Validation of pH Calculation Model of AnCheBi in the Presence of Organic Impurities

Yoonhee Lee[a,b] *and Yong Jin Cho[a]

[a] Korea Institute of Nuclear Safety
62 Gwahak-ro, Yuseong-gu, Daejeon, Korea 34142
[b] University of Science and Technology Korea
217 Gajeong-ro, Yuseong-gu, Daejeon, Korea 34113
Corresponding author: yooney@kins.re.kr

1. Introduction

Due to the importance on the radiological impact during a severe accident, analysis on the behaviors of iodine is always set as high priority in the source term analysis. In addition, since the thermophysical conditions in the containment of a severe accident, i.e., radiation filed with high temperature and humidity makes iodine have various chemical forms such as aerosol, organic, inorganic, elemental, etc., iodine chemistry is an area of particular relevance in the source term analysis during a severe accident [1].

In the chemical behaviors of iodine, one of the most important parameters is pH, which affects the volatility of the iodine in the aqueous phase. During a severe accident, pH is affected not only by additives injected according to accident management guidelines but also by organic impurities dissolved from the painted surface of the sump [1].

In this paper, we develop a pH calculation model in the presence of organic impurities which is based on the minimization of the least squares of the differences between analytic solutions of the model and the experimental results. We, then, implement the model in to AnCheBi [2]. Then the validation is performed on P10T2 [3] and P11T1 [4] obtained via OECD/NEA BIP project [1].

2. Calculation of pH for the Injection of Organic Impurities

2.1 Evolution of pH from organic impurities

During a severe accident, pH of the sump in the containment, i.e., concentration of H^+ ion can be evolved from organic impurities such as additives, dissolution from the painted surfaces, injection of MIBK, etc. Under the severe accident condition, the organic impurities are decomposed into carbon dioxide in the aqueous phase ($CO_{2(aq)}$). The chemical reaction between organic impurities and $CO_{2(aq)}$ is shown as below :

$$ORGIMP_{(aq)} \rightarrow n_{ORGIMP} \cdot CO_{2(aq)}, \qquad (1)$$
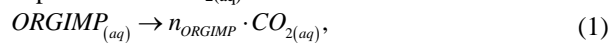
where

n_{ORGIMP} : number of carbon atoms in organic impurities.

The chemical reaction (1) is expressed in the form of following differential equation to obtain the change of concentration :

$$\frac{d\left[CO_{2(aq)}\right]}{dt} = n_{ORGIMP} \cdot k_{ORGIMP} \cdot \left[ORGIMP_{(aq)}\right], \qquad (2)$$

where

[Species] : Concentration of species (mole/dm³),

k_{ORGIMP} : decomposition rate of ORGIMP into CO_2 in aqueous phase.

Then, $CO_{2(aq)}$ is in equilibrium with H_2CO_3 in the aqueous phase as expressed below

$$CO_{2(aq)} \leftrightarrow H_2CO_{3(aq)}. \qquad (3)$$

The aforementioned reaction can be expressed as the following differential equation for numerical analysis :

$$\frac{d\left[H_2CO_{3(aq)}\right]}{dt} = k_{CO_2f} \cdot \left[CO_{2(aq)}\right] - k_{CO_2b} \cdot \left[H_2CO_{3(aq)}\right], \qquad (4)$$

where

k_{CO_2f} : reaction rate on the formation of $H_2CO_{3(aq)}$ from $CO_{2(aq)}$,

k_{CO_2b} : reaction rate on the formation of $CO_{2(aq)}$ from $H_2CO_{3(aq)}$.

H+ ion is then produced from the decomposition of $H_2CO_{3(aq)}$ as follows :

$$H_2CO_{3(aq)} \leftrightarrow H^+_{(aq)} + HCO^-_{3(aq)} \qquad (5)$$
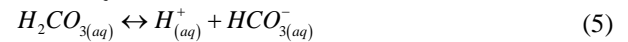
$$\frac{d\left[H_2CO_{3(aq)}\right]}{dt} = -k_{H_2CO_{3f}} \cdot \left[H_2CO_{3(aq)}\right] + k_{H_2CO_{3b}} \cdot \left[H^+_{(aq)}\right] \cdot \left[HCO^-_{3(aq)}\right], \qquad (6)$$

where

$k_{H_2CO_{3f}}$: reaction constant on the decomposition of $H_2CO_{3(aq)}$ to produce $H^+_{(aq)}$ and $HCO_{3(aq)}^-$.

$k_{H_2CO_{3b}}$: reaction constant on the formation of H_2CO_3 from $H^+_{(aq)}$ and $HCO_{3(aq)}^-$,

H+ ions are also produced by the decomposition of $HCO_{3(aq)}^-$ as follows :

$$HCO^-_{3(aq)} \leftrightarrow H^+_{(aq)} + CO^{2-}_{3(aq)} \qquad (7)$$

$$\frac{d\left[HCO^-_{3(aq)}\right]}{dt} = -k_{HCO_{3f}} \cdot \left[HCO^-_{3(aq)}\right] + k_{HCO_{3b}} \cdot \left[H^+_{(aq)}\right] \cdot \left[CO^{2-}_{3(aq)}\right], \qquad (8)$$

where

$k_{HCO_{3f}}$: reaction constant on the decomposition of HCO_3^- to produce H^+ and CO_3^{2-} in the aqueous phase,

$k_{HCO_{3b}}$: reaction constant on the formation of HCO_3^- from H^+ and CO_3^{2-} in the aqueous phase.

Under the radiation field, water radiolysis can also produce H^+ ion. The following simplified reaction is considered in the analysis for the efficient calculation :
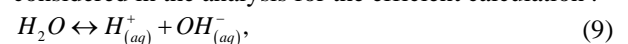
$$H_2O \leftrightarrow H^+_{(aq)} + OH^-_{(aq)}, \qquad (9)$$

$$\frac{d[H_2O]}{dt} = -k_{H_2O_f} + k_{H_2O_b} \cdot [H^+_{(aq)}] \cdot [OH^-_{(aq)}], \qquad (10)$$

where

$k_{H_2O_f}$: reaction constant on the decomposition of H_2O to produce H^+ and OH^- in the aqueous phase,

$k_{H_2O_b}$: reaction constant on the formation of H_2O from H^+ and OH^- in the aqueous phase.

For the injection of MIBK through organic solution, the following reaction and equations are considered for the calculation :

$$MIBK_{(aq)} \rightarrow MIBKInt_{(aq)} \rightarrow ORGIMP_{(aq)}, \qquad `$$

$$\frac{d[MIBK_{(aq)}]}{dt} = -k_{MIBK} \cdot [MIBK_{(aq)}], \qquad (11)$$

$$\frac{d[MIBKInt_{(aq)}]}{dt} = -k_{MIBKInt} \cdot [MIBKInt_{(aq)}] \\ + k_{MIBK} \cdot [MIBK_{(aq)}], \qquad (12)$$

$$\frac{d[ORGIMP_{(aq)}]}{dt} = k_{MIBKInt} \cdot [MIBKInt_{(aq)}], \qquad (13)$$

where

$MIBKInt_{(aq)}$: intermediate product from decomposition of MIBK into organic impurities,

k_{MIBK} : reaction rate on the decomposition of MIBK into intermediate product in the aqueous phase,

$k_{MIBKInt}$: reaction rate on the decomposition of intermediate product of MIBK into organic impurities in the aqueous phase.

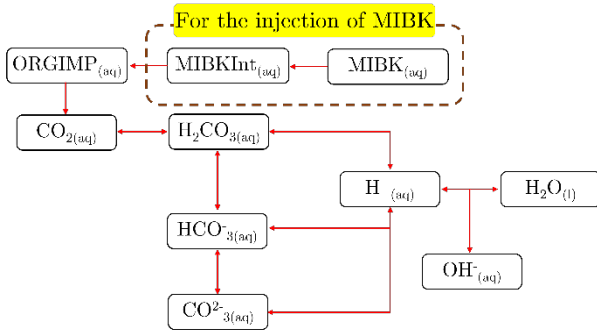The reaction chain for the evolution of pH is summarized in Fig. 1.

Fig. 1. Reaction chain on pH evolution in the sump

2.2 Determination of the reaction coefficients for calculation of pH

A system of ordinary differential equations is constructed with Eqs. (2), (4), (6), (8), (10), (11), (12), and (13). With some algebra on the eigenvalues and the eigenvectors of the matrix on the aforementioned system, the analytic solution on the concentration of H^+ ion is obtained and it is expressed as the following form :

$$[H^+] = f_{H^+}(t, k_{ORGIMP}, k_{CO_2f}, k_{CO_2b}, k_{H_2CO_3f}, k_{H_2CO_3b}, \\ k_{HCO_3f}, k_{HCO_3b}, k_{H_2Of}, k_{H_2Ob}, k_{MIBK}, k_{MIBKInt})$$

$$= A_1 + B_1 \cdot \exp(-k_{ORGIMP} \cdot t) + C_1 \cdot \exp(-k_{CO_2f} \cdot t)$$
$$+ D_1 \cdot \exp(-k_{CO_2b} \cdot t) + E_1 \cdot \exp(-k_{H_2CO_3f} \cdot t)$$
$$+ F_1 \cdot \exp(-k_{H_2CO_3b} \cdot t) + G_1 \cdot \exp(-k_{HCO_3f} \cdot t)$$
$$+ H_1 \cdot \exp(-k_{HCO_3b} \cdot t) + I_1 \cdot \exp(-k_{H_2Of} \cdot t)$$
$$+ J_1 \cdot \exp(-k_{H_2Ob} \cdot t) + K_1 \cdot \exp(-k_{MIBK} \cdot t)$$
$$+ M_1 \cdot \exp(-k_{MIBKInt} \cdot t), \qquad (14)$$

where the coefficients $A_1, \ldots, M_1$ are expressed as the combination of the reaction coefficients, i.e., $k_{ORGIMP}, \ldots,$ $k_{MIBKInt}$. The next step is a procedure to determine the reaction coefficients. The idea is to match Eq. (14) with experimental results on the evolution of H^+ ion. The way to match the analytic solution and experimental results is through the least squares of the differences between the two aforementioned ones, i.e., the procedure is to find the reaction coefficients that minimize the following functional expression :

$$F(k_{ORGIMP}, k_{CO_2f}, k_{CO_2b}, \ldots, k_{MIBK}, k_{MIBKInt})$$
$$= \sum_{i=1}^{N_{exp}} \left\{ f_{H^+}(t_i, k_{ORGIMP}, \ldots, k_{MIBKInt}) - [H^+]_i^{exp} \right\}^2, \qquad (15)$$

where

N_{exp} : number of experimental data applied to Eq. (15),

$[H^+]_i^{exp}$: i th experimental data on the concentration of H^+ ion.

3. Numerical Results

We implemented the aforementioned pH calculation model into AnCheBi code and it is applied to analyses on P10T2 and P11T1 experiments. The experimental conditions of P10T2, and P11T1 are summarized in Tables 1 and 2, respectively.

Table 1. Experimental condition of P10T2

Parameters	Data
Purpose	Iodine behavior in an epoxy painted vessel
Vessel	Epoxy painted
Initial concentrations (CsI)	$(3.2 \pm 0.2) \times 10^{-4}$
Temperature [K]	298
pH	Initially 10 for 45h then uncontrolled
Dose rate [kGy/h]	0.61
Duration of irradiation	283

Table 2. Experimental condition of P11T1

Parameters	Data
Purpose	Iodine behavior during continuous feed of MIBK
Vessel	Stainless steel
Initial concentrations (CsI)	$(3.2 \pm 0.2) \times 10^{-4}$
Temperature [K]	298
pH	Initially 10 for 24h then uncontrolled for 116h Controlled for 24h as 8 Then uncontrolled again for remaining hrs
Dose rate [kGy/h]	0.61
Duration of irradiation	306

In P10T2 experiment, the organic impurities exist at initial due to dissolution of paint from the surface submerged in the sump. In the case of P11T1 experiment, MIBK is being injected as continuous feed. The injection rates during the experiment are 0.8 mL/h with 0.026M from 24h to 140h and 4 mL/h with 0.026 from 164h to 284h. The computation conditions of AnCheBi code are shown in Table 3.

Table 3. Computation conditions in AnCheBi

Parameters	Data
Time discretization	Implicit Euler method
Time step control	Step doubling method
Time step size [sec]	7.0E-03 ~1.0E+00

The changes of pH are shown in Figs. 2 and 3, respectively. Note that the pH changes obtained from AnCheBi are in good agreement with experimental results.
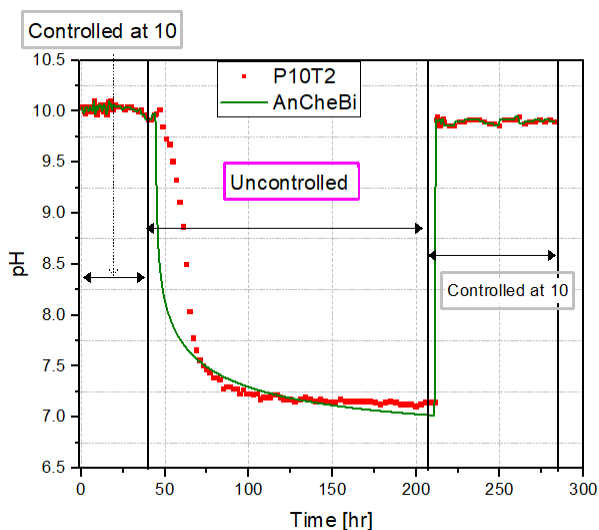

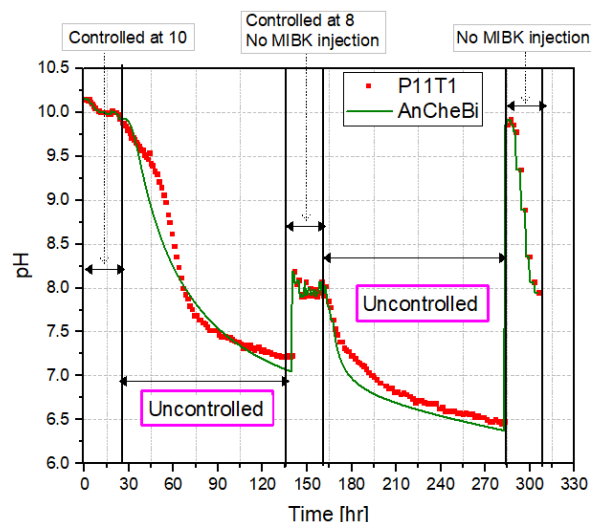Fig. 2. Change of pH in P10T2 experiment

Fig. 3. Change of pH in P11T1 experiment

4. Conclusions

In this paper, we developed the pH calculation model in the presence of organic impurities and implemented it into AnCheBi code. The model was based on the kinetics between chemical species involved in the production of H$^+$ ion. The reaction coefficients on the model are obtained by matching the analytic solution on the concentration of H$^+$ ion in the model and experimental results.

The validation was done by comparing the results from AnCheBi with the experimental results of P10T2 and P11T1 in terms of pH. The numerical results showed in good agreement with experimental results.

As future work, we will compare the numerical results from AnCheBi with experimental results in terms of the concentrations of the iodine species for the validation on the integration of iodine chemistry model and the pH calculation model.

ACKNOWLEDGEMENTS

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