RAIM — A MODEL FOR IODINE BEHAVIOR IN CONTAINMENT UNDER SEVERE ACCIDENT CONDITION

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Abstract

Following a severe accident in a nuclear power plant, iodine is a major contributor to the potential health risks for the public. Because the amount of iodine released largely depends on its volatility, iodine’s behavior in containment has been extensively studied in international programs such as International Source Term Programme-Experimental Program on Iodine Chemistry under Radiation (EPICUR), Organization for Economic Co-operation and Development (OECD)-Behaviour of Iodine Project, and OECD-Source Term Evaluation and Mitigation. Korea Institute of Nuclear Safety (KINS) has joined these programs and is developing a simplified, stand-alone iodine chemistry model, RAIM (Radio-Active Iodine chemistry Model), based on the IMOD methodology and other previous studies. This model deals with chemical reactions associated with the formation and destruction of iodine species and surface reactions in the containment atmosphere and the sump in a simple manner. RAIM was applied to a simulation of four EPICUR tests and one Radioiodine Test Facility test, which were carried out in aqueous or gaseous phases. After analysis, the results show a trend of underestimation of organic and molecular iodine for the gas-phase experiments, the opposite of that for the aqueous-phase ones, whereas the total amount of volatile iodine species agrees well between the experiment and the analysis result.

1. Introduction

Following a severe accident in a nuclear power plant, iodine is a major contributor to the potential health risks for the public, especially with regard to the thyroid. During a core meltdown, a large fraction of iodine in the core can be released into the containment in aerosols form, containing metal iodides and gaseous iodine, as found in Phébus tests [1–3]. Gaseous iodine released from the reactor coolant system (RCS) is depleted mainly through trapping on the containment surface, which can result in the production of organic iodide through interactions between iodine and paint [4–6]. The gaseous molecular iodine could also react with air radiolysis products (ARPs) such as ozone, to form iodine oxide; an aerosol-borne iodine species [7,8]. Organic iodides are also depleted by radiolytic decomposition. However, most metal-iodide...
particulates can be readily dissolved in sump water resulting in iodide ions. These will be oxidized to form volatile inorganic iodide ($I_2$) through many reactions such as radiolysis and hydrolysis. The organic radicals, made from organics such as paint in the sump water, react with the molecular iodine to produce organic iodides. These gaseous iodine species move from the sump water to the containment atmosphere mainly by diffusion and natural convection [9].

The amount of iodine that could be released from the containment largely depends on the volatility of the various kinds of its species [1] and their retention by filters used in the containment venting systems. Therefore, iodine behavior has been a major topic of international research programs such as International Source Term Programme (ISTP) [7,8,10], Organization for Economic Co-operation and Development-Behaviour of Iodine Project (OECD-BIP) [11] and Organization for Economic Co-operation and Development-Source Term Evaluation and Mitigation (OECD-STEM) [12]. The major research areas of these programs are iodine chemistry, surface reactions, mass transfer, modeling of iodine chemistry and its applications to severe accident assessment, and accident management. Qualified tools for modeling these phenomena have been developed and validated experimentally.

ISTP was carried out by the IRSN (Institut de Radioprotection et de Sûreté Nucléaire) for 5 years until the end of 2010 in order to reduce uncertainties when evaluating the environmental release of radioactive products such as iodine or ruthenium following a core meltdown accident in a pressurized water reactor (PWR). Among its various experimental topics, EPICUR and PARIS programs provided experimental data on the physicochemical transformations of iodine (formation and destruction of volatile iodine species) under the effect of radiation in the reactor containment. OECD-BIP was organized by the Organization for Economic Co-operation and Development, Nuclear Energy Agency (OECD/NEA) and has been operated by Canadian Nuclear Laboratories (former AECL) since 2008, performing work in the following three areas: adsorption and desorption of iodine on surfaces, organic iodide formation from containment paints load with iodine from the gas or aqueous phases, and provision of Radiiodine Test Facility (RTF) experimental data from historical experiments. OECD-STEM was launched in 2011 to better address known phenomenological uncertainties relevant to radioactive iodine release in the mid and long term time frame, especially in terms of the stability of iodine aerosol particles under radiation, the long-term gas/deposition equilibrium in a containment, and iodine interactions with paints. Ruthenium chemistry was also investigated in this study.

The Korea Institute of Nuclear Safety (KINS) has been studying the iodine chemistry issue as one of the regulatory research topics, and has joined international programs with other Korean organizations such as the Korea Atomic Energy Research Institute (KAERI). In the course of this study, a simplified, stand-alone iodine chemistry model, RAIM (Radio-Active Iodine chemistry Model) has been developed in order to deal practically with iodine chemistry in the containment [13,14]. This model is based on the semiempirical IMOD methodology [15,16] in terms of the simplification of the chemical species, reaction mechanisms, (especially for the aqueous phase), and reaction rate constants. The gas-phase models are largely based on other previous studies carried out by Bosland et al [7,17] and Funke [18]. Although RAIM is still under development, attempts have been made to couple it with the MELCOR code [19] in order to model organic iodides and to simulate Phébus FPT1 and FPT3 tests [20]. However, the MELCOR-RAIM estimation of the organic iodide concentration was very small compared to the measured data, which showed the need for the further development of its homogeneous reaction model of organic iodide formation. This article summarizes the activities concerning the development of the RAIM model and the benchmarks of the ISTP-EPICUR S1 and S2 series and OECD-BIP P1OT2 experiments.

2. Model development

In order to develop an iodine chemistry model, the existing methodologies have been reviewed. There are two types of iodine behavior models: mechanistic and semiempirical models. Mechanistic models such as LIRIC [21,22], INSPECT [23], and MELCOR [19] are based on detailed data established through extensive analysis of iodine reactions; they also include mechanisms and intermediate products of iodine reactions. However, empirical models such as IMOD have an advantage with regard to their compatibility with integrated severe accident codes due to their simplified scheme, even though they may have limitations in terms of providing accurate calculations for such complicated iodine reactions [9,13].

Following previous studies, we decided to develop our own model based on the LIRIC methodology [20,21], but aiming for a smaller and simpler model similar to IMOD [15,16]. Therefore, reactions in the aqueous phase and volatile species for mass transfer were reduced. For the simplification of reactions and rates, single species were used in the gas and aqueous phases. For instance, the iodine species to be examined were volatile $I_2$, organic iodides of high volatility (HVRI) and low volatility (LVRI), nonvolatile, nonaqueous iodine, iodine oxide aerosols (IOx), and iodine adsorbed on the surface ($I_{ad}$) in the gaseous phase [16,17]. HVRI refers to all of the organic iodides that are volatile, e.g., CH$_3$I which is more volatile than $I_2$, whereas LVRI includes all of the organic iodides that are less volatile. Nonvolatile iodine species in the aqueous phase consists of mainly iodide ion, $I_{(aq)}$, with minor components of species such as HOI, I$_3$ and IO$_2$ including IO$_3$.

Nonaqueous iodine species are those bound on the surfaces in contact with the aqueous phase, e.g., AgI colloids and solids, or iodine adsorbed on surfaces in contact with the aqueous phase [16]. Several other materials participating in the iodine reactions, e.g., organics and organic radicals, and ARPs such as ozone, are also dealt with. Fig. 1 shows the reactions and the transport processes of the iodine species that are modeled by RAIM.

The reaction rate constants suggested by previous studies [8,15–18,21,22] have been adopted; some data from them were given as functions of temperature or the associated activation energy. Reactions with no available rate constants were determined through simulation and sensitivity analysis of EPICUR and RTF experiments. The differential equations for the kinetics of the reaction schemes are solved numerically.
using an explicit method. Until now, the behavior of iodine in condensing water film on surfaces in the containment atmosphere ($I_{\text{con}}$) and the formation of organic iodides through homogeneous reaction between inorganic iodine and organics in the gaseous phase are not modeled by RAIM. Deposition of iodine oxide aerosols in the surface and the subsequent decomposition [24] are not dealt with, either. In any case, the rate constants for the reactions involving CO$_2$ and CO$_3^{2-}$/CO$_3^{2-}$, which can affect the sump pH, have not yet been determined.

2.1. Reactions in the liquid phase

Chemical reactions associated with the formation and destruction of iodine species and surface reactions in the containment sump and the atmosphere, are treated in a simple manner. As described by Wren et al [15,16,21,22], the aqueous-phase reaction model includes the following reactions.

(1) Reactions between nonvolatile iodine species and volatile inorganic iodine species [15].

Stoichiometry:

NonVol$_{(aq)}$ ↔ Vol$_{(aq)}$

Kinetics:

\[
\frac{d[\text{NonVol}_{(aq)}]}{dt} = -k_f[\text{NonVol}_{(aq)}] + k_b[\text{Vol}_{(aq)}] \\
\frac{d[\text{Vol}_{(aq)}]}{dt} = -k_f[\text{Vol}_{(aq)}] + k_b[\text{NonVol}_{(aq)}]
\]  

where $[\text{NonVol}_{(aq)}]$ is the concentration of nonvolatile aqueous iodine species (mol·m$^{-3}$), $[\text{Vol}_{(aq)}]$ is the concentration of volatile inorganic iodine, i.e., I$_2$, in the aqueous phase (mol·m$^{-3}$), $k_f$ (s$^{-1}$) and $k_b$ (s$^{-1}$) are the rate constants for forward and backward reactions, respectively.

(2) Iodine and surface interaction in the aqueous phase [15].

Stoichiometry:

Vol$_{(aq)}$ ↔ NonaqI

NonVol$_{(aq)}$ ↔ NonaqI

Kinetics:

\[
\frac{d[\text{Vol}_{(aq)}]}{dt} = -k_{\text{fVol}}[\text{Vol}_{(aq)}] + k_{\text{bVol}}[\text{NonaqI}] \\
\frac{d[\text{NonaqI}]}{dt} = k_{\text{fVol}}[\text{Vol}_{(aq)}] + k_{\text{bVol}}[\text{Vol}_{(aq)}] - k_{\text{fNonaqI}}[\text{NonaqI}] - k_{\text{bNonaqI}}[\text{Vol}_{(aq)}]
\]

where $[\text{NonaqI}]$ is the concentration of iodine species bound on the surfaces in contact with the aqueous phase (mol·m$^{-3}$), $k_{\text{fVol}}$ (s$^{-1}$) and $k_{\text{bVol}}$ (s$^{-1}$) are the rate constants for forward and backward reactions between Vol$_{(aq)}$ and NonaqI$_{(aq)}$, respectively, $k_{\text{fNonaqI}}$ (s$^{-1}$) and $k_{\text{bNonaqI}}$ (s$^{-1}$) are the rate constants for forward and backward reactions between NonVol$_{(aq)}$ and NonaqI, respectively.
(3) Organic iodide formation and decomposition [22].

Organic solvents are dissolved from painted surfaces into the aqueous phase. Then, the organic compounds are destructed through radiolysis, which results in the formation of organic radicals, ORG. The organic radicals react with inorganic iodine, and so organic iodides are formed, whereas the organic iodides are decomposed by hydrolysis and radiolysis. Following the LIRIC or IMOD approach [15,21,22], the organic iodides were classified as highly volatile organic iodides [HVRI(aq)] and low volatiles [LVRI(aq)] which were assumed to follow the same kinetics as that of HVRI(aq) with different weighting factors for reaction rate constants.

### Stoichiometry:

\[
\begin{align*}
\text{ORG}_{\text{org}}(\text{aq}) & \rightarrow \text{ORG}_{\text{org}}(\text{aq}) \\
\text{ORG}_{\text{org}}(\text{aq}) + \cdot \text{OH} & \rightarrow 6 \cdot \text{ORG}_{\text{org}}(\text{aq}) \\
\cdot \text{ORG}_{\text{org}}(\text{aq}) + \text{VolI}_{\text{aq}} & \rightarrow \text{HVRI}_{\text{aq}}(\text{aq}) \\
\text{HVRI}_{\text{aq}}(\text{aq}) + e^- & \rightarrow \text{NonVolI}_{\text{aq}}(\text{aq}) + \cdot \text{ORG}_{\text{org}}(\text{aq}) \\
\end{align*}
\]

### Kinetics:

\[
\begin{align*}
\frac{d[\text{ORG}_{\text{org}}(\text{aq})]}{dt} &= k_{\text{Diss}} ([\text{ORG}_{\text{org}}(\text{aq})]_{\text{eq}} - [\text{ORG}_{\text{org}}(\text{aq})]) \\
\frac{d[\cdot \text{ORG}_{\text{org}}(\text{aq})]}{dt} &= 6 \cdot k_{\text{Dec}} [\text{ORG}_{\text{org}}(\text{aq})] \cdot \cdot \text{OH} \\
\frac{d[\text{HVRI}_{\text{aq}}(\text{aq})]}{dt} &= k_{\text{RadHV}} [\cdot \text{ORG}_{\text{org}}(\text{aq})] [\text{VolI}_{\text{aq}}(\text{aq})] - (k_{\text{RadHV}} [e^-] + k_{\text{HydroHV}}) [\text{HVRI}_{\text{aq}}(\text{aq})]
\end{align*}
\]

where [ORG_{org}(aq)] (mol m^{-3}) and [ORG_{org(aq)}]_{eq} (mol m^{-3}) are the amount of organic compound at a specific time and at infinitely long time periods in the aqueous phase, respectively, [HVRI_{aq}] is the concentration of highly volatile organic iodides in the aqueous phase (mol m^{-3}), [OH] is the concentration of hydroxyl radicals (mol m^{-3}), [e^-] is the concentration of aqueous electron (mol m^{-3}), k_{\text{Diss}} (s^{-1}) is the dissociation rate constant of organic compound, and k_{\text{Dec}} (m^3mol^{-1}s^{-1}) is the rate constant for organic degradation process reaction, and k_{\text{RadHV}} (m^3mol^{-1}s^{-1}) is the rate constant for formation of highly volatile organic iodides from organic radicals and I_{2(aq)}, and k_{\text{RadHV}} (m^3mol^{-1}s^{-1}) and k_{\text{HydroHV}} (s^{-1}) are the rate constants for organic iodide decomposition by radiolysis and hydrolysis, respectively.

(4) Aqueous–gaseous phase interfacial mass transfer of volatile iodine [15].

### Stoichiometry:

\[
\text{VolI}_{\text{aq}} \rightarrow \text{VolI}_{\text{g}}
\]

### Kinetics:

\[
\begin{align*}
\frac{d[\text{VolI}_{\text{g}}]}{dt} &= k_{\text{MTVI}} A_{\text{int}} \left[ \frac{[\text{VolI}_{\text{aq}}]}{V_g} \right] - \frac{[\text{VolI}_{\text{g}}]}{V_g} \frac{H_{\text{VolI}}}{H_{\text{HVRI}}}
\end{align*}
\]

\[
\begin{align*}
\frac{d[\text{HVRI}_{\text{g}}]}{dt} &= k_{\text{MTVI}} A_{\text{int}} \left[ \frac{[\text{HVRI}_{\text{aq}}]}{V_g} \right] - \frac{[\text{HVRI}_{\text{g}}]}{V_g} \frac{H_{\text{HVRI}}}{H_{\text{HVRI}}}
\end{align*}
\]

where k_{\text{MTVI}} is the overall mass transfer coefficient of volatile inorganic iodine between the aqueous and gaseous phases (m s^{-1}), 1/k_{\text{MTVI}} = 1/[k_{\text{aq}} + H_{\text{VolI}}/k_{\text{g}}], where k_{\text{aq}} and k_{\text{g}} are the mass transfer coefficients for the aqueous- and gas-phase, respectively, and H_{\text{VolI}} is the partition coefficient of the volatile inorganic iodine. Similarly, k_{\text{MTVI}} is the overall mass transfer coefficient of highly volatile organic iodine (m s^{-1}), 1/ k_{\text{MTVI}} = 1/[k_{\text{aq}} + H_{\text{HVRI}}/k_{\text{g}}], where H_{\text{HVRI}} is the partition coefficient of the organic iodide species. A_{\text{int}} is the interfacial mass transfer surface area (m^2), and V_g and V_{\text{aq}} are the volumes of the gas and aqueous solution (m^3), respectively.

2.2. Reactions in the gaseous phase

Reactions in the gaseous phase were modeled after the existing models, including the stoichiometric, kinetic rate laws and kinetic constants, suggested by Bosland et al [8,17] and Funke et al [25]. In the model, formation of organic iodides, represented by CH3I, by radiolysis or thermal reaction between molecular iodine and organics was considered. The model also deals with formation of ARPs and iodine oxides under irradiation, decomposition of organic iodides, and iodine oxides by radiolysis. It also includes the model for adsorption and desorption of volatile iodine on the paint surface.

(1) Formation and destruction of ARP [8,17].

ARPs are produced by air radiolysis. In this model the ARPs are represented by ozone (O_3) and formed from oxygen. ARP decomposition induced by irradiation and by surface reaction was included.

### Stoichiometry:

\[
3\text{O}_2 + \gamma \rightarrow 2\text{O}_3
\]

### Kinetics:

\[
\frac{d[\text{ARP}_{\gamma}]}{dt} = D_\gamma (k_{\text{O3,1}} - k_{\text{O3,2}}) \left[ \frac{[\text{ARP}_{\gamma}]}{V_g} \right] - \frac{[\text{ARP}_{\gamma}]}{V_g} (k_{\text{O3,3}}S_{\text{pd}})
\]

where [\text{ARP}_{\gamma}] is the concentration of ARP represented by ozone (mol m^{-3}), D_\gamma is the average dose rate in the containment atmosphere (Gy s^{-1}), k_{\text{O3,1}} (mol m^{-3}Gy^{-1}) and k_{\text{O3,2}} (Gy^{-1}) are the rates of formation and decomposition of ARPs by radiolysis, respectively, k_{\text{O3,3}} (m s^{-1}) and k_{\text{O3,4}} (m s^{-1}) are the rates of decomposition of ARPs at painted and steel surfaces, respectively, S_{\text{pd}} is the area of the painted gas surfaces (m^2), S_{\text{sd}} is the area of steel gas surfaces (m^2) and V_g is the volume of the gaseous phase (m^3).
(2) Formation and destruction of iodine oxide [8,17,18].

Iodine oxides (IOx), symbolized by the IO3, are formed by the reaction between molecular iodine [I2 or VolI(g)] and ARPs [18,25]. Radiolytic destruction of iodine oxide was also considered.

Stoichiometry:
\[ I_2 + 2O_3 \rightarrow I_2O_6 + \cdots \rightarrow 2IO_3(g) \]

Kinetics:
\[
\frac{d[VolI(g)]}{dt} = k_{VolO} [ARP(g)] [VolI(g)] \frac{1}{2} k_{IOx} \frac{D_g}{[IO_3(g)]} 
\]  

where \([VolI(g)]\) and \([IO_3(g)]\) are the concentrations of molecular iodine and iodine oxides (mol m\(^{-3}\)), respectively; \(k_{VolO}\) (m\(^3\) mol\(^{-1}\) s\(^{-1}\)) and \(k_{IOx}\) (Gy\(^{-1}\)) are the rates of formation and decomposition of iodine oxides, respectively, and \(D_g\) is the average dose rate in the containment atmosphere (Gy\(^{-1}\) s\(^{-1}\)).

(3) Formation and destruction of organic iodides (RIs) in the gaseous phase [8,17].

High volatile organic iodides [HVRI(g)], represented by CH\(_3\)I, are released from paint through a thermal process and a radiolytic process [1,5,6,26]. The radiolytic destruction of RIs in the presence of steam was also considered. Low volatiles \([LVRI(g)]\) were assumed to follow the same kinetics as that of HVRI(g), but with different weighing factors for reaction rate constants.

(i) Formation of HVRI(g) by radiolysis [8,17].

Stoichiometry:
\[
\frac{1}{2} I_2(\text{absorbed onto paints}) + R \rightarrow CH_3I
\]

Kinetics:
\[
\frac{d[HVRI(g)]}{dt} = k_{HVRI,D} [Iad(g)] \frac{0.56 S_{Ad}}{V_g} 
\]  

where \(k_{HVRI,D}\) is the rate of destruction of RIs in the gaseous phase (mol\(^0.5\) m\(^{-1}\) s\(^{-1}\)), \(T_g\) is the temperature of the gaseous phase (K), and X\(_{H_2O}\) is the steam molar fraction.

(ii) Formation of HVRI(g) by thermal reaction [8,17].

Stoichiometry:
\[
\frac{1}{2} I_2(\text{absorbed onto paints}) + R \rightarrow CH_3I
\]

Kinetics:
\[
\frac{d[HVRI(g)]}{dt} = k_{HVRI,T} [Iad(g)] \frac{0.56 S_{Ad}}{V_g} 
\]  

where \(k_{HVRI,T}\) is the rate of formation of RIs on the iodine-loaded paint by thermal reaction (mol\(^0.5\) m\(^{-1}\) s\(^{-1}\)).

(iii) Destruction of organic iodides in the gaseous phase [8,17].

Stoichiometry:
\[
10CH_3I \rightarrow I_2(g) + 8IO(g)
\]

Kinetics:
\[
\frac{d[VolI(g)]}{dt} = k_{IOx} I_{ad} \frac{1}{V_g} 
\]  

where \(k_{IOx}\) is the rate constant of adsorption and desorption, respectively; SAT is the saturation capacity of gaseous phase surfaces for iodine (mol m\(^{-2}\)) and \(X_{H_2O}\) is the steam molar fraction.

(iv) Adsorption and desorption [8,22].

For adsorption of volatile molecular iodine on the gaseous phase surface and desorption from the surface,
\[
\frac{d[VolI(g)]}{dt} = k_{ad} [VolI(g)] \frac{1 - \frac{[Iad]}{SAT} - k_{des} \frac{A_g}{V_g} [Iad]}{\frac{1}{11} \frac{1}{V_g}} 
\]  

where \([VolI(g)]\) is the concentration of molecular iodine in the gaseous phase (mol m\(^{-3}\)), \([Iad]\) is the concentration of iodine (mol m\(^{-2}\)) adsorbed and retained on the surface, \(K_{ad}\) (s\(^{-1}\)) and \(K_{des}\) (s\(^{-1}\)) are the rate constants of adsorption and desorption, respectively; SAT is the saturation capacity of gaseous phase surfaces for iodine (mol m\(^{-2}\)), \(A_g\) is the surface area (m\(^2\)), and \(V_g\) is the volume of the gaseous phase (m\(^3\)).

3. Simulation of iodine behavior tests

After the establishment of the iodine reaction models, RAIM has been applied to the simulation of separate effect tests such as the ISTP-EPICUR S1 and S2 series, and OECD-BIP P1072, which deal with iodine behavior under severe accident conditions.
3.1. ISTP-EPICUR tests

The EPICUR program, which was operated by the IRSN as a part of the ISTP, dealt with the kinetics of organic iodide formation through reactions with paint, reactions in the gaseous phase and formation of volatile iodine in the liquid phase. Fig. 2 shows a schematic diagram of the EPICUR loop, in which the irradiation vessel and a May-pack device are connected by a stainless steel tube. Volatile species produced in the irradiation vessel are transferred to the May-pack device via the gas bubble. The May-pack system is composed of several steps with a quartz fiber filter, knit-mesh filters, and impregnated charcoal filters. Therefore, \( \text{IO}_x, \text{I}_2, \) and RI can be captured and quantified serially. Online \( \gamma \) measurement is provided by the NaI (Tl) counters placed on top of each stage of the filter of the May-back device [1].

The EPICUR program consists of several test series; the S1 series tests were conducted to study the organic iodide formation from a painted coupon in the iodine solution, whereas the S2 series was carried out with a painted coupon loaded with molecular iodine and placed in gaseous phase. Among them the S1-9, S1-11, S2-6-5-2, and S2-6-14 tests were chosen to be analyzed by RAIM; the first two represent the aqueous-phase tests, and the last two stand for the gas-phase tests. The test conditions are shown in Table 1. For comparison with the experimental data, the online measurement data were used with corrections taking into account its difference from the post-test results. However, the missing mass balance was

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**Table 1 – Experimental conditions of the selected tests.**

<table>
<thead>
<tr>
<th>Test</th>
<th>Test objective</th>
<th>S1-9</th>
<th>S1-11</th>
<th>S2-6-5-2</th>
<th>S2-6-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial iodine concentration on the painted coupon (mol, ( \cdot \text{m}^{-2} ))</td>
<td>No coupon in gas phase</td>
<td>No coupon</td>
<td>2.5 ( \times ) 10^{-4}</td>
<td>1.7 ( \times ) 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Liquid volume (mL)</td>
<td>2,000</td>
<td>2,009</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Gas volume (mL)</td>
<td>2,800</td>
<td>2,791</td>
<td>4,800</td>
<td>4,800</td>
<td></td>
</tr>
<tr>
<td>% RH</td>
<td>–</td>
<td>–</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>( T_{\text{irradiation vessel}} ) (°C)</td>
<td>66.6 ( \rightarrow ) 71.5</td>
<td>80.5</td>
<td>80 ( \rightarrow ) 120</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7</td>
<td>7</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Gas flow in the liquid phase (L/min)</td>
<td>0.25 ( \rightarrow ) 0.50</td>
<td>0.25 ( \rightarrow ) 0.50</td>
<td>0.21 ( \rightarrow ) 0.41</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Dose rate (kGy, h^{-1})</td>
<td>1.81</td>
<td>No coupon</td>
<td>1.66</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>Painted coupon</td>
<td>2.29</td>
<td>2.34</td>
<td>2.30</td>
<td>1.87</td>
<td></td>
</tr>
<tr>
<td>Gaseous phase</td>
<td>2.84</td>
<td>2.90</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Sump average</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
not considered, even though it was 11–20% of the initial iodine inventory, because there was no reasonable way to determine the distribution of each iodine species.

### 3.2 Analysis of the aqueous-phase tests (S1-9 and S1-11)

Figs. 3–5 show the estimated quantity of volatile inorganic iodine, organic iodide, and IOx aerosols for the S1-9 test [27], respectively. Even though the logarithmic scale does not show the concentrations of zero value in the early period of the test, which appear more clearly with the linear scale in Fig. 3, it can cover a wide range of values. Similarly, Fig. 6 shows the quantities for the S1-11 test [28]. Both the results for S1-9 and S1-11 show that the concentrations of inorganic molecular iodine and IOx were overestimated by RAIM, while that of organic iodide was slightly underestimated at first and then overestimated for S1-9. As the S1-11 test did not use any painted coupon, no organic iodide was expected, although in the experiment it was detected by the equivalent amount of S1-9. The organic iodide measured on the impregnated charcoal is probably due to the presence of a small amount of organic compounds (pollution) in the experimental loop. Moreover, the amount of iodine measured on the Knit-mesh might have been slightly underestimated because a fraction of molecular iodine might have been retained on the charcoal stage instead of the Knit-mesh stage due to a low efficiency of the Knit-mesh [28].

### 3.3 Gaseous-phase test (S2-6-5-2 and S2-6-14)

Figs. 7–9 show the estimated amount of volatile inorganic iodine, organic iodide, and IOx aerosols for the S2-6-5-2 test [29], respectively. Similarly, Fig. 10 shows the corresponding amount for the S2-6-14 test [30]. Because the online measurement data was obtained with different time spans for the two knit-mesh filter stages during the S2-6-14 test, the amount of inorganic iodine, which came from the sum of the radioactivity on those filter stages, was estimated by using the interpolation method for vacant data. As shown in these figures, the amount of inorganic iodine and organic iodide were underestimated for the gas-phase tests, which is opposite to...
that of the previously mentioned aqueous tests. However, the amount of iodine oxides was consistently overestimated.

3.4. OECD-BIP P10T2 test

The BIP provided the RTF experimental data from experiments performed in the 1990s. The RTF was an intermediate scale test facility that was designed to study iodine behavior under postulated postaccident conditions, including under radiation. Fig. 11 shows a schematic of the RTF. The facility consisted of a replaceable cylindrical main vessel partially filled with water and containing a radiation source. The vessel was connected to various flow loops such as the ones for gas ventilation, gas- and aqueous recirculation, gas- and aqueous sampling. BIP members selected five tests for inclusion in the program, where the main focus was on organic paints and impurities. The tests demonstrated the dissolution of residual paint solvents and their subsequent radiolytic degradation and formation of organic iodides. They also demonstrated the relative importance of various iodine sinks. Among them, the P10T2 test was chosen to be analyzed in this study. Table 2 shows the summary of the experimental conditions [11,31].

Approximately 2 days before the main test, the vessel was filled with ~25 L of distilled water. During the next 48 hours the release of organic compounds from the paint and the pH change associated with the radiolytic degradation of these compounds was monitored. Iodine was introduced, with a fresh charge of water, at the start of the main portion of the test, during which the pH was held at 10 for 45 hours, after which the pH control was released [11].

Figs. 12–14 show the estimated concentrations of volatile inorganic iodine, and high and low volatile organic iodides for the P10T2 test, respectively. Because no measurement data were available for iodine oxide, comparison was not made for that species. As shown in these figures, the concentrations of all the iodine species were overestimated for the first period, and then reasonably estimated until the last period of sharp increase in inorganic iodine concentration. Figs. 12 and 13 show the dominant effect of pH on the iodine volatility and RI formation. They seem to imply that not only the change of pH but also some important parameters other than pH should
Table 2 — Experimental conditions of the Radioiodine Test Facility P10T2 test.

<table>
<thead>
<tr>
<th>Test objective</th>
<th>To study iodine behavior for an irradiated solution of iodide in a painted vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel</td>
<td>Epoxy paint (Amerlock)</td>
</tr>
<tr>
<td>Iodine solution (M)</td>
<td>$1 \times 10^{-5}$</td>
</tr>
<tr>
<td>Liquid volume (dm$^3$)</td>
<td>25</td>
</tr>
<tr>
<td>Gas volume (dm$^3$)</td>
<td>315</td>
</tr>
<tr>
<td>$T_{\text{irradiation vessel}}$ (°C)</td>
<td>25</td>
</tr>
<tr>
<td>pH</td>
<td>Initially 10 for 45 hr, then uncontrolled</td>
</tr>
<tr>
<td>Dose rate (kGy·h$^{-1}$)</td>
<td>0.61</td>
</tr>
<tr>
<td>Duration (hr)</td>
<td>283</td>
</tr>
</tbody>
</table>
be considered more carefully in order to improve the RAIM estimations.

4. Discussion

There is a trend with the RAIM estimation for aqueous and gaseous tests; the amount of organic and molecular iodine is overestimated within two orders of magnitude for the aqueous experiments, whereas the opposite trend is shown for the gaseous tests with a similar range of bias. However, the amount of iodine oxides was consistently overestimated for all EPICUR tests. The experimental data for IOx was based on the activity measured on the quartz fiber filter. Because the residence time of air in the irradiation vessel is less than 10 minutes, there might not be sufficient time for ARPs such as ozone to be produced to react with iodine. As a result, there is an argument that the iodine captured by the quartz filter may be inorganic iodine instead of IOx. If this argument is confirmed, the discrepancy between the experiment and the RAIM estimation becomes larger for IOx aerosols. Meanwhile, Fig. 15 shows that the total amount of volatile iodine species for EPICUR S2-6-5-2 (i.e., the sum of iodine oxides, and molecular and organic iodine) makes little difference between the experiment and the estimation. It means that iodine volatility can be estimated with reasonable accuracy by RAIM, whereas the chemical composition of the species is estimated with some bias. All these judgments are considered to be valid for EPICUR tests, even taking into account the missing balance that could be composed mostly of inorganic iodine and small amounts of IOx, because it is significantly less than the difference between the experiment and the estimation. With regard to the P10T2 test, both amounts of HVRI and LVRI were well estimated for most of the test period as described previously.

Therefore, it seems that further work is needed to elaborate on reaction models and the rate constants, including those for mass transfer between aqueous and gaseous phases. The adjustment of the rate constants for mass transfer between the phases using a sound technical base seems to reduce the biased estimation of iodine species in the aqueous and gaseous phases. In addition, the development of missing models should be pursued. Important subjects of interest are likely to be the formation of organic iodides through homogeneous reaction, and the deposition of iodine oxide aerosols in the surface and the subsequent decomposition and volatilization of iodine species [24]. It is expected that the addition of those models may reduce the amount of IOx and increase organic and inorganic iodine. With regard to the experimental side, improvements in the provisions for better speciation of the iodine species, especially I2 and IOx, will be very helpful in improving reaction models.

5. Conclusions

RAIM, a model for iodine behavior in the reactor containment under severe accident conditions, has been developed based on the methodology of IMOD and other previous studies. This model deals with chemical reactions associated with formation and destruction of iodine species, the surface reactions in the containment atmosphere and the sump in a simple manner. For the simplification of reactions, single species were used in the gas and aqueous phases. After that, RAIM was applied to simulation of several tests including four ISTP-EPICUR tests and one RTF test, which were carried out mostly with a painted coupon loaded with iodine in the aqueous or gaseous phases. The analysis results show a consistent trend of underestimation of molecular and organic iodine for the gas-phase experiments, the opposite of that for the aqueous ones, whereas the total amount of volatile iodine species shows good agreement between the experiment and the estimation. Therefore, further elaboration of the reaction models and the rate constants may be needed to obtain better estimations. Gas-phase models for organic iodide formation through homogeneous reactions, and IOx deposition and decomposition are currently missing and need to be developed for reliable estimation of iodine species in the gaseous phase. On the experimental side, improvements in the provisions for better iodine speciation will be helpful to advance the iodine chemistry modeling.

Conflicts of interest

All authors have no conflicts of interest to declare.

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