2. THE IODINE BEHAVIOUR CODES

The iodine behaviour codes used in this comparison exercise were IODE 4.2 (IPSN), LIRIC 3.2 (AECL), IMOD 2.0 (AECL), INSPECT (AEAT), IMPAIR (GRS) and modified IODE(NRIR). The purpose of each of these codes is to describe chemical and physical processes that influence iodine behaviour, under conditions that are relevant to post-accident containment. Therefore, the fundamental components of each of these codes are similar. Each code contains sub-models for key processes, such as

1. the interconversion between non-volatile iodine species (e.g., I^-, IO_3^-) and volatile iodine species (I_2) in the aqueous and gas phases,
2. the formation and destruction of organic iodides,
3. the transport of volatile species (e.g., I_2, RI) across a liquid-gas interface,
4. the transport of iodine species to (adsorption) and from (desorption) surfaces, and
5. the transport of iodine species to condensing films and to the bulk aqueous phase by condensation flows.

A brief description of the method by which the codes model each of these processes is provided below.

2.1 Interconversion Between Iodine Species

The iodine behaviour codes used in the current exercise model the hydrolysis of molecular iodine in essentially the same way [1, 2]:

$$I_2 + H_2O = HOI + I^- + H^+ \tag{1}$$

$$HOI = OI^- + H^+ \tag{2}$$

$$3HOI = IO_3^- + 2I^- + 3H^+ \tag{3}$$

Therefore, it is only in the radiolytic reaction subset that the interconversion of iodine species is modelled differently[1].

In LIRIC and INSPECT, a mechanistic model is used to calculate the concentrations of the water radiolysis species that subsequently react with various iodine and organic species to produce volatile iodine species, and reduce these volatile species back to non-volatile iodide. The key radiolytic reactions are

<u>Primary water radiolysis</u>

$$4.1\ H_2O \xrightarrow{h\nu} 2.6\ e_{aq}^- + 0.6\ {\bullet}H + 2.7\ {\bullet}OH + 0.7\ H_2O_2 + 2.6\ H^+ + 0.45\ H_2 \tag{4a}$$

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[1] IMOD does not explicitly contain the I_2 hydrolysis reactions. However, IMOD was constructed from LIRIC; the overall rates for volatile iodine production and decomposition used in IMOD reflect the hydrolysis processes.

where the coefficients in Reaction (4a) are the G-values for the primary production from γ-radiolysis of water in units of molecules per 100 eV absorbed dose.

<u>Secondary reactions of the primary water radiolysis products with each other and with organic and inorganic impurities</u> (4b)

<u>Oxidation and reduction of iodine species</u>[2]

$$2I^- + 2{\bullet}OH \rightarrow I_2(aq) \qquad (5)$$

$$I_2(aq) + 2O_2^- \rightarrow 2I^- + 2O_2 \qquad (6)$$

$$I_2(aq) + H_2O_2 \rightarrow 2I^- + 2H^+ + O_2 \qquad (7)$$

Reactions (5–7) in LIRIC and INSPECT are dependent upon the dose rate. Reactions (1–3) and (6) and (7) are extremely dependent upon the aqueous pH, and Reactions (1) and (7) have strong temperature dependences.

IODE and IMPAIR use two equations to model the radiolysis of iodine species in the aqueous phase. In IODE, the equations are

$$2I^- \xleftrightarrow{\quad h\nu \quad} I_2 \qquad (8)$$

$$I_2 + 3\,O_2 \xleftrightarrow{\quad h\nu \quad} 2\,IO_3^- \qquad (9a)$$

The pH and dose rate dependence of molecular iodine formation in IODE is incorporated into the rate equations in the following manner:

$$\text{Rate of } I_2 \text{ production by (8)} = d[I_2]/dt = k_8\,[I^-]\cdot[H^+]^n\cdot D - k_{-8}[I_2] \qquad (10)$$

$$\text{Rate of } I_2 \text{ production by (9a)} = d[I_2]/dt = k_{-9a}\,[IO_3^-]\cdot[H^+]^n\cdot D - k_{9a}[I_2] \qquad (11a)$$

where D is the dose rate in $Gy\cdot s^{-1}$, and n is a user-defined exponential term.

IMPAIR also contains Reaction (8) with a rate expression similar to that for IODE, but with different values for the rate constants and the exponent, and with D expressed in units of $kGy\cdot h^{-1}$. IMPAIR also contains the forward reaction of (9a); however, instead of I_2 being reversibly converted to IO_3^-, the iodine oxidation reaction is an irreversible process that is represented by

$$I_2 + 3\,O_2 \rightarrow 2\,IO_3^- \qquad (9b)$$

with the following rate equation:

$$d[I_2]/dt = -\,k_9[I_2] \qquad (11b)$$

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[2] Note that Reactions (5) through (7) are written as overall reactions that consist of more than one step. The codes model the individual steps separately.

Iodate is then irreversibly converted to iodide:

$$2IO_3^- \xrightarrow{h\nu} I^- + 3O_2 \qquad (12)$$

with its rate defined as

$$d[IO_3^-] / dt = -k_{12}[IO_3^-]^n \cdot D \qquad (13)$$

IMOD uses Reaction (8) to represent the overall (both thermal and radiolytic) interconversion of iodine species in the aqueous phase, with the rate expression formulated to reproduce, as closely as possible, the overall pH, temperature and dose rate dependence of overall volatile iodine production predicted by LIRIC, over a wide range of conditions. That is, Reactions (1–7) and any iodate formation and reduction in LIRIC are represented by Reaction (8) in IMOD. In IMOD, the rate equation is further simplified such that the rate of production of volatile iodine species (i.e., the forward rate of Reaction (8)) is dependent only on dose rate and is independent of pH and temperature. In contrast, the backward rate (reduction of I_2 to I^-) is pH-, temperature- and dose-rate-dependent.

2.2 Organic Iodide Formation and Decomposition

The sub-models for the radiolysis of organic species and the formation and decomposition of organic iodides are treated quite differently in each of the various iodine behaviour codes. LIRIC and IMOD contain essentially the same sub-model to describe these processes. These codes, along with IODE(NRIR), assume that organic iodide formation is primarily an aqueous-phase process, initiated by the radiolytic decomposition of organic solvents in the aqueous phase (Reactions (14–16)). The decomposition of organic iodides by hydrolysis (Reaction (17)) and radiolysis (Reaction (18)) is also incorporated into these codes.

The model for organic iodide formation in LIRIC and IMOD is[3]

$$RH + \bullet OH \rightarrow R\bullet + H_2O \qquad (14)$$

$$R\bullet + O_2 \rightarrow RO_2\bullet \rightarrow\rightarrow CO_2 \qquad (15)$$

$$R\bullet + I_2/HOI \rightarrow RI + I\bullet \qquad (16)$$

$$RI + H_2O/OH^- \rightarrow I^- + H^+ + ROH \qquad (17)$$

$$RI + e^-_{aq} \rightarrow I^- + R\bullet \qquad (18)$$

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[3] The organic sub-models in LIRIC and IMOD differ only in the way they calculate the OH concentration. In LIRIC, the OH concentration is modelled in detail using the full water radiolysis reaction set, whereas in IMOD, the OH concentration is expressed using a simple algebraic formula.

In these models, the formation of organic iodides is dose-rate-dependent, because the rate of production of both R• and I_2 are dependent upon the dose rate (•OH radical concentration affects both production rates). However, because RH and I^- compete with each other for •OH radicals, an increase in the dose rate by a given factor does not result in a linear increase in both the amount of I_2 and R•. The dose rate dependence of organic iodide formation in LIRIC and IMOD is not as strong as it is in some of the other codes, which assume that the formation of I_2 and the formation of organic iodides each have separate and additive dependences on the dose rate (see Reactions (22–27) below).

In LIRIC and IMOD, the concentration of the organic species RH(aq) is assumed to be dependent upon its rate of accumulation in the aqueous phase, as a result of dissolution from wetted or immersed painted surfaces (as well as being dependent upon its rate of depletion by Reaction (14)). The rate of accumulation is described as a temperature-dependent, first-order kinetic process:

$$[\mathrm{RH(aq)}]_t = [\mathrm{RH(aq)}]_\infty \cdot \left(1 - \exp\left(-k_{\mathrm{DIS}} \cdot t\right)\right) \qquad (19)$$

where $[\mathrm{RH(aq)}]_t$ and $[\mathrm{RH(aq)}]_\infty$ represent the concentrations of organic compound in the aqueous phase at time t, and when dissolution is complete, respectively, and k_{DIS} is the dissolution rate constant (s^{-1}). $[\mathrm{RH(aq)}]_\infty$ ($mol \cdot dm^{-3}$) is determined by the initial amount of solvent that is available in the paint polymer to be released into a given volume of water, and is a function of temperature, coating thickness and paint age. The rate constant k_{DIS} is also dependent upon these parameters.

IODE(NRIR) formulates organic iodide formation in the aqueous phase using a simple first-order equation (see Reaction (20) below), and does not incorporate an organic solvent accumulation process into the model; instead, it assumes an initial [RH](aq) that is independent of temperature, and is user-defined. For this exercise, IODE(NRIR) assumed an initial concentration of 1×10^{-3} $mol \cdot dm^{-3}$ for all calculations. In addition, the organic iodides are modelled in IODE(NRIR) to decompose only by hydrolysis, (Reaction (17)), and not by radiolysis (Reaction (18)).

In IODE(IPSN) and IMPAIR, organic iodide formation can occur both by aqueous-phase processes and heterogeneous processes:

a. Aqueous homogeneous thermal process

$$I_2(aq) + 2\ CH_3R(aq) \rightleftarrows 2\ CH_3I(aq) + 2\ R\ (aq) \qquad (20)$$

with the rate defined as

$$d[CH_3I(aq)]/dt = k_{20}\ [I_2(aq)]\ [CH_3R(aq)] - k_{-20}\ [CH_3I(aq)] \qquad (21)$$

b. Heterogeneous thermal and radiolytic process

Paint + $I_2(s)$ or $I^-(s) \rightleftarrows CH_3I(g,aq) + R(s)$ (22)

with the rate defined as

in IMPAIR: $d[CH_3I]/dt = (A/V_g)\,(k_{22} + k_{22}^{rad} D)\,[H^+]^{0.24}\,(2\,[I_2(s)] + [I^-(s)])$ (23a)
in IODE(IPSN): $d[CH_3I]/dt = (A/V_g)\,(k_{22} + k_{22}^{rad} D)\,[H^+]^{0.24}\,(2\,[I_2(aq)] + [I^-(aq)])$ (23b)

where A is the total (dry and submerged) paint surface area, V is the volume of the gas phase, and (s) refers to deposited species. In IMPAIR, the concentrations of deposited species ($I_2(s)$ and $I^-(s)$) are calculated by the iodine absorption sub-model. Note that although Reaction (22) in IODE(IPSN) is a surface process, the rate of production of CH_3I is formulated using the aqueous-phase concentrations of I_2 and I^-, rather than the surface concentrations. The implicit assumption is that the surface concentrations of the iodine species are proportional to the aqueous concentrations.

Organic iodide formation is very pH dependent as a result of the formulation of Equation (23). This direct pH dependence, resulting from the $[H^+]^{0.24}$ term, is augmented by the dependence of $I_2(aq)$ or $I_2(s)$ on pH. As a result, organic iodide formation in both of these codes is more strongly dependent on pH than it is in LIRIC and IMOD.

The dose rate dependence of organic iodide formation in IMPAIR is a function of the amount of iodine that is predicted to be deposited on surfaces. The overall rates of organic iodide formation via Reactions (20) and (22) are proportional to the dose rate, because the rate of production of I_2 is dose-rate-dependent. In addition, Reaction (22) has an extra dose rate dependence resulting from the $k_{22}^{rad}D$ term. However, if appreciable I^- is deposited on the surface, and if k_{22} is larger than k_{22}^{rad}, then there is a pathway to the formation of organic iodides that is independent of the dose rate.

The initial concentration of organic species, $[CH_3R]$, is a user-defined input in both IODE(IPSN) and IMPAIR. For this exercise, calculations using these codes assumed that the concentration was 0, with the exception of Case 8, where the amount of organic species was specified. Therefore, for all the other cases, both codes modelled organic iodide formation as a surface process alone.

The decomposition of CH_3I by hydrolysis, Reaction (17), is included in both IODE(IPSN) and IMPAIR. IMPAIR calculations assumed that there was radiolytic decomposition of organic iodides in both the gas and aqueous phases (Reaction 24), with k_{24} defined as $1.6\times10^{-4}\ s^{-1}$, and $3\times10^{-4}\ s^{-1}$ respectively. However, although IODE(IPSN) contains the same radiolytic decomposition mechanism (but only in the aqueous phase), the calculations performed for this exercise did not use this decomposition process:

$CH_3I(g,aq) + h\nu \longleftrightarrow I_2(g,aq) + 2\,CH_3\bullet\,(g, aq)$ (24)

$$-\,d[CH_3I]/dt = k_{24}\,D\,[CH_3I] - k_{-24}\,[I_2]\,[CH_3\bullet] \tag{25}$$

INSPECT assumes that all of the organic iodides are produced by a surface process that is based on a model developed by Funke [2], which is similar to that in Reaction (22):

$$\text{Paint} + \text{DEP} \rightleftarrows CH_3I(g) + R\bullet \tag{26}$$

$$d[CH_3I(g)]/dt = (A/V_g)\,(k_{26} + k_{26}^{rad}\,D)[DEP] - k_{dec}[CH_3I(g)]D \tag{27}$$

where $[CH_3I(g)]$ = CH_3I concentration in the gas phase ($mol\cdot m^3$)
k_{26}^{rad} = rate constant for radiation-induced RI formation
k_{26} = rate constant for thermal-induced RI formation
[DEP] = iodine deposited on paint (both dry and submerged) ($mol\cdot m^2$)
A = total (submerged and dry) painted surface area (m^2)
V_g = gaseous volume (m^3)
k_{dec} = rate constant for decomposition of organic iodide (gas phase)
D = dose rate ($kGyh^{-1}$)

The production of organic iodides from this process is virtually independent of temperature up to about 100°C (i.e., $k_{26}^{rad} > k_{26}$); thermal processes contribute at higher temperatures. The overall production rate is somewhat dependent upon pH, since the concentration of I_2 in either the gas or aqueous phase has some effect on the amount of iodine deposited on the surfaces. INSPECT also incorporates hydrolysis and radiolytic decomposition of CH_3I in the aqueous phase in the same way as IMPAIR. As is the case for IODE(IPSN) and IMPAIR, the predicted dose rate dependence of the rate of production of organic iodides in INSPECT could be much greater than in IMOD or LIRIC, depending on whether the amount of iodine deposited on the surfaces is a function of the dose rate.

2.3 Deposition of Iodine on Ag

All of the codes have a similar model for the deposition of iodine on silver surfaces. Deposition is treated as a first-order process, dependent upon the surface area of the Ag:

$$I_2 \quad + \quad 2Ag \quad \rightarrow \quad 2AgI \tag{28}$$

$$d[AgI]/dt = k_{28}[I_2]A_{Ag}/\,V_{aq} \tag{29}$$

where A_{Ag} (m^2) is the total surface area of Ag, and V_{aq} (m^3) is the aqueous phase volume.

IODE(IPSN) and INSPECT also include a two-step reaction, in which a fraction of the silver becomes oxidized and reacts with I^- to produce AgI:

$$Ag \quad \rightarrow \quad Ag_{ox} \qquad \text{slow} \tag{30a}$$

$$Ag_{ox} + I^- \rightarrow AgI \qquad \text{fast} \qquad (30b)$$

$$d[Ag_{ox}]/dt = k_{30a}\ A_{Ag}/V_{aq} - k_{30b}\ [I^-]\ A_{ox}/V_{aq} \qquad (31)$$
$$d[AgI]/dt = k_{30b}\ [I^-]\ A_{ox}/V_{aq} \qquad (32)$$

where A_{ox} is the area of oxidised silver (m^2), V_{aq} is the aqueous volume (m^3), and A_{Ag} is the total surface area (m^2) of silver. If A_{ox} is less than A_{Ag}, then the kinetics of silver oxidation determine the rate of iodide reaction with Ag_{ox}, with $d[Ag]/dt = - k_{30a}\ A_{Ag}/V$ and $d[AgI]/dt = k_{30b}\ [I^-]\ A_{ox}/V$. If A_{ox} is greater than or equal to A_{ag}, then an oxide layer surrounds the silver particle and the reaction corresponds to the reaction of iodide ions with the silver oxide. The kinetics are determined by the mass transfer of iodide ions to the Ag particle surface and are therefore first-order relative to iodide. The rate of Reaction (30a) is pH-dependent, with the pH dependence of k_{30} being user-defined.

In IMPAIR, I^- is assumed to react directly with Ag in one step, and the reaction is independent of pH:

$$Ag + I^- \rightarrow AgI(s) \qquad (33)$$

2.4 Gas-Phase Reactions

Another difference between the codes is the participation of gas-phase reactions or reactants. Reactions of particular importance involve the production of nitric acid by the radiolysis of air, for the calculation of pH in IODE(IPSN) and the gas phase reaction between molecular iodine and ozone to form iodate in IMPAIR. In IODE(IPSN), nitric acid production and the release of CO_2 from molten core concrete interactions (MCCI) into containment are responsible for the pH changes that are induced when pH is not controlled (see Case 5 calculations, Appendix C). The release of CO_2 is provided as an input to IODE(IPSN) from upstream calculations, whereas nitric acid formation is calculated within the code using a G-value, which results in a linear increase in nitric acid concentration as a function of time.

The iodate formation reaction incorporated in IMPAIR is

$$I_2(g) + 2O_3(g) \rightarrow 2IO_3^-(g) \qquad (34)$$

The reaction is modelled as a first-order decomposition of I_2, with a rate constant of $1.1\times10^{-4}\ s^{-1}$. The removal of iodate aerosol by absorption into steam, or by aerosol removal mechanisms is not modelled in the current exercise. Reaction (34) results in IMPAIR predicting that a significant fraction of the iodine inventory is converted to iodate over the course of several hours. Note that Reaction (34) is also included in IODE(IPSN), but was not used in this exercise.

2.5 Interfacial Mass Transfer and Surface Adsorption

Mass transfer and surface adsorption (excluding adsorption on Ag) are modelled in a similar manner in all of the codes. The approach uses a standard two-resistance model. The values recommended for this exercise for the mass transfer coefficients and partition coefficients can be found in Appendix A. The adsorption of I_2 on containment surfaces (both wet and dry) is described as a first-order process, with recommended rate constants as given in Appendix A. Some of the codes also provide the option of modelling I^- absorption in the aqueous phase, and IMPAIR calculations used this option for this exercise.

2.6 Condensation

The effect of the condensation of steam on iodine volatility is modelled in LIRIC and IMOD using a two-step kinetic scheme. Molecular iodine (but not organic iodides) is assumed to be absorbed into a condensing film covering the surfaces, in a simple first-order process that is identical to that of absorption. Once absorbed into the condensing steam, it is assumed to be hydrolysed to I^- and returned to the sump by the condensate flow. The absorption of molecular iodine on non-immersed surfaces in the presence of steam is assumed to be slower than its absorption on the same surfaces under non-condensing conditions:

$$\frac{d\left([I_2(con)]\right)}{dt} = k_{AD}^{cw} \cdot [I_2(g)] \cdot \frac{V_g}{V_{con}} \qquad (35)$$

$$\frac{d\left([I_2(g)]\right)}{dt} = -k_{AD}^{cw} \cdot [I_2(g)] \qquad (36)$$

where V_{con} is the volume of the condensate on the wall in dm^3, V_g is the volume of the gas phase, and k_{AD}^{CW} is the rate constant for the absorption of iodine in condensing water. k_{AD}^{CW} is further defined as

$$k_{AD}^{CW}\ (s^{-1}) = v_{AD}^{CW} \cdot (A_{con}/V_g) \qquad (37)$$
$$v_{AD}^{CW}\ (dm \cdot s^{-1}) = (7 \pm 2) \times 10^{-4} \qquad (38)$$

where A_{con} is the surface area of the condensing water film in units of dm^2.

The mass transport rate of iodine from wall condensate to the aqueous phase depends on the condensation rate of water, therefore, it depends on the steam concentration, the temperature difference between the gas phase and the wall, and to a minor extent, the type of surface. The process is incorporated as a first-order process in both models:

$$\frac{d\left([I_2(con)]\right)}{dt} = -k_{con} \cdot [I_2(con)] \qquad (39)$$

$$\frac{d\left([I^{-}(aq)]\right)}{dt} = 2\ k_{con} \cdot [I(con)] \cdot \frac{V_{con}}{V_{aq}} \qquad (40)$$

$$k_{con}\ (s^{-1}) = F_{con}/V_{con} \qquad (41)$$

where F_{con} is the flow rate of condensate going into the aqueous phase ($dm^3 \cdot s^{-1}$), and V_{con} is the volume of condensate on the walls in dm^3. Recommended values for V_{con} and F_{con} can be found in Appendix A.

In IODE(NRIR), IODE(IPSN), INSPECT and IMPAIR, the fraction of gaseous iodine removed by condensation and transported to the bulk water phase is assumed to be the same as the fraction of the mass of steam that is condensed into the bulk phase. These codes assume that organic iodides are also removed by steam condensation, whereas LIRIC and IMOD do not. They also differ from LIRIC and IMOD in that they do not assume that I_2 and CH_3I are hydrolysed to I^-; rather, these species remain in the same form when they are transferred to the bulk water phase.

Regardless of the model used, the condensation sub-model results in a first-order rate of removal of gaseous iodine species from the gas phase.