

Empirical Correlation on Iodine Concentration in Aqueous Solution under Irradiation

Thi Thanh Thuy Nguyen^{a,b}, Kwang Soon Ha^{b*}, Jin Ho Song^{a,b}, Sung Il Kim^b

^aUniversity of Science and Technology, 217 Gajeong-ro, Yuseong-gu, Daejeon, Korea

^bKorea Atomic Energy Research Institute, 1045 Daedeok-daerok, Yuseong-gu, Daejeon, Korea

*Corresponding author: tomo@kaeri.re.kr

1. Introduction

It has been recognized that radioiodine is potentially one of the most hazardous fission products that can be released from the fuel of nuclear reactors during a severe accident. According to the thermodynamic calculations and various experiments under the severe accident condition, the iodine released from the fuel would be primarily in its reduced state as cesium iodide (CsI) in the containment [1]. Iodide, which is one of the major iodine species if the CsI solution is dissolved in cooling water, is easily diffused into the gas phase after being oxidized into gaseous I₂ by gamma irradiation [2]. Overall, the behavior of I₂ is an important component used to evaluate and predict the radioactivity at an early stage of a severe accident, and for accidents involving steam and water, iodine may collect in the aqueous phase and undergo a variety of reactions depending on the oxidation potential and pH solution.

Many experiments have been conducted to evaluate the radiolytic oxidation of iodide ions in aqueous solutions, most of which used iodide concentrations within in a range of 10⁻³ to 10⁻⁶M and a pH range from mildly acid to mildly alkaline with the dose rates were fixed. The range of their conditions is close to those anticipated in the case of a severe accident. The modeling effect has also been pursued to predict the iodine chemistry behavior under severe accident conditions. The empirical models are practically used in the severe accident codes, such as IODE, ASTEC, IMPAR, *etc.*, when modeling the iodine species with a limited set of reactions and the typical codes adapted in the mechanistic approach are INSPECT (IodiNe SPECiation and Transport) developed in AEAT, which has been integrated with some changes into MELCOR 1.8.5 and the LIRIC model (Library of Iodine reactions in containment) developed at AECL.

Although there are many experimental results and correlations to estimate the volatile iodine in an aqueous phase, but there are significant differences between iodine models due to the uncertainties on the boundary conditions, such as the pH solution, occur if not controlled. Therefore, a new empirical model to estimate the produced concentration of volatile iodine at 5.0x10⁻³ to 10⁻⁴ M irradiated CsI solutions at an initial pH of 3.0 to 9.0 and high irradiation dose rates (several kGy/hr) was proposed in the aqueous phase.

2. Methods and Results

The Jung's and T. I. Gorbovitskaya's experiments were conducted to evaluate the production of volatile iodine concentration in iodide concentrations of 1.0 and 5.0 mM without the control of pH under high irradiation dose rates. Based on these experimental results, the oxidation and reduction rate of the kinetic reactions between the CsI solution and radiolysis products were estimated in this paper.

2.1 Empirical Model

The products of water radiolysis are continuously generated under effects of radiation, thus the kinetics reaction between the CsI solution and radiolysis products is important to determine the iodine behavior in the aqueous solution. Under high radiolysis condition, the most important reactions are oxidation of hydroxyl radical ·OH, the reduction of I₂ species in an acid medium by either e⁻ under the absence of dissolved oxygen or by O₂⁻ under the presence of dissolved oxygen and in a neutral or basic medium by the hydrolysis of I₂ followed by the reduction of I⁺(HIO/IO⁻) oxidation state by H₂O₂ [3].

To estimate the behavior of volatile iodine in a liquid solution, the semi-empirical approach is being developed in this paper. In this approach, the radiolysis reaction ($2I^- + \gamma \rightarrow I_2$) were initiated by Furrer et al., is modeled as Eq.1,

$$\frac{d[I_2]}{dt} = k_1 [I^-] D [H^+]^{0.5} - k_2 [I_2] \quad (1)$$

where

[I⁻] : concentration of iodide in liquid phase (mol/l)

[I₂] : concentration of iodine in liquid phase (mol/l)

[H⁺]:concentration of init. hydrogen (mol/l)

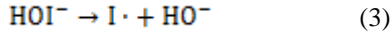
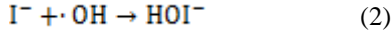
D : dose rate expressed as (Gy/s)

k₁: kinetic constant for the oxidation reactions (mol^{-0.5}.Gy)

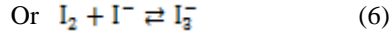
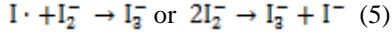
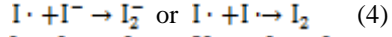
k₂ : kinetic constant for the reduction reactions (s⁻¹)

n : a constant equal to 0.5.

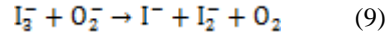
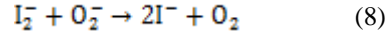
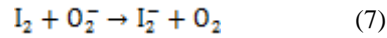
Using the same approach method as IODE model, the formation rate of I₂ is the competition of the oxidation of I⁻ by ·OH (hydroxyl radical) and reduction reactions of I₂, modeled as Eq.(1). This process is described as the following reactions [12, 13]:



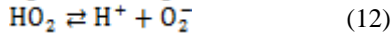
where $\cdot OH$ is a water radical product formed under the irradiation. The $I \cdot$ radicals combine ultimately to form either I_2 or I_3^- , which depends on the $[I^-]$ concentration and pH values in the aqueous solution.



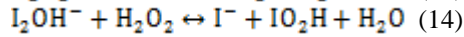
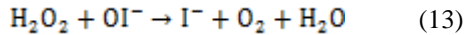
These reactions are competing with the reactions of the reduction of I_2 in an acid medium, either by e^- in the absence of dissolved oxygen or by superoxide (O_2^-) in the presence of dissolved oxygen.



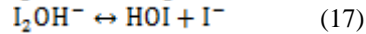
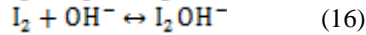
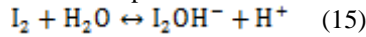
The dissolved oxygen formed through the reaction of the solvated electron or atomic hydrogen with dissolved oxygen:



In addition, in a neutral or basic medium by the hydrolysis of I_2 followed by the reduction of the $I+1(HOI/IO^-)$ oxidation state by H_2O_2 (hydrogen peroxide),



This mechanism is expressed in more detailed steps:



2.2 Methods for developing a new correlation

To developing a new model using the same approach, we try to find the oxidation rate of the forward reaction in this simplified formulation, as shown in Eq. (1). In the presence of a strong irradiation field and a high concentration of iodide, the oxidation of iodide ions into I_2 by $\cdot OH$ is very fast or the effect of reverse reactions can be ignored. If the concentration of I^- available is sufficient for stabilizing I_2 by the equilibrium reaction ($I_2 + I^- \rightleftharpoons I_3^-$), the formation of I_3^- is favored. By measuring the curve of $(I_3^-)I_2$ concentration at the beginning time, $t = 0.0$, the k_1 value was evaluated is $0.63 \text{ (mol)}^{-0.5}/\text{kGy}$.

To determine the reduction rate of reactions, the balance between the oxidation and reduction reactions of I_2 is considered. For these states, the term $d[I_2]/dt$ in Eq.(1) should must be zero.

$$\frac{d[I_2]}{dt} = 0$$

$$k_1[I^-][H^+]^{0.5}D = k_2[I_2] \quad (18)$$

The remaining $[I^-]$ concentration in aqueous phase can be determined as follows.

$$[I^-]_t = [I^-]_{t-1} - 2[I_2]_t \quad (19)$$

By substituting Eq. (18) into Eq. (17), we have Eq. (20).

$$k_1([I^-]_{t-1} - 2[I_2]_t)[H^+]^{0.5}D = k_2[I_2]_t \quad (20)$$

This balance can be seen clearly in a series of experiments was performed by T.I. Gorbovitskaya at different initial pH of 3.0 to 9.0. With k_1 value is 0.63, and then the value of k_2 is calculated from these experiments:

$$k_1 = 0.63$$

$$k_2 = 0.82$$

$$n=0.5$$

2.3 Comparison of Gorbovitskaya's experiment with the correlation [4]

The experiment was performed by T. I. Gorbovitskaya et al.[4] as a part of a research program to investigate the escape of volatile forms of radioiodine from the coolant water in severe accident. The solution studied was 10^{-5} to 10^{-3} M cesium iodide solution at 323 K, and the initial pH of the solution was a variable at $3 < \text{pH} < 9$ for a dose range of 1-30 kGy.

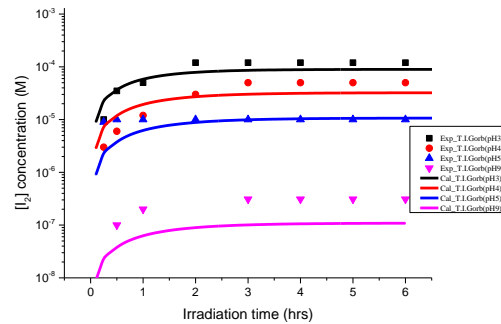


Fig. 1: Comparison of the experiment data with calculated iodine concentration by model: 10^{-3} M CsI solution, pH 3, 4, 5 and 9

Under these experimental conditions, the molecular iodine concentrations that changed during irradiation were calculated according to model and compared with the experimental results. Fig. 1 shows that the predicted I_2 concentrations are well matched with the observed

data in acid solutions (pH 3, 4 and 5), which increases with the irradiation time and reached stability after 0.5 hour irradiation at 4.5 kGy/hr, but it is slightly smaller in magnitude the measured I_2 concentrations in the case of the alkaline solution (pH9).

2.4 Others experiment results and correlation

K. Ishigure et al.[5] carried out some experiments to investigate the effects of radiation on the chemical forms of iodine species under the condition of nuclear reactor accidents. It was found that several factors such as the initial CsI concentration, pH, and O_2 concentration have a large influence on the oxidation and reduction reactions in the radiolysis of the iodide solutions.

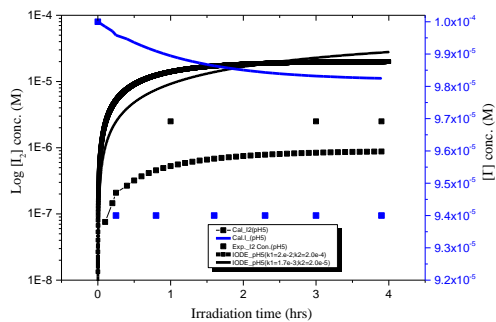


Fig. 2: The prediction radiolysis iodine concentrations using IODE model, our model, and experiment data: CsI= 10^{-4} M, dose rate = 0.38 Mrad/h (3.8kGy/h) at initial pH 5 (not buffered)

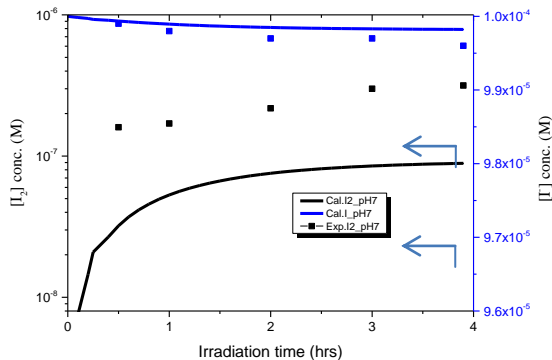


Fig. 3: Radiolysis products of CsI = 10^{-4} M, dose rate = 0.38 Mrad/h (3.8 kGy/h) at initial pH 7 (not buffered)

To verify the code, K. Ishigure et al experiment in case of 10^{-5} CsI solution at pH5 and 7 was used to compute the profile of concentration of I_2 and I^- during the irradiation time induced. Fig. 2 and 3 shows a comparison between calculated their concentration by model, the calculated I_2 by IODE code and the observed I_2 and I^- concentrations at pH5 and neutral pH7. The I_2 and I^- concentration profiles which calculated by code with increasing irradiation time were similar in both cases of pH values. However, the calculated I^- concentration is well match with observed I^-

concentration but the predicted I_2 lower than measured data in the case of pH7.

3. Conclusions

A new empirical model is proposed to estimate the volatile iodine in an aqueous phase according to the pH and irradiation dose rate in the pool. The model was evaluated by comparison with available experimental results and these comparisons showed that the volatile iodine can be predicted at various initial pH levels for the 10^{-3} M to 10^{-4} CsI solution with good agreement. However, the predicted iodine concentration was an order of magnitude lower than the observed experiment results in the 10^{-5} M solution.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT) (No. NRF-2017M2A8A4015280)

REFERENCES

- [1] B. Clement, L.Cantrel, G. Ducros, F. Funke, L. Herranz, A. Rydl, G. Weber, C. Wren, "State of the art report on iodine chemistry", NEA/CSNI/R(2007)1, OECD-NEA, 23 Feb, 2007.
- [2] C. C. Lin, "Chemical effects of gamma radiation on iodine in aqueous solutions", J. Inorg. Nucl. Chem. 42 (1980) 1101-1107
- [3] C. Poletiko, D. Jacquemain, C. Hueber, "The volatility of iodine from irradiated iodide solutions in the presence or absence of painted surfaces: Modelling on the IODE code at IPSN", Nuclear Technology, 126, p. 215-228 (1999)
- [4] T.I. Gorbovitskaya, et al. "Radiolysis of dilute aqueous Cesium iodide solutions", 1992.
- [5] K.Ishigure, et. al. "Radiation chemistry of aqueous iodine systems under nuclear reactor accident conditions", August 1987.