Iodine Chemistry Model Development in ISAAC 2.0 Code

Y.M. Song*, S.Y. Park
Thermal Hydraulic and Safety Research Dept., Korea Atomic Energy Research Institute
P.O.Box 105, Yusong, Taejon, Korea, 305-600
Tel:+82-42-868-2663 , Fax: +82-42-861-2574 , Email:ymsong@kaeri.re.kr

1. Introduction

The iodine escaping from damaged fuel is usually released in the form of a gas (I₂, 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 I₂ and CsI are as shown in the table below (at atmospheric pressure).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I₂</td>
<td>114</td>
<td>184.3</td>
</tr>
<tr>
<td>CsI</td>
<td>626</td>
<td>1,280</td>
</tr>
</tbody>
</table>

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.

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
- I₂ hydrolysis: $\text{I}_2 + \text{H}_2\text{O} \rightleftharpoons \text{I}^- + \text{H}_2\text{O}^+ + \text{HOI}$
- HOI disproportionation: $3\text{HOI} \rightleftharpoons \text{I}_2 + 2\text{HOI}$
- Oxidation of I⁻ by dissolved O₂: $2\text{I}^- + \text{O}_2 + 2\text{H}^+ \rightleftharpoons \text{I}_2 + 2\text{H}_2\text{O}$
- I⁺ radiolysis: $2\text{I}^+ + \text{hv} \rightleftharpoons \text{I}_2 + 2\text{e}^-$
- IO₃⁻ radiolysis: $2\text{IO}_3^- + \text{hv} \rightleftharpoons \text{I}_2 + \text{I}^- + 3\text{O}_2$
- CH₃I formation: $2\text{CH}_3 + \text{I}_2 \rightleftharpoons 2\text{CH}_3\text{I}$

### Heterogeneous reactions in aqueous phase
- Silver iodide formation: $2\text{Ag}^+ + \text{I}_2 \rightleftharpoons 2\text{AgI}$
- CH₃I formation by reaction of I₂ and I⁻ with painted surfaces: $\text{I}_2 (+ \text{paint}) \rightleftharpoons 2\text{CH}_3\text{I}$

### Mass transfer between phases
- Liquid/vapor equilibrium: $\text{I}_2(g) \leftrightharpoons \text{I}_2(aq)$
- CH₃I (g) \leftrightharpoons CH₃I (aq)

### Heterogeneous reactions in gaseous phase
- I₂ absorption by painted surface: $\text{I}_2(g) \rightarrow \text{I}_2(\text{ad,g})$
- I₂ desorption from painted surface: $\text{I}_2(\text{ad,g}) \rightarrow \text{I}_2(g)$

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, I₂; the strength of this reaction increases as the pH decreases, i.e., becomes more acidic;
- Formation of organic iodide CH₃I (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 I₂ molecules in 3 different phases and CH₃I in two different phases.

<table>
<thead>
<tr>
<th>Index No.</th>
<th>Chemical Species</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>I₂</td>
<td>gaseous phase</td>
</tr>
<tr>
<td>1-2</td>
<td>I₂</td>
<td>aqueous phase</td>
</tr>
<tr>
<td>1-3</td>
<td>I₂</td>
<td>adsorbed in walls</td>
</tr>
<tr>
<td>2.</td>
<td>I⁻</td>
<td>aqueous phase</td>
</tr>
<tr>
<td>3.</td>
<td>IO₃⁻</td>
<td>aqueous phase</td>
</tr>
<tr>
<td>4-1</td>
<td>CH₃I</td>
<td>gaseous phase</td>
</tr>
<tr>
<td>4-2</td>
<td>CH₃I</td>
<td>aqueous phase</td>
</tr>
<tr>
<td>5.</td>
<td>CH₃</td>
<td>aqueous phase</td>
</tr>
<tr>
<td>6.</td>
<td>HOI</td>
<td>aqueous phase</td>
</tr>
</tbody>
</table>

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 m² 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 I₂ and CH₃I in both aqueous and gaseous phases.

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 ISAAAC 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 ISAAAC 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, I₂ and CH₃I) 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.

ACKNOWLEDGMENTS

This project has been carried out under the Nuclear R&D Program by Ministry of Science and Technology (MOST) in Korea.

REFERENCES