The radiolytic oxidation of iodine in the gas phase is a fast and efficient process to convert $I_2$ into iodine oxides. With respect to the removal of volatile iodine from the gas phase, it competes with the deposition at surfaces. The question then arises about the nature of the depositing iodine species. Deposition at surfaces is usually studied in non-irradiated conditions and using volatile $I_2$. Derived models from such experiments could therefore be non-representative for irradiated conditions, as e.g. the intermediate-scale RTF or CAIMAN tests. There is obviously a need to revisit the interpretation of these tests that form an important part of the validation of iodine chemistry codes [76].

### 3.4.5 Summary of remaining issues

Re-suspension from iodine loaded surfaces: Coupling of thermal-hydraulics with iodine chemistry is still an open question. The current ThAI project using a large-scale facility with a 60 m$^3$ volume will provide such data. Temperature, relative humidity and steam condensation are dominant parameters that influence the re-suspension rates by orders of magnitude. Current work in ThAI is focused on the re-suspension of $I_2$.

Condensing conditions: experimental work is on-going (ThAI).

Organic iodide production: experimental work is on-going (EPICUR).

Radiolytic oxidation of inorganic and organic iodine: experimentally to clarify the transition between volatile $I_2$ and non-volatile Iodine oxide; analytically to revisit the interpretations of intermediate scale RTF and CAIMAN tests with respect to the radiolytic oxidation of iodine.

## 3.5. EXCHANGES BETWEEN THE SUMP AND THE CONTAINMENT ATMOSPHERE

Mass transfer kinetic between sump and gas is a recurrent problem for iodine modelling in the severe accident (SA) codes because this parameter has a direct influence on airborne iodine concentrations. In most of the codes devoted to iodine behaviour modelling, the mass transfer phenomenon is described according to the two-film theory [101], which considers two resistances, one located in each phases, liquid and gas. At the interface, the species are considered to be at the equilibrium. The equilibrium value corresponds to the Henry's constant or more commonly used the partition coefficient, H, which is the ratio between the gas concentration and the liquid concentration at the interface.

The volatile forms of iodine are $I_2$ and organic iodides whose the more volatile is methyl iodide ($CH_3I$) that is over more probably the dominant organic iodides compounds in relevant conditions. For ethyl iodide ($C_2H_5I$) is about three times less volatile than methyl iodide [102].

Partition coefficients for $I_2$ and $CH_3I$ are displayed on Figure 10r. Wren et al. [103] report a 25ºC-value of 4.8 for the liquid-to-gas partition coefficient of $CH_3I$. This is in close agreement with the values of 4.5 and 1 respectively at 20°C and 70ºC, reported by Evans et al. [104], but somewhat lower than the value of 6.6 calculated using the expression in ASTEC/IODE, which originates from the review by Borkowski [105]. Anyway, this source of discrepancy only represents a minor source of uncertainty in the calculations.
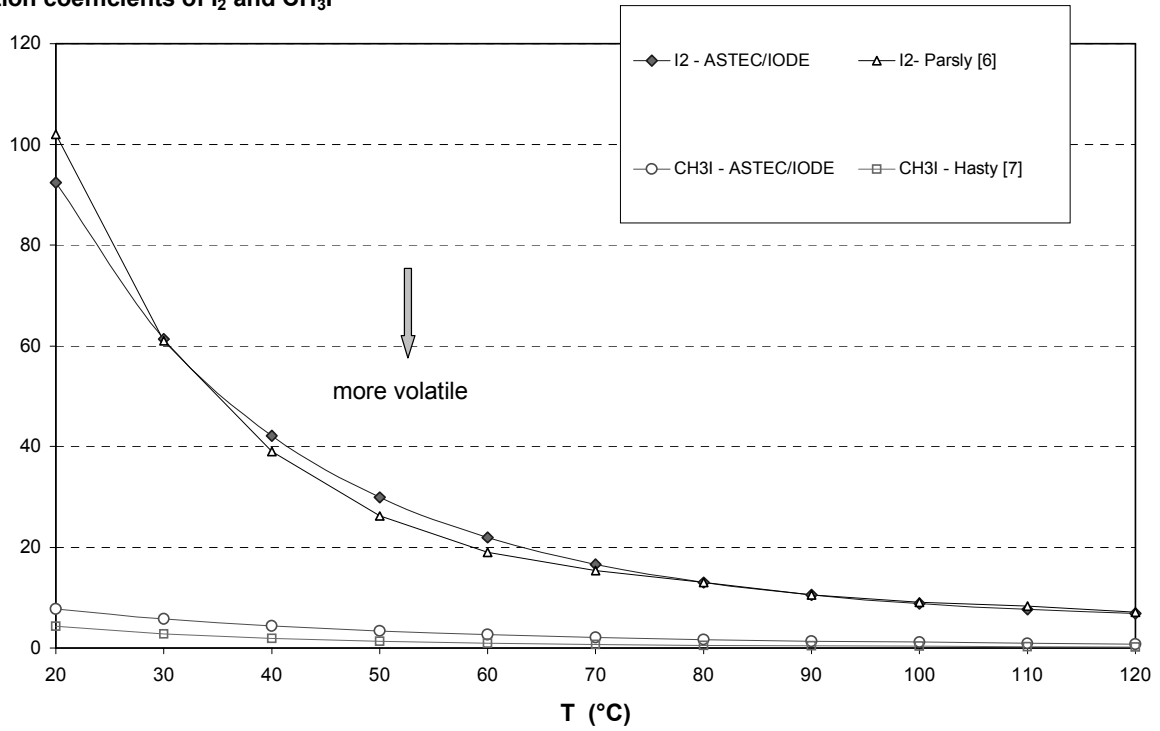
**Partition coefficients of I$_2$ and CH$_3$I**



**Figure 10: Partitions coefficients for I$_2$ and CH$_3$I as a function of temperature**

The equations (E-I) and (E-II) describing the transfer flow of iodine species, according to the two-film theory, referred respectively to the gas side or to the liquid side can be written as:

$$\phi = A_{int} \, k_g \left( C_g - C_g^{int} \right) \qquad \text{(E-I)}$$

or,

$$\phi = A_{int} \, k_L \left( C_L^{int} - C_L \right) \qquad \text{(E-II)}$$

with,

$A_{int}$, is the interfacial surface area, in m$^2$

$k_L$, is the individual mass transfer coefficient in the liquid side, in m.s$^{-1}$, equal to $\dfrac{D_{i\text{-}L}}{\delta_L}$

$k_g$, is the individual mass transfer coefficient in the gas side, in m.s$^{-1}$, equal to $\dfrac{D_{i\text{-}g}}{\delta_g}$

$C_L^{int}$ and $C_g^{int}$ are the interfacial concentrations in liquid and gas phases, in mol.m$^{-3}$

$C_L$ and $C_g$ are the bulk concentrations in liquid and gas phases, in mol.m$^{-3}$

$\delta_L$ and $\delta_g$ are respectively the boundary layer thicknesses in liquid and gas side, in m

One can derive new relationships (E-III) and (E-III) for the transfer flow as:

$$\phi = A_{int}\ K_L \left( C_g\ H - C_L \right) \qquad\qquad \text{(E-III)}$$

with,

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{H}{k_g} \qquad\qquad \text{(E-IV)}$$

$K_L$ being the overall mass transfer coefficient. $K_L$ is most often defined as an input parameter.

To illustrate the influence of $K_L$-value on iodine gas concentrations, they were computed with ASTEC/IODE code [106] for a French 900 MWe PWR geometry with two different values of $K_L$, $10^{-4}$ m/s and $10^{-3}$ m/s, no silver was considered in order to enhance mass transfer influence, and for the first two days pH was fixed at 5 and for the last two, 9.
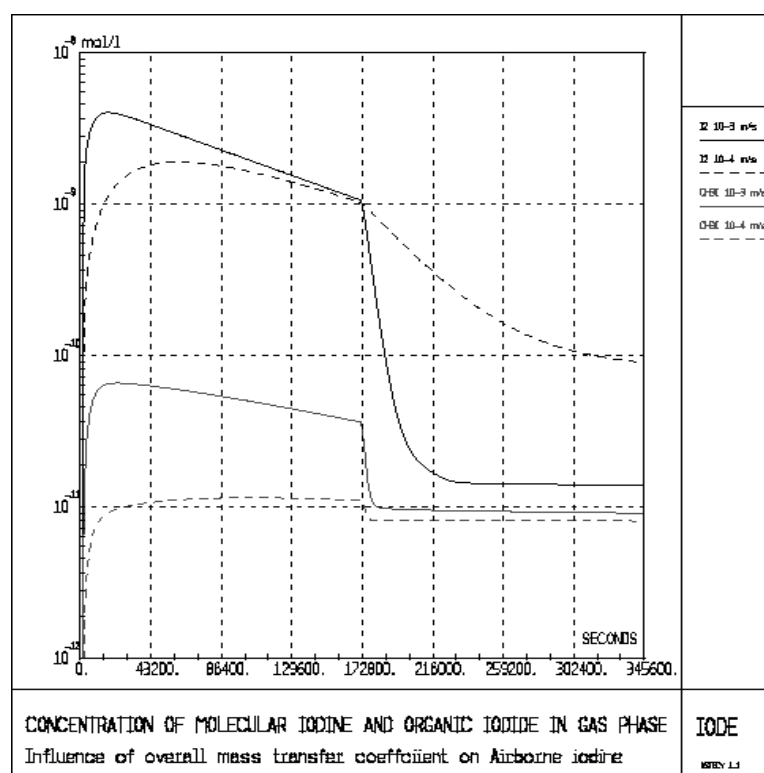


**Figure 11: Gas concentrations of $I_2$ and $CH_3I$ as a function of temperature**

In reactor conditions, the mass transfer process is generally governed by the natural convection due to thermal gradients inside the containment. So it is difficult to extrapolate with confidence mass transfer coefficients estimated on iodine experiments (RTF facility, CAIMAN facility …) which are small scale experiments compared to real size containment.

Anyway, it could be assumed that the sump will be well mixed because several phenomena promote the mixing. The first is the presence of the gas flowing through the sump due to MCCI interactions. The second effect is the decay heat of fission products which can induce convection loops inside the sump and

finally for different reactor designs and scenario, the possible existence of a liquid circulation loop for the safety-equipment requirements.

For the resistance in the gas phase, some correlations are available in the literature [107,108] which permit us to estimate $k_g$-value in assuming flat plate geometry at the interface. These correlations depend on diffusion coefficients of the species which is transferred, of a characteristic length and of dimensionless numbers according to the transfer regime involved (Grashof, Reynolds, Schmidt …).

Recently, in support to PHEBUS FP programme, a specific experimental programme devoted to mass transfer study was carried out at IRSN [109]. This programme had two advantages in comparison to other works performed in the past on this subject. The first is that the influence of specific regime like evaporating conditions or natural convection was investigated and the second is that the relative big size of the vessel, 10 $m^3$, which allows us to validate some correlations to calculate $k_g$ and $k_L$ values that could be extrapolated to reactor geometry with a rather good confidence. In evaporating conditions, it has been observed that evaporation speeds up mass transfer kinetics from the sump to the gas and decreases the equilibrium concentrations within the sump. To sum up, the two-film modelling is able to interpret with success the mass transfer experiments performed in natural convection without evaporation. For evaporating conditions, it is no more the case, as specific modelling is needed.

To conclude this modelling aspect of iodine behaviour, the dataset of experiments and knowledge is high enough in this field in order to complete/improve the existing modelling in the S.A codes.

## 3.6. SOURCE TERM TO THE ENVIRONMENT

Several pathways exist for the release to the environment. The first one is associated to the natural leaks of a containment in accident situation. The retention in the leakage paths is not well known and generally not credited for in safety studies aiming at giving a conservative value. The second one is associated with containment venting through filters in case of overpressure, for those reactors using such a procedure. Certain venting procedures involve filters having a very high retention for aerosols, a low one for $I_2$ and a negligible one for organic iodides. The third one is associated to basemat penetration by molten corium/concrete interaction. The filtering medium is then the soil and the assumption that retention is the same as for filtered venting is often made.

A second series of pathways is associated with containment by-pass sequences, of which Steam Generator Tube Sequences (SGTRs) are risk-dominant for PWRs and will be discussed in the next section.

### 3.6.1. Iodine under SGTR Sequences

Steam Generator Tube Rupture (SGTR) sequences are dominant-risk in Pressurised Water Reactors (PWR's) since they entail a direct path for radioactivity from the primary circuit to the environment. SGTR source term studies under severe accidents or Design Basis Accidents (DBAs) are not well known and PSA studies typically assume little or no retention of fission products in the secondary side of the failed steam generator. Presumably, however, some source term attenuation should be expected in the tube bank, support plates, separators and dryers, even in the total absence of water. In order to tackle with the issue, the SGTR project [110] was launched within the 5th Framework Programme of the CEC and, at present, the international ARTIST project is underway with the final goal of supporting safety assessments with a unique database and analytical models.

Three different scenarios may be identified regarding source term behaviour [111]:

−   A severe accident sequence with a dry secondary side.

- A severe accident sequence with water present at the secondary side.

- A DBA with the primary coolant in a liquid and superheated state with respect to the secondary side.

The ongoing research (i.e., the ARTIST project) is essentially focused in the aerosol behaviour under the two first scenarios, although some studies are planned on specific aspects of the DBA conditions. Anyway, no chemical considerations are foreseen.

Regardless of whether iodine emerging from a steam generator tube breach is in vapour or particulate form, little is known at present about its behaviour within the secondary side under severe accident conditions. This lack of knowledge is even further marked in the presence of water, since hydrodynamics of carryover gas is entirely unknown. The jet velocities reached by the gas at the secondary side entry point as well as the tube bank immersion in the aqueous phase are conditions unexplored so far. In addition, chemically relevant conditions for iodine behaviour, like dose rates and pHs, have not been specifically addressed in iodine chemistry studies (more focused on containment conditions).

Concerning the SGTR DBA scenarios, three distinct mechanisms exist for transport of iodine to environment: partitioning of iodine dissolved in the Secondary Coolant System (SCS), flashing of the reactor coolant system because of the temperature and pressure differences between primary and secondary sides of the steam generator, and droplet entrainment with the flashing fraction. Adams [112] demonstrated that the flashing mechanism was the dominant one and recommended, in view of the lack of data, to carry out further experiments. This iodine transport in vapour bubbles will be studied under low pressure conditions in the Phase VI of the ARTIST project.

# 4. MODELS AND CODES

## 4.1. MODELLING ASPECTS

Reliable estimates based on computer codes or models of the volatile iodine formation and behaviour under postulated severe accident conditions are the final goal of the experimental and theoretical work on containment iodine chemistry. Usually, we are trying to obtain best estimate predictions (i.e., not conservative predictions) because under a severe accident conditions it is sometimes difficult to say what is conservative and what is not.

The criteria for assessing the predictive capabilities of the models and codes have been debated for a long time. The optimum seems to be the ability of the model to predict the gas phase volatile iodine concentration approximately within a range of one order of magnitude (it is, of course, important particularly for those cases where the concentration of volatile iodine in the atmosphere is high enough to be a safety issue).

The ability to predict gas phase iodine concentrations is closely linked with the ability of the model to predict pH profile in the sump water as a function of time (pH is one of the most important parameters influencing iodine volatility: the more acidic the pH the higher amounts of volatile iodine are produced in water and then partitioned to the atmosphere). Predicted pH changes would not such a problem if the sump water could be guaranteed to remain alkaline for some time during and after an accident and this is the case for sumps treated by chemical additives. However, pH prediction for an untreated sump under prototypical accident conditions is certainly a challenge.

Another aspect of the question of the model predictive capabilities is the ability to differentiate properly between $I_2$ and organic iodides (or even other volatile species) in the atmosphere, and even between low volatility RI and high volatility RI.

The most important reactions to model are volatile iodine formation and decomposition in aqueous phase (water in the containment sump), mass transfer of the volatile iodine from water to the containment atmosphere and gas phase volatile iodine formation and behaviour including iodine interactions with painted surfaces in containment.

There exist two basic approaches to modelling of iodine interactions, namely, either mechanistic models or empirical models. Currently, the empirical models are those of the practical use since they are being incorporated into big containment codes while mechanistic models are more important as a scientific tool for studying the basic principles.[13] Mechanistic modelling tries to represent the whole set of elementary radiochemical reactions (typically all the important elementary reactions in water which can amount to much more than one hundred reactions) and solves for the kinetics of these reactions using some ordinary differential equation solver. The empirical models, on the other hand, are using only small number of correlations suitable for the whole range of conditions under a postulated accident. These

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[13]  exception being mechanistic model INSPECT which has been integrated into MELCOR 1.8.5; proper modelling of organic iodide formation and behavior is still missing in MELCOR so its applicability is limited so far

correlations are based on theoretical evaluations of experimental findings and/or on results of mechanistic calculations for a pre-defined range of conditions.

Typical representatives of the mechanistic approach are the INSPECT reaction set [113,114] (IodiNe SPECiation and Transport), developed in AEAT, which has been integrated with some changes into MELCOR 1.8.5 [45], and the LIRIC model [53] (Library of Iodine Reactions in Containment) developed in AECL. Typical representatives of the empirical codes are the French code IODE [115,116], used in many European countries, also as a part of the European code ASTEC, and the IMPAIR code [117,118] which was developed in PSI Switzerland and is used in Germany and also in Japan. The Canadian code IMOD [119] is an empirical code that was developed based mainly on the knowledge coming from mechanistic approach (from LIRIC).

Nowadays, intensive efforts have been spent in the further development of the French code IODE (at IRSN), Canadian IMOD (together with LIRIC, at AECL) and Swiss mechanistic code PSIODINE and the semi-empirical code IMPAIR3 (at PSI).

Passive coupling or integrated use of important empirical models, i.e., IODE, IMOD, IMPAIR3 together with the containment codes provide best estimate treatment of iodine behaviour in conjunction with the affecting thermal-hydraulic and aerosol parameters in the aqueous and gas phases as well as the transfer of volatile species between them

The treatment of governing processes in the aqueous phase for the generation of volatile iodine species, i.e., the models for radiolytic oxidation of non-volatile iodide, $I^-$, to volatile molecular iodine, $I_2$, and reduction back to iodide, is currently quite close in IODE and in IMOD.

The Taylor-Liger model in IODE 5.1 of organic iodide (RI) formation in water is again much closer to Canadian IMOD than it used to be in the previous versions of IODE. RI formation in water is now in both codes based on reactions of $I_2$ with organics leaching from paints (submerged painted containment walls).

Other processes taking place in the sump water (including formation of insoluble AgI and radiolysis and hydrolysis of RI) are generally modelled in a similar way in IODE, IMOD and IMPAIR.

There are differences between the two codes in the way they predict the pH changes in the sump water and also in the way they differentiate between volatile and less volatile (groups of) organic iodides.

The two-resistance model with the overall mass transfer coefficients, to be provided as user-input parameters is the commonly used treatment for the mass transfer of volatile iodine species between water and the atmosphere in most the iodine codes. A further improvement in this treatment could be modelling those coefficients using time dependent thermal-hydraulic quantities as calculated by the containment thermal-hydraulic or integral system codes.

In summary, for the treatment of the aqueous phase models and mass transfer, there is a great deal of similarities in codes such as IODE and IMOD in terms of representing very complex reaction paths including many intermediate reactants by considering only the key reaction species and a few semi-empirical reaction sets with empirical reaction constants. The jump from phenomenological (mechanistic) treatment of all the reactions with all the participating reactants to representing a set of reactions for the key phenomena is great, however, it is important to achieve fast running codes, The semi-empirical treatment is then valuable provided that the empirical rate constants used in the formulations cover boundary conditions anticipated in the reactor accidents. Therefore, similarities of models for the main reaction paths in such different codes provide the confidence to the code developers and users associated

with the applicability and quality of the models. The current status of semi-empirical as well as the mechanistic codes certainly represents a significant progress achieved since the last10 years.

A rather different situation exists for the modelling of volatile iodine formation and behaviour in the gas phase. Sorption of $I_2$ on various surfaces of the containment atmosphere is recognised to be very important process by all of the code developers. The models associated with the sorption and desorption -without chemical changes- are similar in most of the codes.[14] On the other hand, production of volatile iodine species in the containment atmosphere, or on surfaces exposed to the gas phase, is the most controversial issue. In some codes these processes are not modelled at all while in others they are claimed to be the crucial issue to model at least under certain conditions. For example, some modellers assume that the organic iodide production from interactions of iodine with painted surfaces of the containment atmosphere could be the most important route of volatile iodine formation, especially for the case where volatile organic iodine transfer from the sump is suppressed.

Another subject debated among modellers is the significance of radiolytic oxidation of iodine in the containment atmosphere to higher oxidation levels of iodine e.i.,$I_2O_5$ and $I_4O_9$ . Such iodine species are solid and non volatile and might constitute the final stage of the oxidation products. This is due to the fact that the available data base is not comprehensive and detailed enough to follow various stages of the radiolytic oxidation at various prototypical conditions.

In summary, the common understanding established for modelling the key aqueous phase processes within the international community has not ye been achieved for the gas phase processes. Further efforts in the area of supporting experimental programs and accompanying analytical efforts are necessary to achieve a similar common level for the significant reaction routes for the gas phase.

In the various iodine models, there are also descriptions of some other phenomena generally of less importance than those already discussed. Maybe it is worth mentioning the effect of steam condensation on volatile iodine in the atmosphere. This phenomenon is modelled in some codes in more or less consistent manner resulting in a first-order rate of removal of iodine species in aerosol or gaseous form from the gas phase.

### 4.2 Use of Codes for Plant Studies

International Standard Problems (ISPs) provide a good opportunity to assess calculation tools at a common ground and provide a forum for specialists to exchange experience and know-how to establish a common understanding of modelling different phenomena. It provides also the opportunity for the new comers to receive the experience from the senior scientists. . Both ISP-41 and ISP-46, recently completed, have provided useful information regarding the present status of iodine chemistry models and codes [51]. This has allowed us to draw conclusions for modelling and integral aspects, as well as implications for plant studies

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[14] Generally the sorption models use  first order rate behavior of iodine sorption on various types of surfaces. This treatment is just an integral approximation of the observed data without deeper knowledge of the deposition kinetics and even without deeper knowledge of chemical nature of the sorbed iodine. In the ISP 41 exercise, large variations in the predictions stem from a wide spread in the user-input adsorption/desorption rate values. It may be envisioned that the deposition kinetics could be influenced by the type of the surface, temperature and humidity of the atmosphere. Possible concentration gradients in the gas phase might additionally complicate the mass transfer of the iodine to the surface.

A strong *user effect* is visible in results from ISP-46, as was evident in previous ISP's, therefore the user effect in plant studies cannot be ruled out. A major objective must be to limit the consequences of this user effect on the quality of the study. It is recommended that this could be achieved by: checking that previous training has been efficient; using adequate procedures for controlling the results and peer reviewing, involving experienced specialists in the field; and by checking that enough support is provided by developers when necessary. The use of code options or input parameter values differing from default or recommended ones might be necessary depending on specific conditions but should be duly justified.

The *quality of the models* must also be taken into account. A number of necessary improvements in codes and models have been identified, the main ones being: a better estimation of structural material release, especially for control rod elements, the possibility to take into account the presence of gaseous iodine in the RCS; and the definition of optimum parameters for iodine chemistry codes. As not all the necessary improvements can be achieved in a short term, users have to be well aware of the validation status of codes and must take into account their limitations when performing plant studies.

*Sensitivity studies* should be performed as a usual good practise. In addition, an important lesson from the integral ISP-46 is that iodine calculations may suffer from propagation of errors coming from other modules in integral calculations, as iodine chemistry in the containment is at the end of the calculation chain. It was recommended, at the THENPHEBISP (ISP46) application workshop [120] that iodine chemistry stand-alone calculations can be used to complement integral calculations, as necessary. These calculations should use boundary conditions, such as the silver amount or gaseous iodine from the RCS that are different from the ones calculated by integral codes.

Severe accident codes are *difficult to handle*, and their *validation is not complete*. They should not be used as "black boxes", i.e. their results have to be interpreted, according to the goal of the study for which they are used. Extensive training of new users should be mandatory, and efficient quality assurance procedures for reactor studies have to be used, involving a review of the results by experienced experts not directly involved in the work.

Finally, users should not trust automatically the results of their calculation, but make a critical analysis! Do the results seem consistent and reasonable ("reality check")?

# 5. CONCLUSIONS

At the beginning of 60's, when the reactor site criteria of most nuclear reactors were set the radiological importance of iodine recognised. At that time, some rather crude hypotheses were taken concerning its behaviour under accident conditions. For instance, in the US TID 18444 document, it was considered that:

− half of iodine core inventory is instantaneously available in the containment,

− half of in-containment iodine is deposited onto surfaces rapidly.

− most of iodine entering the containment (91%) was supposed to be in the form of volatile molecular iodine ($I_2$) and the rest were almost equally distributed in particulate form (5%) and organic species (4%).

Since that time, the Rasmussen WASH 1400 report and the TMI2 accident triggered a large effort on severe accidents, both in the experimental and modelling fields. Concerning iodine, this allowed to improve our understanding of iodine behaviour in severe accident conditions, and to build models incorporated in codes used for safety studies. The dominant phenomena have been identified. A way to select the most important ones in a risk perspective is to look at those which mainly govern the evolution of the gaseous iodine concentration in the gas phase of the containment.

Considerable progresses have been made in our understanding of iodine behaviour under severe accident conditions, particularly over the last 15 years since the intermediate engineering-scale integrated-effects test facilities that could provide radiation environments, such as the RTF at AECL and later CAIMAN at IRSN Cadarache, became available. Together with the ThAI facility (non-radiation facility), these facilities, having some control of test conditions and on-line measurements, have been used for systematic and parametric studies in multi-components environments, and have been instrumental to the interpretation of a much-larger scale PHEBUS-FP experiments. The integrated effects tests performed in the intermediate scale and large scale facilities have facilitated in prioritising and establishing key phenomena affecting iodine volatility and have been crucial for developing and validating whole system models on iodine behaviour under post-accident containment conditions.

Nevertheless, the results from the intermediate test facilities still show the net effects of many contributing phenomena or processes. Some of these processes are highly dependent on geometric scale of the test containment, while the other processes are independent of the scale. Thus, the results from the intermediate scale facilities are often difficult to interpret and cannot be directly applied to the real containment conditions not even to the PHEBUS conditions. For the same reason, the PHEBUS results cannot be directly applied to real containment conditions. Thus, the international iodine community over the last decade or so has performed very valuable underlying experimental and modelling activities in support of the intermediate and large engineering scale studies. Studies on the radiation induced iodine reactions and iodine-surface interactions have been and will be performed under the AECL-COG Reactor Safety Containment behaviour projects and the AECL-UWO Collaborative Research projects, and under the European Framework Projects Iodine Chemistry and ICHEMM, French EPICUR and PARIS projects and several other projects carried out at various European laboratories, such as PSI, Chalmers and former Siemens-Erlangen (currently FRAMATOME-ANP Erlangen); studies on high temperature RCS chemistry

under the CHIP project. These research activities at more fundamental levels have made and will make possible the interpretation of the results from the intermediate and large scale studies, and the development of iodine models with better predictive capabilities.

As the result of the concerted programs of the international iodine community, ranging from the large-scale PHEBUS tests to intermediate-scale RTF, CAIMAN and ThAI tests to the smaller underlying studies, there has been an explosion in our stride to understanding of iodine behaviour under severe accident conditions over the last decade. Most of the knowledge gained has been slowly incorporated into and improve on safety analysis iodine codes. The iodine models in safety analysis codes describe iodine behaviour in varying degrees of sophistication. Mechanistic codes, such as LIRIC, INSPECT and MELCOR-I, PSIODINE attempt to model all foreseeable radiochemical reactions involved and are generally used for detailed studies and thorough understanding. Semi-explicit treatment of the iodine chemistry involving only limited but representative number of reaction paths involving only the main iodine species, such as IODE, IMPAIR, AIM and IMOD, is generally incorporated in system-level codes. The development and continual improvement on these models over the last decade has been impressive. Particularly, over the last 7 years, the international iodine community has collaborated in the improvement of the iodine models through OECD/CSNI sponsored ISP-41 and ISP-46 code comparison exercises. The models and codes have been validated at varying degrees against separate-effect tests, intermediate-scale and integral experiments. However, during these validations, most of them required many user-defined model parameters and the input parameters that were not well defined in the tests and hence estimated or calculated by other models dealing for instance with thermal-hydraulics or aerosol physics.

Although there has been a significant progress in our understanding of iodine behaviour over the last decade, the results from the relatively new integrated effects tests have revealed the many unexpected and synergistic effects that were not previously recognised, and emphasised the complexity of underlying iodine phenomena. Considerable efforts to address newly emerged issues have been made. However, there are many areas that require additional efforts to come to the closure of the iodine issues. The current status of our understanding of key phenomena is briefly described, followed by the areas that require additional efforts to bring the iodine issue to the closure.

The main phenomena that would govern the evolution of the gaseous iodine concentration in the containment atmosphere following an accident are considered to be:

- the fraction of iodine released from the RCS in gaseous form into the containment,

- the radiolytically induced volatile iodine ($I_2$ and organic iodides) formation in the bulk water phase (sump, pool on the floor, etc),

- the iodine adsorption/desorption on a wide variety of surfaces, both in the aqueous and gas phases,

- the aqueous-gas phase interfacial mass transfer and partitioning of volatile iodine species

- the interactions of volatile iodine with air radiolysis products and the fate of the resulting oxidation products.

The following phenomena, although not directly involving iodine species, would influence the gaseous iodine concentration, because of their impacts on the iodine reactions and transport processes:

- certain reactions involving impurities compete with reactions involving iodine for the water radiolysis products; those impurities if available in significant concentrations, even if they do not

interact with iodine species, should be tracked in the codes for an improved treatment of the iodine behaviour.

- the dissolution of organic solvents from painted surfaces or organic compounds from oil and grease into the containment sump water as it affects the organic iodide formation,

- air radiolysis product behaviour in the presence of containment surfaces and aerosols as it affects the formation of oxidised iodine species, the radiolytic decomposition of organic iodides and nitric acid formation in the gas phase.

Although the relative importance given to the different phenomena are still debated somewhat, it is generally agreed that semi-empirical iodine models should incorporate some descriptions of these phenomena, either as overall rate constants or as detailed sub-models.

The relative importance given to the different phenomena has evolved with time and is still debated. The importance of liquid phase phenomena, considered in the past from the results of small scale tests, has been reinforced by the results from intermediate-scale experiments such as RTF and CAIMAN. The possibility of gaseous iodine source term from the RCS to the containment was considered in source term evaluations especially for the accident scenarios involving early containment failures, and the results of the Phébus-FP programme have confirmed this possibility and however also shown the complexity of underlying phenomena. It was also realised that the interactions of iodine with paints in the gas phase could be an important contributor to organic iodide formation and could even dominate under certain circumstances. The importance of the gaseous iodine release from the RCS has been recognised lately and has triggered ongoing research activities.

The degree of confidence that can put on the predictive capability of models and codes depend on the adequacy of the underlying knowledge of phenomena and on the validation status of the models/codes under prototypical accident conditions.

Concerning the knowledge, a number of points should be better addressed:

a.   The gas phase chemistry and the formation of volatile iodine in the primary circuit.

This is one of the two main routes leading to the presence of volatile Iodine species in the containment atmosphere. The results of Phébus-PF have underlined the complexity of phenomena and it is expected to gain valuable information from the newly launched CHIP programme.

b.   The desorption rate of organic iodide from painted surfaces.

This phenomenon is a contributor to the organic iodide concentration in the gas phase. Time-dependent data are expected from the ongoing EPICUR programme, helping the validation of existing models and/or their improvement.

c.   The interactions of iodide ions with wet painted surfaces after steam condensation and the potential subsequent release of volatile iodine

Due to the lack of data base it is currently not possible to determine the Importance of these interactions which might (or not) lead to the formation of volatile iodine species. Simple but controlled experiments under irradiation could be very helpful to identify the significance of the issues.

d.   The effect of impurities on oxidation and reduction of iodine species in liquid phase.

Though the effect of dissolved impurities on the net conversion rate of non-volatile species has been realised relatively recently, considerable progress has been made for the effect of some selected ones but not all. The other issues regarding the impurities are the determination of the type and their concentrations under in real situations.

e.    The iodine behaviour in the secondary side of the steam generator.

There is a nearly complete lack of data on the subject and this leads to use very crude hypotheses in safety evaluations. An extension of the ARTIST programme to iodine behaviour, as initially foreseen, would be very valuable.

f.    The interactions of volatile iodine with air radiolysis products in the containment atmosphere., especially the nature and fate of oxidation products.

The existing knowledge needs to be extended to the nature and fate of the resulting iodine oxidation products, together with the depletion in air radiolysis products by reactions with surfaces. New information is expected from the current PARIS programme.

Concerning the validation, the effort is being and must be further pursued, especially for:

g.    The homogeneous formation of organic iodide in liquid phase

A variety of organic residuals may be present in a sump water originating from the leached solvents from the paints, oils, etc., which may after many reactions steps lead to the generation of low to high volatile organic iodides. The processes are rather complex. Efforts have been spent to simplify the existing detailed models for use in the semi-empirical codes. Further validation work on existing data and already launched programmes such as EPICUR are ongoing.

h.    The organic iodide formation by reaction with submerged paints.

Although there is a considerable debate between the modellers for assigning the main route for the organic iodides in the water phase, direct generation on the submerged surface could also contribute to the overall generation of the organic iodides in the aqueous phase in addition to that by homogenous formation. The existing models based on the test data for the net organic iodide generation assume that the submerged surface-iodine reaction is the main rout. Validity of these models are limited to the extent of the conditions of the tests (e.g., these tests do not consider the availability of other organic sources) and should be used with caution during the plant applications.

Boundary conditions are used for iodine chemistry calculations, and some of them are not enough accurately predicted.

i.    pH evolution in the sump water.

If pH is not controlled by engineering measures, its evolution will depend on the amount and nature of materials released into the containment's sump. Sound hypotheses have to be made for plant studies, and recommendations should be given on how to tackle the problem.

j.    determination of the dose rate and type of the dose in the containment

Integrated analysis of iodine behaviour in a complete treatment of severe accident phenomenology requires proper prediction of the time dependent dose rates in the containment atmosphere and the sump water. For multi-compartment applications this becomes more critical since the distribution of the activity

between different compartments follow the transport driven by the intercompartmental flows. Type of the dose and its associated dose, i.e., beta and alphas emissions, should bring the attention to the level of local dose especially for those reactions for which not only the bulk dose rate but high local dose rate is important, e.g., surface reactions, radiolytic stability of certain iodine species.

k.   Amount of silver and its oxidation state in sump water.

Silver release from the core is often badly calculated by fuel degradation codes. Improvements should be made in that field. There are only few data on its oxidation state coming from Phébus integral experiments. It is expected that the current PARIS programme will provide new information. Note that this phenomenon is important only for reactors with silver-indium-cadmium control rods.

The iodine chemistry codes also suffer from the fact that the values of some crucial parameters are user-defined but no physical models are built in to calculate them. These are:

l.   Mass transfer parameters.

Improvements have been made in certain codes such as IODE by using the coupling between thermal-hydraulic and iodine chemistry calculations for the coefficients regarding interfacial mass transfer between the water and gas phases. This should be extended to other codes.

The THAI experimental programme could offer the possibility to validate the coupling between phenomena introduced in the codes, providing also information about the added value of treating iodine chemistry with a multi-compartment description in lumped parameter codes.

m.   Adsorption velocities and desorption rates on/from different surfaces

The current iodine codes expect code users to define the adsorption and desorption velocities on/from different surface using the available experimental data or engineering judgements where the data is not available (e.g. deposition/desorption on concrete surface). A large variation in the values by different users using even the same codes has been evidenced in recent ISPs. It would be valuable if a commonly agreed set of values for these parameters can be agreed upon for a range of prevailing conditions with a clear guidance for the code users. This necessitates an assessment of the available data in the literature which might point out to and the need for new data.

The severe accident research, development and application community is aging and loosing expertise as the number of retired experts overwhelming the number of the newcomers. The number of experts with the right expertise in the field of iodine behaviour is becoming scarcer. This poses a problem for the organisations who introduce relatively inexperienced scientists or analysts to perform reactor safety studies including iodine chemistry. It is therefore particularly important that code developers provide proper guidance about the validation status of the calculation tools, recommendations for the user input values and the selection of the code options as well organise efficient training courses.

Finally, an international consensus on the degree of satisfaction with the code prediction capabilities should be established. As an example should the level of sophistication of the code models be regarded satisfactory when the code is shown to predict the gaseous iodine concentrations measured in all the relevant tests covering a broad range of conditions prototypical for the severe accident conditions within an order of magnitude? Should the goal depend on the gaseous iodine concentration perhaps with a less demanding requirement for low concentration? Answers to these questions will probably depend on the nature of the safety studies (e.g. do we want conservative or best-estimate studies). They may also be dependent on the accident scenario as well as the type of the plant in question.

In summary, this report reviews the progress made in the last ten years on the understanding of phenomena governing iodine chemistry and release in the case of reactor severe accident. It evaluates the current status of iodine chemistry knowledge and tools used for source term prediction in connection with accident management and emergency planning. The remaining weaknesses have been identified and proposals have been made for improvement.

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