

## Implementation of pH Calculation Module for Chemical Behavior of Iodine in the Containment during Severe Accident

Yoonhee Lee<sup>a,b,\*</sup> and Yong Jin Cho<sup>a</sup>

<sup>a</sup>Korea Institute of Nuclear Safety

62 Gwahak-ro, Yuseong-gu, Daejeon, Korea 34142

<sup>b</sup>University of Science and Technology Korea

217 Gajeong-ro, Yuseong-gu, Daejeon, Korea 34113

\*Corresponding author: [yooney@kns.re.kr](mailto:yooney@kns.re.kr)

### 1. Introduction

Iodine is one of the most important contributors to the potential health risk for the public since it has high affinity to thyroid of a human and relatively long half-life. Therefore, for the consequence analysis of a severe accident in nuclear power plants, iodine behavior in the containment is one of the important topics in the severe accident analysis.

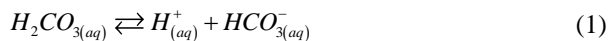
Under the conditions of the severe accidents, i.e., radiation field with high temperature, and humidity in the containment, iodine has multiplicity of the oxidation states, which leads to have various chemical forms, e.g., aerosol, organic, inorganic, and etc. Considering that effective dose coefficients, which are essential to evaluate the public risk, are various [1], chemical behavior of the iodine is an area of particular relevance in the source term studies of the nuclear accident, especially for the best-estimate consequence analyses during the severe accidents.

In the analyses of the chemical behaviors of iodine, pH of the water in the sump is one of the most important parameters, since it affects the amount of production of volatile molecular iodine, I<sub>2</sub>, in the gas phase, i.e., the lower pH, the higher production of I<sub>2</sub>.

In this paper, we will implement pH calculation module in the iodine chemistry code to predict chemical behaviors of the iodine species more accurately and realistically. The validation of pH calculation module is done against experimental data of P10T2 and P11T1 performed by AECL [2].

### 2. pH Calculation Module in the Iodine Chemistry Code

Since pH is concentration of hydrogen ion, H<sup>+</sup>, in the aqueous phase, chemical species related with formation and destruction of H<sup>+</sup> are considered in the calculation module. The first species in the module is H<sub>2</sub>CO<sub>3</sub>, which is made from H<sup>+</sup> and organic impurities in the aqueous phase. The chemical reaction on the species is shown as below :



The aforementioned reaction can be expressed as the follow differential equation

$$\frac{d[H_2CO_{3(aq)}]}{dt} = -k_{H_2CO_{3f}} \cdot [H_2CO_{3(aq)}] + k_{H_2CO_{3b}} \cdot [H^+_{(aq)}] \cdot [HCO^-_{3(aq)}], \quad (2)$$

where

[Species] : Concentration of species,

$k_{H_2CO_{3b}}$  : reaction constant on the formation of H<sub>2</sub>CO<sub>3</sub> from H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>,

$k_{H_2CO_{3f}}$  : reaction constant on the destruction of H<sub>2</sub>CO<sub>3</sub> to produce H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup>.

The next species is HCO<sub>3</sub><sup>-</sup>. Chemical reaction and differential equation on the reaction are shown as the following Eqs. :



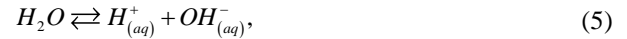
$$\frac{d[HCO^-_{3(aq)}]}{dt} = -k_{HCO_{3f}} \cdot [HCO^-_{3(aq)}] + k_{HCO_{3b}} \cdot [H^+_{(aq)}] \cdot [CO^{2-}_{3(aq)}], \quad (4)$$

where

$k_{HCO_{3b}}$  : reaction constant on the formation of HCO<sub>3</sub><sup>-</sup> from H<sup>+</sup> and CO<sub>3</sub><sup>2-</sup>,

$k_{HCO_{3f}}$  : reaction constant on the destruction of HCO<sub>3</sub><sup>-</sup> to produce H<sup>+</sup> and CO<sub>3</sub><sup>2-</sup>.

Water radiolysis is also important phenomenon in the calculation of pH. For efficient calculations in the iodine chemistry code, the complicated reactions are simplified to the following two reactions :



The reactions are expressed as the following differential Eqs. Note that we assume that the reaction rate in Eq. (8) is assumed to be saturated depending on the concentration of H<sup>+</sup>.

$$\frac{d[H_2O]}{dt} = -k_{H_2O_f} + k_{H_2O_b} \cdot [H^+_{(aq)}] \cdot [OH^-_{(aq)}], \quad (7)$$

$$\frac{d[H^+_{(aq)}]}{dt} = k_{H_f} - k_{H_b} \cdot [H^+_{(aq)}], \quad (8)$$

where

$k_{H_2O_b}$  : reaction constant on the formation of H<sub>2</sub>O from H<sup>+</sup> and OH<sup>-</sup>,

$k_{H_2O_f}$  : reaction constant on the destruction of H<sub>2</sub>O to produce H<sup>+</sup> and OH<sup>-</sup>,

$k_{H_b}$  : reaction constant on the formation of H<sub>2</sub>O from H<sup>+</sup> in the simplified radiolysis reaction,

$k_{H_j^+}$  : reaction constant on the destruction of  $H_2O$  to produce  $H^+$  in the simplified radiolysis reaction.

The constants used in the module are taken from references [3, 4] and they are explained on the code manual [5] in detail.

In the calculation, the aforementioned differential equations are set to a system of the Eqs. And they are solved numerically by the implicit Euler method for accurate and stable calculations.

### 3. Numerical Results

The validations are done with experimental data of P10T1 and P10T2, which show rapid variation in pH during the experiments. The experimental conditions are shown in Table 1.

Table 1. Experimental conditions of P10T2 test

Parameters	P10T1	P10T2
Vessel	Epoxy painted vessel	
Initial iodine species (CsI)	$\sim 8.9 \times 10^{-6} M$	$\sim 8.6 \times 10^{-6} M$
Liquid volume [dm <sup>3</sup> ]	28.1	25
Gas volume [dm <sup>3</sup> ]	311.2	315
Operating temperature [°C]	25	60
pH	Initially 10 for 45h, then uncontrolled	Initially 10 for 72 h then uncontrolled
Dose rate [kGy·h <sup>-1</sup> ]	0.61	0.67
Duration [hrs]	283	300

As computation conditions, the implicit Euler method is used for time discretization on the pH calculation module. The size of time step is determined by the step doubling method and it is between  $7.0E-3 \sim 1$  sec, depending on the errors estimated by the method.

The changes of pH during experiments are shown in Figs. 1 and 2, respectively.

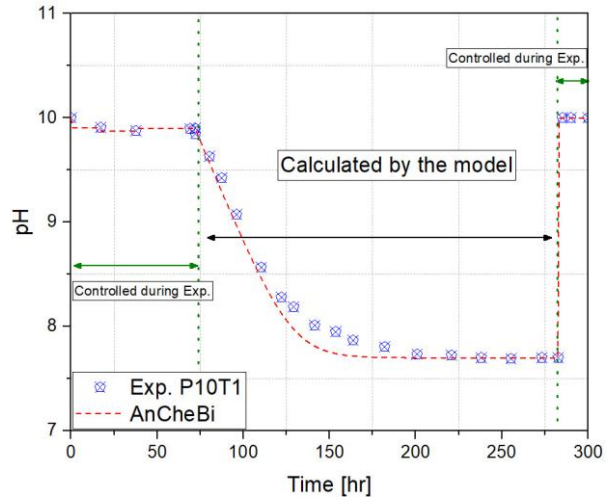


Fig. 1. Change of pH in P10T1 experiment

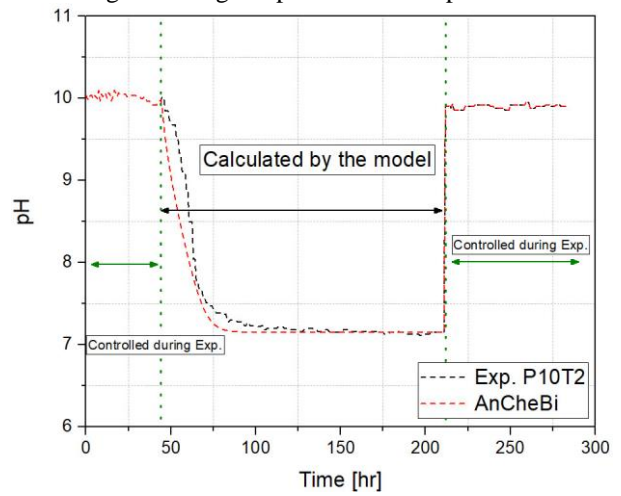


Fig. 2. Change of pH in P10T2 experiment

As shown in Figs. 1 and 2, changes of pH obtained from the iodine chemistry code shows excellent agreement with those of experimental data. Especially, the numerical results follow the rapid change of pH as soon as pH becomes uncontrolled.

### 4. Conclusions

In this paper, we implemented pH calculation module in the iodine chemistry code in order to perform analyses on the chemical behavior of iodine species in the containment during severe accidents more accurately and realistically. The pH calculation module is based on the chemical species and reactions related with formation and destruction of  $H^+$  ion in the aqueous phase.

The calculation module was validated with experimental data of P10T1 and P10T2 performed by AECL. The numerical results showed excellent agreement with that of experimental data.

As future work, we will validate the pH calculation module coupling with the analysis module on the chemical behaviors of the iodine species.

## ACKNOWLEDGEMENTS

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