Iodine Chemistry Model Development in ISAAC 2.0 Code

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1. Introduction

The iodine escaping from damaged fuel is usually released in the form of a gas (I_2, for example), into the reactor vessel. However, it may very rapidly react with other chemical elements released at the same time, in particular cesium, which are present in large amounts. The compounds formed, such as CsI, will condense into droplets, or even solidify, either as they pass through the reactor coolant system or when they reach the containment, given that the melting and boiling points for I_2 and CsI are as shown in the table below (at atmospheric pressure).

Compound	Melting Point (°C)	Boiling Point (°C)
I_2	114	184.3
CsI	626	1,280

There is a high probability that the iodized aerosols formed will fairly quickly reach the aqueous phase. They may settle down and join the water present on the floor or in sumps; they may be deposited on the cold walls, where the steam also condenses and then be carried away in the run-off water; they may be trapped directly by the spray droplets; or, if they are hygroscopic (case of CsI), they may themselves be the site of steam condensation.

Some iodized compounds, such as CsI, are highly soluble. They may dissociate in aqueous phase and release iodine in the form of I^- iodide ions. These ions will then be able to re-react in a variety of ways within the aqueous phase. The iodized compounds formed may be volatile, and may return to the gaseous phase.

Whether in aqueous or gaseous phase, the iodine may react with the containment walls: by adsorption or desorption in the original form; by combining with paint elements; etc. These surface reactions are termed "heterogeneous," as opposed to the "homogeneous" reactions occurring in the aqueous or gaseous volumes.

The reactions governing iodine development in the containment under accident conditions can then be divided into five categories:

1. homogeneous reactions in aqueous phase;
2. heterogeneous reactions in aqueous phase;
3. mass transfer between phases linked to a liquid/vapor equilibrium (volatile compounds);
4. homogeneous reactions in gaseous phase; and
5. heterogeneous reactions in gaseous phase.

2. Chemistry models

Table 1 lists the set of chemical reactions included in the iodine chemistry model in the ISAAC 2.0 code.

Homogeneous reactions in aqueous phase	
I_2 hydrolysis	$I_2 + H_2O \Leftrightarrow I^- + HOI + H^+$
HOI disproportionation	$3HOI \Leftrightarrow IO_3^- + 2I^- + 3H^+$
Oxidation of I^- by dissolved O_2	$2I^- + 1/2O_2 + 2H^+ \Leftrightarrow I_2 + H_2O$
I^- radiolysis	$2I^- + h\nu \Leftrightarrow I_2 + 2e^-$
IO_3^- radiolysis	$2IO_3^- + h\nu \Leftrightarrow I_2 + 2e^- + 3O_2$
CH_3I formation	$2CH_3 + I_2 \Leftrightarrow 2CH_3I$
Hydrolysis of CH_3I	$CH_3I + H_2O \Leftrightarrow I^- + CH_3OH + H^+$ $CH_3I + OH^- \Leftrightarrow I^- + CH_3OH$
CH_3I radiolysis	$2CH_3I + h\nu \Leftrightarrow I_2 + 2CH_3$
Dissociation of water molecules	$H_2O \Leftrightarrow H^+ + OH^-$ (MAAP4's pH model)
Heterogeneous reactions in aqueous phase	
Silver iodide formation	$2Ag + I_2 \Leftrightarrow 2AgI$
CH_3I formation by reaction of I_2 and I^- with painted surfaces	$I_2(+ \text{ paint}) \Leftrightarrow 2CH_3I$ $I^- (+ \text{ paint}) \Leftrightarrow CH_3I$
Mass transfer between phases	
liquid/vapor equilibrium	$I_2(g) \Leftrightarrow I_2(aq)$ $CH_3I (g) \Leftrightarrow CH_3I (aq)$
Heterogeneous reactions in gaseous phase	
I_2 absorption by painted surface	$I_2(g) \rightarrow I_2(ad,g)$
I_2 desorption from painted surface	$I_2(ad,g) \rightarrow I_2(g)$

Table.1 Chemical reactions in iodine chemical model

Safety studies are primarily interested in the concentration and chemical form of iodine in gaseous phase. From this point of view, the main reactions are the following:

– radiolysis of I^- in aqueous phase, causing its transformation into a volatile compound, I_2; the strength of this reaction increases as the pH decreases, i.e., becomes more acidic;
– formation of organic iodide CH_3I (highly volatile) from paints, mainly in aqueous phase;
– aqueous phase - gaseous phase exchange of volatile iodized compounds;
– adsorption/desorption of different forms of iodine in gaseous phase by and from the walls; and

It should be noted that there is no model of a

radiolysis reaction in gaseous phase because water molecules are not numerous enough for the effects of radiolysis to be significant in the gaseous phase.

The followings summarize the chemical species taken into account in the model. There are six chemical species with I_2 molecules in 3 different phases and CH_3I in two different phases.

Index No.	Chemical Species	
1-1	I_2	in gaseous phase
1-2	I_2	in aqueous phase
1-3	I_2	adsorbed in walls
2.	I^-	in aqueous phase
3.	IO^-_3	in aqueous phase
4-1	CH_3I	in gaseous phase
4-2	CH_3I	in aqueous phase
5.	CH_3	in aqueous phase
6.	HOI	in aqueous phase

3. Methods and Results

3.1 Analyzing Scenarios

A large LOCA is analyzed that is a transient sequence initiated by a guillotine break in the reactor outlet header (ROH) with an area of 0.259 m^2 in one loop. For the bounding calculation, any safety or mitigating systems were assumed to be unavailable. Major accident progression and a detailed trend of the important variables for the thermal hydraulics can be referred to from the Wolsong level 2 PSA final reports [1].

3.2 Calculational Results

Figure 1 shows the mass concentration of I_2 and CH_3I in both aqueous and gaseous phases.
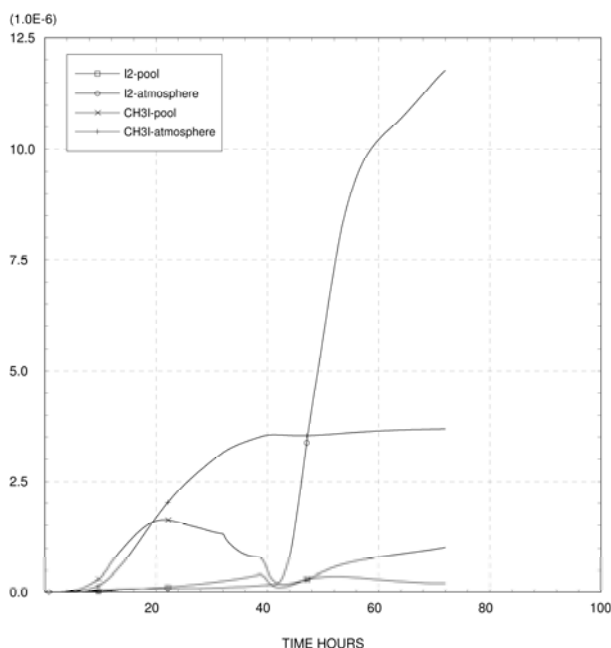

Figure.1 I_2 and CH_3I mass concentration [kg]

The concentration of iodine ions naturally follows that of an iodine aqueous phase in the water pool (including water droplets) which was a 57% peak concentration at 3 days into the accident [2]. It is noted that the methyl iodide gaseous phase reaches a peak equilibrium concentration before 40 hours while the concentration of the elemental iodine gaseous phase increases rapidly after 40 hours when CCI occurs actively. But the contribution to the iodine atmospheric concentration by the elemental iodine and the methyl iodide gaseous phases was very small whose maximum concentration corresponds to about 0.0025% of the initial iodine inventory. Though the iodine reaction with the containment walls by combining with paint elements is not considered in this analysis, an ISSAC 2.0 sensitivity study [2] (which is not addressed here) shows that the absorbed amount by painted surfaces increases continuously until 3 days into the accident following the amount of an iodine aqueous phase in the water pool.

4. Conclusion

As old fission product models in ISAAC 1.0 version [3] treat the iodine species only as inorganic compounds like CsI and RbI, a new chemistry model is incorporated into the new ISAAC 2.0 version [4] to trace the elemental or organic iodine forms. This chemistry model comes from the latest MAAP4 code [5] that is used for a PWR severe accident analysis worldwide and has been validated for a long time. When CsI is deposited into the water pool (including water droplets), CsI dissociates immediately changing its form into I^- iodine ions and its deposition rate becomes a source rate for the iodine in the pool. Throughout the accident, most iodine in the water pool exists as iodine ions (> 99.99%) while very small portions form highly volatile iodized compounds (such as, I_2 and CH_3I) and return to the gaseous phase. This study will help users to predict the trace of an iodine atmospheric concentration via sump iodine revaporization at a late stage into the severe accident.

REFERENCES

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[5] FAI, "Modular Accident Analysis Program (MAAP4) User's Manual," 2000.