

Importance Analyses on the Model for pH in the Presence of Organic impurities in the Aqueous Phase for a Severe Accident

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1. Introduction

During a severe accident of a nuclear power plant, iodine has a particular relevance due to its high affinity to the thyroid and relatively long duration of the radiological effect from the relatively long half-life natures of the isotopes, among the various radiological materials included in the nuclear source term. In addition to the aforementioned properties, iodine has multiple oxidation states in the containment under severe accident conditions such as high humidity, high radiation field, presence of organic materials, etc. which leads to the formation of various chemical species such as those in gaseous form, aerosol, and organic and inorganic compounds. Since the various chemical forms of iodine have different radiological effect, iodine chemistry is an area of particular relevance to nuclear source term studies.

Among the various thermophysical conditions during a severe accident, pH is one of the most important parameters in the chemical behavior of the iodine, which affects the volatility of iodine in the aqueous phase [1]. Due to its importance on the iodine, the authors have developed a pH analysis model in a presence of organic impurities and it has been implemented in AnCheBi [2].

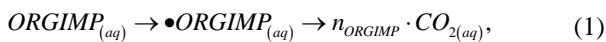
In this paper, with the aforementioned model, we would like to perform the importance analysis on the chemical species of the iodine, which leads to find important reaction coefficients on the change of pH and volatility of iodine species during a severe accident.

2. Summaries of the pH Calculation Model and Framework of Importance Analyses

2.1 Summary of the pH calculation model in the presence of organic impurities

The change of pH is derived from the change of H⁺ ions in the sump. The pH model in AnCheBi is being developed based on the semi-mechanistic approaches via simplification of the mechanistic models in KICHE [3].

The evolution of H⁺ ions from the organic impurities is related with decomposition of carbon bonds in the organic impurities and the formation and decomposition of H₂CO₃ under irradiation in the aqueous phase. The chemical reaction between organic impurities and CO_{2(aq)} is shown as below :



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 :

$$\frac{d[\bullet ORGIMP_{(aq)}]}{dt} = k_{ORGIMP} \cdot [ORGIMP_{(aq)}], \quad (2)$$

$$\frac{d[CO_{2(aq)}]}{dt} = n_{ORGIMP} \cdot k_{O2aq} \cdot [O_{2(aq)}] \cdot [\bullet ORGIMP_{(aq)}], \quad (3)$$

where

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

k_{ORGIMP} : decomposition rate of ORGIMP into CO₂ in aqueous phase,

k_{O2aq} : decomposition coefficient of organic impurity radicals into carbon dioxide in the aqueous phase

Then, CO_{2(aq)} is in equilibrium with H₂CO₃ in the aqueous phase as expressed below



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

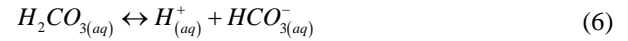
$$\frac{d[H_2CO_{3(aq)}]}{dt} = k_{CO_2f} \cdot [CO_{2(aq)}] - k_{CO_2b} \cdot [H_2CO_{3(aq)}], \quad (5)$$

where

k_{CO_2f} : reaction rate on the formation of H₂CO_{3(aq)} from CO_{2(aq)},

k_{CO_2b} : reaction rate on the formation of CO_{2(aq)} from H₂CO_{3(aq)}.

H⁺ ion is then produced from the decomposition of H₂CO_{3(aq)} as follows :



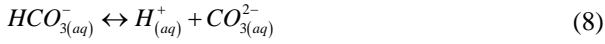
$$\frac{d[H_2CO_{3(aq)}]}{dt} = -k_{H_2CO_3f} \cdot [H_2CO_{3(aq)}] + k_{H_2CO_3b} \cdot [H_{(aq)}^+] \cdot [HCO_{3(aq)}^-], \quad (7)$$

where

$k_{H_2CO_3f}$: reaction constant on the decomposition of H₂CO_{3(aq)} to produce H⁺_(aq) and HCO_{3(aq)}⁻.

$k_{H_2CO_3b}$: reaction constant on the formation of H₂CO₃ from H⁺_(aq) and HCO_{3(aq)}⁻,

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

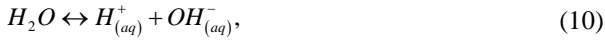


$$\frac{d[\text{HCO}_3^-]}{dt} = -k_{\text{HCO}_3^f} \cdot [\text{HCO}_3^-] + k_{\text{HCO}_3^b} \cdot [\text{H}^+] \cdot [\text{CO}_3^{2-}], \quad (9)$$

where

$k_{\text{HCO}_3^f}$: reaction constant on the decomposition of HCO_3^- to produce H^+ and CO_3^{2-} in the aqueous phase,
 $k_{\text{HCO}_3^b}$: 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 :



$$\frac{d[\text{H}_2\text{O}]}{dt} = -k_{\text{H}_2\text{O}^f} + k_{\text{H}_2\text{O}^b} \cdot [\text{H}^+] \cdot [\text{OH}^-], \quad (11)$$

where

$k_{\text{H}_2\text{O}^f}$: reaction constant on the decomposition of H_2O to produce H^+ and OH^- in the aqueous phase,
 $k_{\text{H}_2\text{O}^b}$: reaction constant on the formation of H_2O from H^+ and OH^- in the aqueous phase.

The reaction coefficients are obtained via minimization of the least squares of the difference between analytic solutions of the model and the experimental results. The detailed procedures are discussed in Ref. 4.

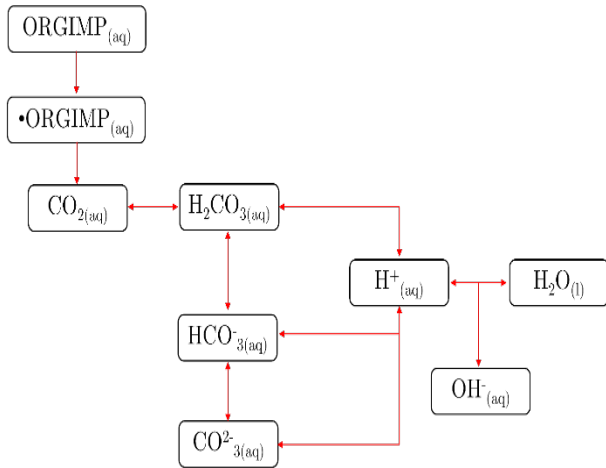


Fig. 1. Summary of reaction chain on pH change in AnCheBi

2.2 Importance Analyses for the pH calculation model

In this work, the importance analyses are performed on the pH calculation model in AnCheBi integrating with the iodine chemistry models to determine the important reaction coefficients for evaluating chemical behaviors of the iodine.

The importance analyses scheme considered in this work is the same as the one in the previous study [5]. via Latin hypercube sampling on the reaction coefficients,

sensitivity analyses of AnCheBi, and calculation of the correlation coefficients between the reaction coefficients and figure of merits (the pH and the concentrations of the various iodine species). The process is summarized on the following figure.

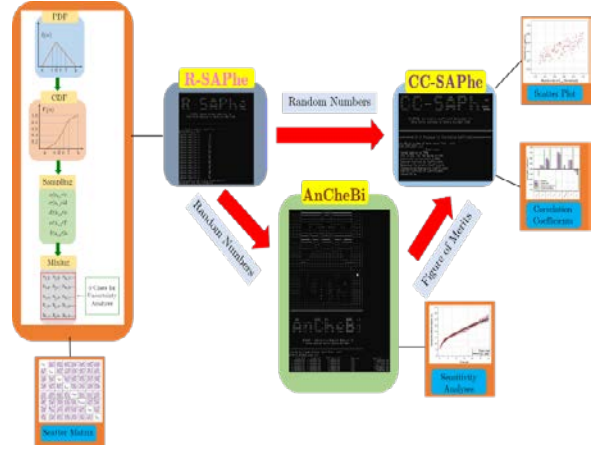


Fig. 2. Summary of reaction chain on pH change in AnCheBi

3. Numerical Results

The procedure discussed in 2.2 is applied to the AnCheBi code integrated with the pH calculation model. The uncertainty range of the reaction coefficients in the pH calculation model and the number of Latin Hypercube sampling are set to be 30% of the values and 2,000, respectively. In the analyses, not only the pH but also the concentrations of the iodine species both aqueous and gas phases are considered as the figure of merits since it is related with volatility of the iodine. We consider two experiments in the importance analyses; the first is P10T2, representing organic impurities via dissolution of paints in the sump [6]. The other is P11T1, representing continuous injection of organic impurities [7]. 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

The sensitivity of pH and the concentrations of the iodine species from the uncertainty range of the reaction coefficients for the pH calculations are shown in Fig. 3.

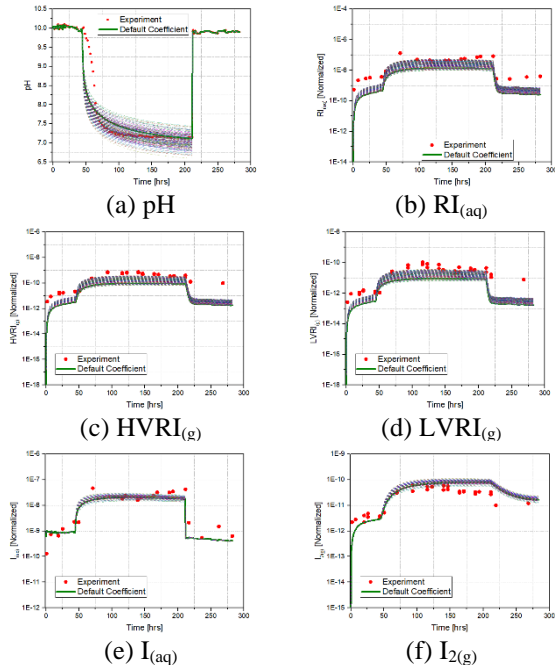


Fig. 3. Change of pH and concentrations of iodine species from sensitivity analyses on P10T2

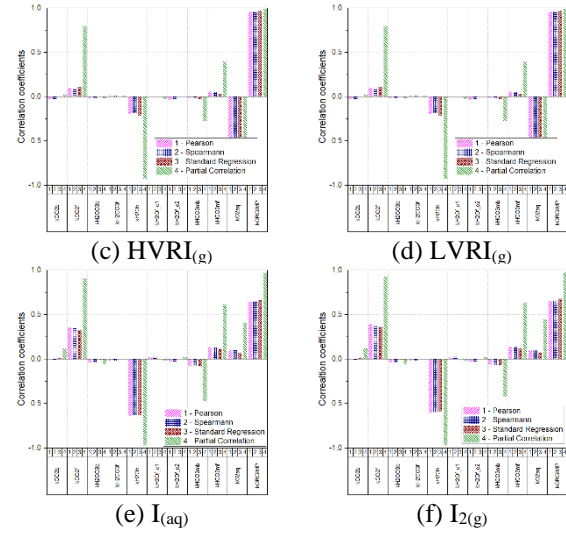
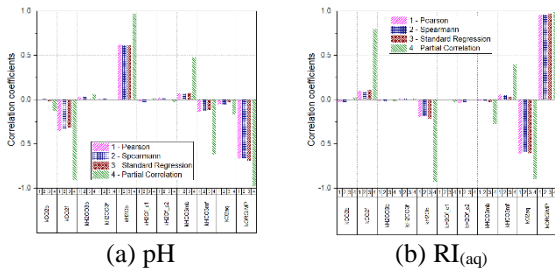


Fig. 4. Correlation coefficients for selected reactions on the pH changes in P10T2

As shown in Figs. 3(a) and 4(a), the pH in the analyses displays a strong linear relationship with the reaction coefficient for the radical formation from organic impurities (k_{ORGIMP}) in the aqueous phase. In other words, the pH decreases as the coefficient increases. The pH also shows a strong linear relationship with the backward reaction in the water radiolysis.

In the case of organic iodide production, similarly with the previous results, Figs. 3(b), 3(c), 4(b), and 4(c) show that the concentrations of organic iodide have strong linear relationship with the reaction coefficients for the radical formation of organic impurities (k_{ORGIMP}) in the aqueous phase.

Figs. 3(d), 3(e), 4(d), and 4(e) show that the concentrations of $I_{(aq)}$ and $I_{2(g)}$ have a strong linear relationship with the reaction coefficients for the radical formation (k_{ORGIMP}). The partial correlation coefficient between $I_{2(g)}$ and k_{CO2f} also indicates that there is a strong linear relationship between the concentration and the formation of H_2CO_3 from CO_2 in the aqueous phase. The results on P11T1 are shown as below.

