Refinement of RAIM via Implementation of Implicit Euler Method

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1. Introduction

In the case of severe accident in a nuclear power plant, iodine is one of the most important nuclides due to its impact on the potential health risk. Therefore, it is important to understand the behaviors of iodine species during the accidents. In order to study such behaviors, many experimental studies, e.g., PHEBUS FP [1], PHEBUS RTF [2], OECD-BIP [3] have been performed.

Based on the aforementioned studies, modeling of the iodine behavior in the containment has been developed. There are two approaches on the modeling. The first approach is a mechanistic approach which is used in LIRIC [4] in which more than 200 reactions are modeled in detail. This approach enables to perform the detailed analysis. However, it requires huge computation burden.

The other approach is a simplified model approach which is used in the IMOD [5], ASTEC/IODE [6], and etc. In this approach, simplified reactions with less numbers than those in the mechanistic approach are used. Since this approach can perform the analysis with short computing time, it is usually coupled with integrated computer codes for severe accident analysis such as ASTEC, etc.

Recently, KINS has developed RAIM (Radio-Active Iodine chemistry Model) based on the simplified model approach [7]. Since the numerical analysis module in RAIM is based on the explicit Euler method, there are major issues on the stability of the module [8]. Therefore, implementation of a stable numerical method becomes essential.

In this study, RAIM is refined via implementation of implicit Euler method in which the Newton method is used to find the solutions at each time step. The refined RAIM is tested by comparing to RAIM based on the explicit Euler method. In the comparison, experimental data of OECD-BIP P10T2 test are used.

2. Modeling and Numerical Method in the Refined RAIM

2.1 Important Reactions in OECD-BIP P10T2 Test

In order to model the iodine behavior, iodine and its associated species are grouped into 22 chemical species. There are 42 reactions between the species considered in RAIM. Among them, 9 reactions, which are important in P10T2 test, are described in this paper. The important reaction chain in P10T2 test are shown in Fig. 1.

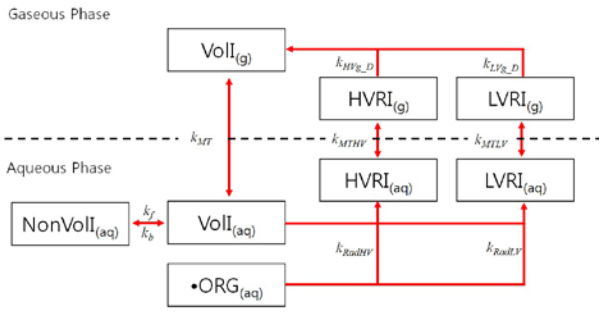

Fig. 1. Important reaction chain in P10T2 test

The kinetics of the reactions shown in Fig. 1 are written as :

i) reactions between nonvolatile iodine species ($\mathrm{NonVolI_{(aq)}}$) and volatile inorganic iodine species ($\mathrm{VolI_{(aq)}}$) in aqueous phase,

$$\frac{d\left[\mathrm{NonVolI_{(aq)}}\right]}{dt} = -k_f\left[\mathrm{NonVolI_{(aq)}}\right] + k_b\left[\mathrm{VolI_{(aq)}}\right], \tag{1}$$

$$\frac{d\left[\mathrm{VolI_{(aq)}}\right]}{dt} = -k_b\left[\mathrm{VolI_{(aq)}}\right] + k_f\left[\mathrm{NonVolI_{(aq)}}\right], \tag{2}$$

where k_f and k_b are the rate constants for forward and backward reactions, respectively,

ii) reactions between $\mathrm{VolI_{(aq)}}$ and high volatility organic iodides in aqueous phase ($\mathrm{HVRI_{(aq)}}$),

$$\frac{d\left[\mathrm{VolI_{(aq)}}\right]}{dt} = -k_{RadHV}\left[\bullet\mathrm{ORG_{(aq)}}\right]\left[\mathrm{VolI_{(aq)}}\right], \tag{3}$$

$$\frac{d\left[\mathrm{HVRI_{(aq)}}\right]}{dt} = k_{RadHV}\left[\bullet\mathrm{ORG_{(aq)}}\right]\left[\mathrm{VolI_{(aq)}}\right], \tag{4}$$

where k_{RadHV} is rate constant for formation of $\mathrm{HVRI_{(aq)}}$ from organic radicals ($\bullet\mathrm{ORG_{(aq)}}$) and $\mathrm{VolI_{(aq)}}$,

iii) radiolytic decomposition of high volatility orgainic iodide in gaseous phase ($\mathrm{HVRI_{(g)}}$) with vapor,

$$\frac{d\left[\mathrm{HVRI_{(g)}}\right]}{dt} = -\frac{d\left[\mathrm{VolI_{(g)}}\right]}{dt}$$

$$= -k_{HVg\_D}\frac{\left(1-0.0013T_g\right)\left(1-0.68\exp\left(-1.7X_{H_2O}\right)\right)}{\left(1.22-\dfrac{0.11}{D_g}\right)} \tag{5}$$

$$\times D_g\left[\mathrm{HVRI_{(g)}}\right],$$

where k_{HVg_D} is destruction rate of $\mathrm{HVRI}_{(g)}$, T_g is the temperature of the gaseous phase (K), and X_{H_2O} is the mole fraction of steam,

iv) interfacial mass transfer between aqueous and gas phase,

$$\frac{d\left[\mathrm{VolI}_{(aq)}\right]}{dt}=k_{MT}\frac{A_{int}}{V_{aq}}\left(2\left[\mathrm{VolI}_{(g)}\right]\cdot H_{VolI}-\left[\mathrm{VolI}_{(aq)}\right]\right), \qquad (6)$$

$$\frac{d\left[\mathrm{VolI}_{(g)}\right]}{dt}=k_{MT}\frac{A_{int}}{V_{g}}\left(\frac{1}{2}\left[\mathrm{VolI}_{(aq)}\right]-\left[\mathrm{VolI}_{(g)}\right]H_{VolI}\right), \qquad (7)$$

$$\frac{d\left[\mathrm{HVRI}_{(aq)}\right]}{dt}=k_{MTHV}\frac{A_{int}}{V_{aq}}\left(\left[\mathrm{HVRI}_{(g)}\right]\cdot H_{HVRI}-\left[\mathrm{HVRI}_{(aq)}\right]\right), \qquad (8)$$

$$\frac{d\left[\mathrm{HVRI}_{(g)}\right]}{dt}=k_{MTHV}\frac{A_{int}}{V_{g}}\left(\left[\mathrm{HVRI}_{(aq)}\right]-\left[\mathrm{HVRI}_{(g)}\right]\cdot H_{HVRI}\right), \qquad (9)$$

where

$$\frac{1}{k_{MT}}=\frac{1}{k_{aq}}+\frac{H_{VolI}}{k_g},$$

$$\frac{1}{k_{MTHV}}=\frac{1}{k_{aq}}+\frac{H_{HVRI}}{k_g},$$

k_{aq} and k_g are the mass transfer coefficients for the aqueous and gaseous phase, respectively, H_{volI} and H_{HVRI} are the partition coefficients for the volatile iodine and high volatility organic iodide respectively, A_{int} is the interfacial mass transfer surface area, and V_g and V_{aq} are the volumes of gas and aqueous solution, respectively.

In the case of low volatility organic iodides in aqueous ($\mathrm{LVRI}_{(aq)}$) and gaseous phase ($\mathrm{LVRI}_{(g)}$), they are assumed to follow the same kinetics as those of $\mathrm{HVRI}_{(aq)}$ and $\mathrm{HVRI}_{(g)}$ with different weighting factors for reaction rate constants.

2.2 Implicit Euler Method for RAIM

After some algebra, reaction kinetics equations can be expressed as forms used in the implicit Euler method. The equations are expressed as a matrix form as follows:

$$F(\vec{X})=0, \qquad (10)$$

where

$$F(\vec{X})=\left[f_1 \quad f_2 \quad \cdots \quad \cdots \quad f_n\right]^T,$$

$$\vec{X}=\left[x_1 \quad x_2 \quad \cdots \quad \cdots \quad x_n\right]^T,$$

f_i and x_i are the reaction kinetic equation expressed as a form used in the implicit Euler method and the concentration for chemical species, i, respectively.

In this study, Eq. (10) is solved by Newton method. The method can be expanded to F about $\vec{X}$:

$$\vec{X}^{t+1}=\vec{X}^{t+1}-\left[F'(\vec{X}^t)\right]^{-1}F(\vec{X}^t)=0, \qquad (11)$$

where t is iteration index in Newton method, and $F'(\vec{X}^t)$ is Fréchet derivative on F at $\vec{X}^t$ and is defined as the Jacobian matrix expressed as follows:

$$\left[F'(\vec{X}^t)\right]=\begin{bmatrix}\frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n}\\ \frac{\partial f_2}{\partial x_1} & \ddots & & \frac{\partial f_2}{\partial x_n}\\ \vdots & & \ddots & \vdots\\ \frac{\partial f_n}{\partial x_1} & \frac{\partial f_n}{\partial x_2} & \cdots & \frac{\partial f_n}{\partial x_n}\end{bmatrix}.$$

Since f_i 's have a simple form, analytic expressions of the elements in the Jacobian matrix can be obtained easily with some algebra. In this study, inverse of the Jacobian matrix is obtained via Gaussian elimination. Computation burden of Gaussian elimination is not large due to a small size of the Jacobian matrix considered in this study (≈20).

3. Numerical Results

The refined RAIM is tested using data of OECD-BIP P10T2 test [3]. Experimental conditions of P10T2 test are summarized in Table 1.

Table 1. Experimental conditions of P10T2 test

Vessel	Epoxy painted vessel
Initial iodine species	$\sim 8.9\times10^{-6}\,M$, CsI
Liquid volume [dm^3]	28.1
Gas volume [dm^3]	311.2
Operating temperature [^{o}C]	25
pH	Initially 10 for 45hrs, then uncontrolled
Dose rate [$kGy\bullet h^{-1}$]	0.61
Duration [hrs]	283

As sizes of time step (Δt), the refined RAIM uses 0.1 and 0.001 s and it is compared to RAIM with explicit Euler method using a small time step size (Δt =0.008 s). Concentrations of organic iodide in aqueous solution (sum of concentrations of $\mathrm{LVRI}_{(aq)}$ and $\mathrm{HVRI}_{(aq)}$), $\mathrm{LVRI}_{(g)}$, $\mathrm{HVRI}_{(g)}$, and $\mathrm{VolI}_{(g)}$ are shown in Figs. 2, 3, 4, and 5, respectively. Note that experimental data does not provide the concentrations of $\mathrm{LVRI}_{(aq)}$ and $\mathrm{HVRI}_{(aq)}$ separately.

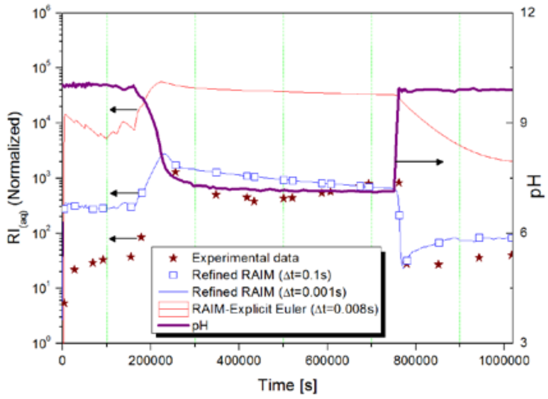

Fig. 2. Concentration of organic iodides in aqueous solution ($\mathrm{RI}_{(aq)}$)

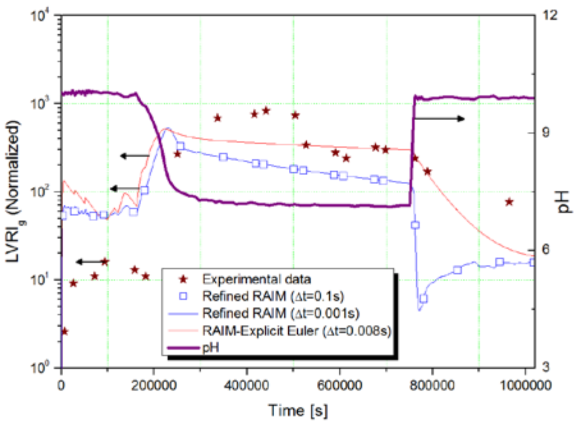

Fig. 3. Concentration of LVRI$_{(g)}$

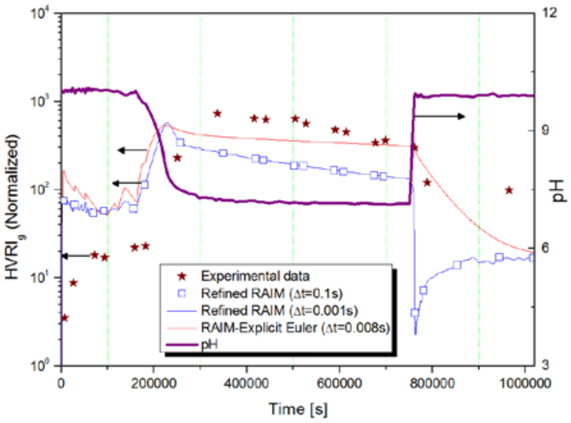

Fig. 4. Concentration of HVRI$_{(g)}$

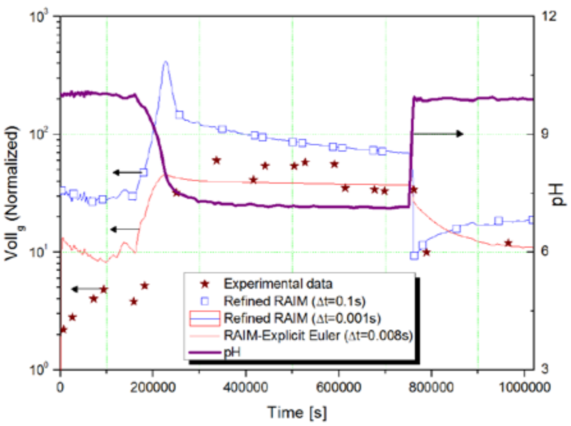

Fig. 5. Concentration of VolI$_{(g)}$

Compared to the results from the explicit Euler method, the refined RAIM shows better agreement to the experimental results. Note that, at time t=800,000 s, the concentrations of RI$_{(aq)}$ from the refined RAIM decrease by two orders of magnitude for 10,000 s, which is affected by the rapidly increased pH for that time. While in the explicit Euler method, the concentrations change slower, i.e., they decrease, at most, by less than one order of magnitude.

With the various time step sizes, the refined RAIM shows good agreement on the results. Meanwhile, RAIM with the explicit Euler method can perform the calculations when the time step size is less than 0.008 s, which is ~12.5 times smaller than that can be used in the refined RAIM.

Computing time of the refined RAIM and the explicit Euler method are compared in Table 2. As shown in the table, the computing time of the refined RAIM is comparable to that of the explicit Euler method.

Table 2. Comparison of computing time

	Time step (Δt) [s]	Computing time [s]
Refined RAIM	0.1	45
	0.001	~4500
RAIM with explicit Euler method	0.008	48

4. Conclusions

In this paper, RAIM was refined by implementing the implicit Euler method. At each time step of the method in the refined RAIM, the reaction kinetics equations are solved by the Newton method in which elements of the Jacobian matrix are expressed analytically.

With the results of OECD-BIP P10T2 test, the refined RAIM was compared to RAIM with the explicit Euler method. The refined RAIM shows better agreement with the experimental data than those from the explicit Euler method. For the rapid change of pH during the experiment, the refined RAIM gives more realistic changes in the concentrations of chemical species than those from the explicit Euler method.

In addition, in terms of computing time, the refined RAIM shows comparable computing time to that with explicit Euler method. These comparisons are attributed to ~10 times larger time step size used in the implicit Euler method, even though computation burden at each time step in the refined RAIM is much higher than that of the explicit Euler method.

Compared to the experimental data, the refined RAIM still shows discrepancy, which are attributed to the coefficients used in the iodine chemistry model. Their dependence on pH, radiation dose, etc. seems not to be negligible. However, some of them, e.g., partition coefficients, are assumed to be independent of such conditions. As future works, we will investigate the condition dependence of coefficients in the modeling.

ACKNOWLEDGEMENTS

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