Estimation of the Oxidation Rate of Iodide Ions under Gamma Irradiation Conditions

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1. Introduction

If a severe accident occurs in a nuclear power plant, fission products from a fuel might be released into the environment. Iodine, which is a major fission product generated in RCS, can enter the containment in several forms including CsI and I_2. The NUREG-1465 report indicated that most of the iodine enters the containment as a particular form as cesium iodine (CsI) (95%), and the remaining is a vapor species such as atomic iodine (I) and hydrogen iodine (HI) (5%) [1].

The iodine species can be dissolved in a liquid phase by converting a non-volatile iodine species into a volatile species I_2, and finally released into the containment. The iodine dissolution may be induced by some hydrolysis processes and reactions with other species generated by water radiolysis. To determine the concentration of iodide ions, I^-, and its contribution to the gaseous phase iodine concentration, the rate of reaction products I_3^- (I_2) should be known as a function of the initial conditions in water, such as the initial iodide ion concentration and pH variation under gamma irradiation. Some correlations have been issued to modeling this process, and used in several codes such as IODE, IMPAIR, and MELCOR code. However, some uncertainties still remain, for example, INSPECT code can estimate well the oxidation rate of iodine (I_2) and iodide ion (I_3^-) when the I^- concentration is about 0.1mM but overestimate them when I^- concentration is larger than 1mM [2].

A new correlation was issued to estimate the iodate concentration in an acidic pool under irradiation conditions by identifying the key reactions and solving the differential equations based on the rate law. The correlation was also verified with experimental data found by Sang et al. [3] using NaI solutions under gamma irradiation.

2. Experiments [3]

An experimental test was conducted by Jung *et al.* [3], the experimental facility for the gamma irradiation was set up as shown in Fig. 1, and the initial conditions of the tests were described in Table I.

The measured pH values and the formation of an I_3^- concentration at various concentrations of NaI solutions of 0.2mM, 1.0 mM, 5.0 mM as a function of irradiation time and gamma dose are shown in Figs. 2 and 3, and Tables II and III. The I_3^- concentration obtained from two experiments was plotted as the gamma doses, as shown in Fig. 4 [3].
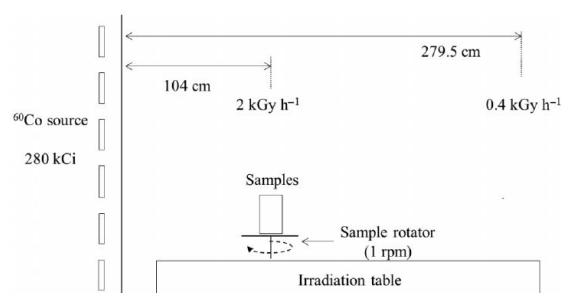

Fig.1. Schematic diagram of ^{60}Co irradiation facility [3]

Table I: Initial conditions of test [3]

Initial conditions	Values
Conc. of NaI solution (mM)	0.2; 1.0; 5.0
pH value	3.0
Gamma dose rate (kGy.h^{-1})	2.0
Temperature at laboratory (^{o}C)	23.0

Table II: The pH values under gamma irradiation [3]

Irrad. time (h)	pH values of NaI solutions after Irradiation		
	0.2 mM NaI	1.0 mM NaI	5.0 mM NaI
0	3.04	3.04	3.04
1	3.2	3.20	3.29
2	3.15	3.28	3.5
4	3.16	3.5	5.92
7	3.16	3.93	6.04

Table III: The pH change and formation of [I_3^-] in 5.0 mM NaI solution as a function of Gamma dose [3]

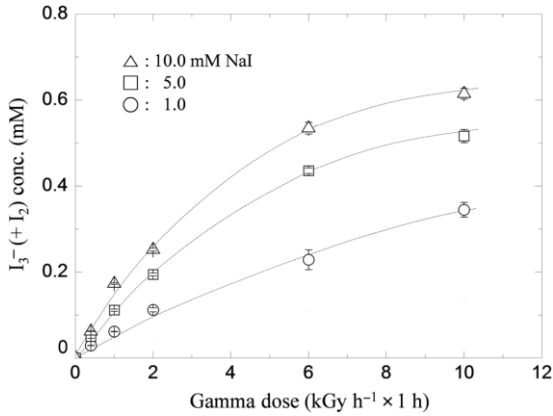| Gamma Dose (kGy.h^{-1} ×1h)	pH value after Irradiation	[I_3^-] calc. from the pH change (mM)	[I_3^-] measured (mM)
1	3.25	0.116	0.110
2	3.40	0.198	0.198
6	4.51	0.382	0.440
10	6.04	0.397	0.545

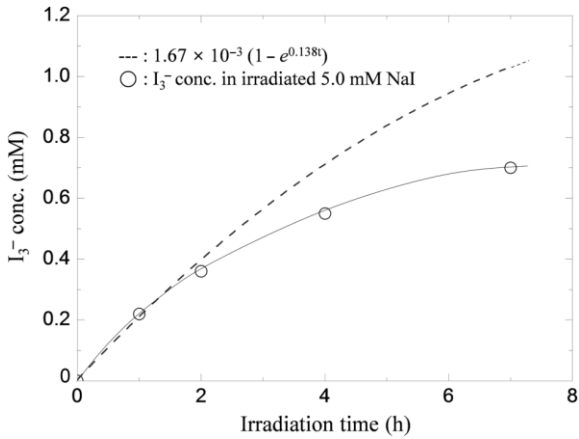Fig.2. Formation of $[I_3^-]$ as gamma dose in various NaI conc. solutions: 1.0, 5.0, 10.0 mM NaI [3]

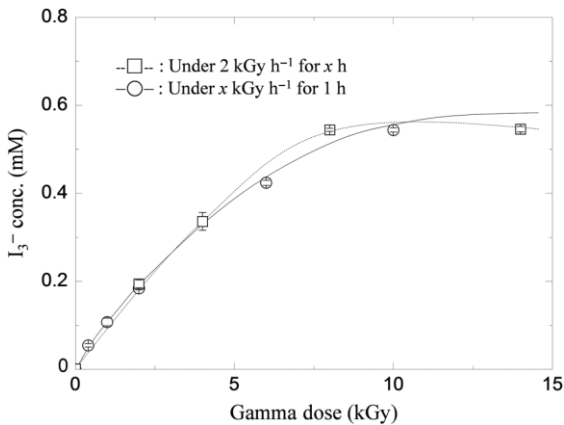Fig. 3. Formation of I_3^- in 5.0 mM NaI solution as a function of irradiation time [3]

Fig. 4. Formation of $[I_3^-]$ as gamma dose in 5.0 mM NaI under x kGy.h^{-1} for 1 h (ϕ), under 2 kGy.h^{-1} for x h ($\square$) [3]

The UV-VIS spectra were used to identify the species in 0.2, 1.0, and 5.0 mM NaI solutions under a gamma dose rate of 2.0 kGyh^{-1} at 0.0, 1.0, 2.0, 4.0, and 7.0 hours of irradiation exposure times. In the case of the 0.2 and 1.0 mM NaI solutions, two components, I_3^- and I_2, were observed, and thus the oxidation of I^- was confirmed as follows: first, I^- ions were oxidized into I_2 with OH·, and most of I_2 was then stabilized into I_3^- as long as the I^- concentration is high. In 5.0 mM NaI solution, few I_2 molecules were observed in the UV-VIS spectra when the concentration of I^- was enough high.

To predict the I_3^- and I_2 concentrations in a low concentration and acidic solution, many researches have been carried out, and several codes have been modeled, such as IODE, IMPAIR, and MELCOR. In general, most of the codes were considered for two important reactions, the first of which reaction is

$$I^- + OH \cdot \rightarrow I \cdot + OH \cdot, \ I \cdot + I \cdot \rightarrow I_2,$$
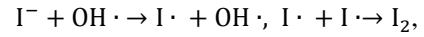
and the second of which is

$$I_2 + I^- \overset{K_5}{\Leftrightarrow} I_3^-$$
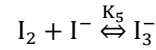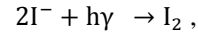
with

$$\log_{10}(K_5) = \{5.55e^2T^{-1} - 2.575\log_{10}(T) + 7.355\} \ /D_w$$

, where D_w : density of water (kg/dm^3).

The first reaction has been considered by the general form which is

$$2I^- + h\gamma \rightarrow I_2 \ ,$$

and the generation rate equation of I_2 species was modeled on

$$\frac{d[I_2]}{dt} = k[I^-][H^+]^nD - k'[I_2] \ ,$$

which the values of k, k' and n were proposed in IMPAIR and IODE as shown in Table IV [2].

Table IV: k, k', and n values [2]

k[H$^+$]^n Unit used for D	IMPAIR kGy/h	IODE Gy/s
n	0.1	0.5
k	4×10^{-6}	1.3×10^{-3}
k$'$	1.0×10^{-15}	2.0×10^{-5}

However, the second equation is only significant if the concentration of I^- is higher than 10^{-4} M. For a higher iodide concentration ($>10^{-3}$M), the iodide concentration is overestimated in these codes. To overcome this limitation, a new correlation for a high I^- concentration in a wide range of pH was suggested by considering the formation and reduction rate of I_3^- after irradiating the I^- solution.
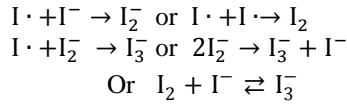
3. Modeling Method

3.1. Modeling Method

Under radiation, water in the solution will form many molecular and radical products, which are usually represented by

$$H_2O \rightsquigarrow H_2O_2, H, H_2, OH, e_{aq}^-, HO_2$$
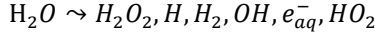
The principal oxidizing species in water are $OH\cdot$ and the secondary radiolysis products are H_2O_2, HO_2, etc. [4]. The primary species can react with the initial molecules through several reactions and produce a secondary species that may take part in further reactions. The primary oxidation mechanisms of I^- to I_3^- with radiolysis products are well known [3]:

$$I^- + OH\cdot \rightarrow HOI^-$$
$$HOI^- \rightarrow I\cdot + HO^-$$
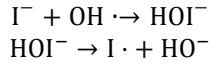
The $I\cdot$ radicals combine ultimately to form either I_2 or I_3^-, and the reaction depends on the $[I^-]$ concentration and pH value in an aqueous solution.

$$I\cdot + I^- \rightarrow I_2^- \text{ or } I\cdot + I\cdot \rightarrow I_2$$
$$I\cdot + I_2^- \rightarrow I_3^- \text{ or } 2I_2^- \rightarrow I_3^- + I^-$$
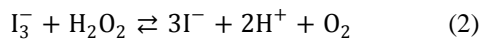$$\text{Or } I_2 + I^- \rightleftarrows I_3^-$$

In a high concentration of I^- and an acidic solution, the formation of I_3^- is proportional to the concentration of I^- and $HO\cdot$, as shown in equation (1):

$$3I^- + 2OH\cdot + 2H^+ \rightarrow I_3^- + 2H_2O \qquad (1a)$$
$$3I^- + 2H_2O_2 + 2H^+ \rightarrow I_3^- + 2H_2O \qquad (1b)$$
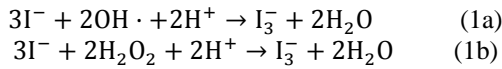
Two reactions enable the modeling of radiolysis in the code:

$$3\,I^- + h\vartheta \rightarrow I_3^-$$
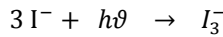
The second reaction is the reduction of I_3^- (or I_2) with H_2O_2 to I^- in an alkaline solution [2]:

$$I_3^- + H_2O_2 \rightleftarrows 3I^- + 2H^+ + O_2 \qquad (2)$$

Ashmore et al. [5] reported that, although hydrogen peroxide is reactant, the oxidation rate decreases as its concentration increases, and it is very effective to eliminate volatile iodine (I_2 reacts with H_2O_2). However, this reaction only occurs at a high pH, which is based on an electrochemistry standpoint of the change in Gibbs free energy of the reaction. For example, the pH reaches around 5.4 if the $[I^-]$ is changed to 0.5mM [3].

To model the radiolysis of an iodine species in an aqueous phase, consecutive first-order irreversible reactions are considered, which are represented by a reaction network with rate constants of k_1 and k_2, as shown in equation (3):

$$I^- \rightarrow I_3^-(I_2) \rightarrow I^- \qquad (3)$$
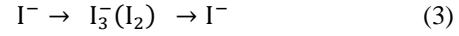
The change in concentration of each species depends on the time, and the rate law can be applied to obtain these simultaneous differential equations:

$$\frac{d[I^-]}{dt} = -k_1[I^-][H^+]^n D \qquad (4a)$$

$$\frac{d[I_3^-]}{dt} = k_1[I^-][H^+]^n D - k_2[I_3^-][H_2O_2]D \quad (4b)$$

At $t = 0.0$, only I^- is presented in the solution, and thus

$$[I^-]_o = [I^-], [I_3^-]_o = 0 \qquad (5a)$$

, where the boundary condition is

$$[I^-]_o = [I^-] + 3[I_3^-] \quad . \qquad (5b)$$

3.2. Determination of reaction rate constants

To determine the reaction rate constants, k_1, k_2, in equation (4), and the parameter of pH dependence, n, the experiment rate constant K_{exp} must be identified. We define an entirely experimental parameter, K_{exp}, which is a function of all $[I_3^-]$ concentration changes during the irradiation time, by equation (6) [6]:

$$K_{exp} = (d[I_3^-]/dt)/[I_3^-] \qquad (6)$$

To obtain the numerical derivative of $[I_3^-]$ using experimental data, two equally spaced points are taken, and the derivative at the central point $[I_3^-]_i$ is then calculated through equation (7).

$$\left(\frac{dI_3}{dt}\right)_i = \frac{[I_3]_{i+1} - [I_3]_{i-1}}{\Delta t} \qquad (7)$$

In equation (7), Δt is the time interval between two points.

From equations (6) and (7), we can obtain the reaction rate constants through an analysis of the experiment data.

3.3. Analysis of the experiment data

As we mentioned before, equation (2) is only active in a solution of higher than pH 5.4 with a high initial I^- concentration. Therefore, we consider two initial I^- concentrations of 2.0×10^{-5} and 5.0×10^{-4}M in all ranges of pH from 3.0 to 6.0.

Case 1: High iodide concentration in acidic solution

During several hours, the formation of tri-iodide ions in equation (1) may become important at a low pH.

Therefore, the modeling of the equation is written as

$$\frac{dI_3^-}{dt} = k_1[I^-][H^+]^n D = k_1([I_o^-] - 3.0[I_3^-])[H^+]^n D$$
$$= K'([I_o^-] - 3.0[I_3^-]) = K_{exp}[I_3^-] \qquad (8)$$

where

$$K' = k_1[H^+]^n D . \qquad (9)$$

Using the measured concentration of $[I_3^-]$ from the experiment, Jung et al. [3] estimated the value of k_1 to be $0.138h^{-1}$. Therefore, the values of K' and k_1 can be obtained. From equation (9), the pH dependence, n, is determined as 0.23 by least-squared-fitting method.

The general form of the differential equation can now be written in this case as

$$\frac{dI_3^-}{dt} = 0.138[I^-][H^+]^{0.23}D \qquad (10)$$

Case 2: High iodide concentration in alkaline solution

In a high initial iodide concentration solution, not only the oxidation reaction but also the reduction reaction of I_3^- should be considered because the high pH value was observed to be 5.92 after 4 h, and the oxidation reaction gradually stops at a pH of above 5.4 owing to H_2O_2 as a reductant. The change in concentrations of [I_3^-] thus depends on time as follows:

$$\frac{dI_3}{dt} = 0.138[I^-][H^+]^{0.23}D - k_2[I_3^-] \qquad (11)$$

$$k_2 = \left[\frac{dI_3}{dt}\right]_{cal} - \left[\frac{dI_3}{dt}\right]_{exp}$$

$\left[\frac{dI_3}{dt}\right]_{cal}$: calculated data from the equation (10)

$\left[\frac{dI_3}{dt}\right]_{exp}$: experimental data at pH>5.6

In equation (11), the k_2 value are obtained as 0.0283 by least-squared-fitting method based on the experimental data of I_3^- concentrations when pH is higher than 5.6.

Combining both cases, the reaction rate of iodide ions is finally modeled as equation (12).

$$\frac{dI_3}{dt} = 0.138[I^-][H^+]^{0.23}D - k_2[I_3^-] \quad (12)$$

$$\begin{cases} k_2 = 0.0 & 3.0 \leq pH \leq 5.6 \\ k_2 = 2.83.10^{-2} & 5.6 \leq pH \leq 6.0 \end{cases}$$

4. Comparisons with Experimental Data

From the above correlation in equation (12), the formation of I_3^- concentration under gamma irradiation as a function of irradiation time, gamma dose, and concentrations of NaI in the solutions was calculated and verified with the experiment data [3].

The initial conditions such as the dose rate, pH value, and initial concentration of [I⁻] shown in Table I were used to analyze the oxidation behavior of iodide ions under gamma irradiation conditions. The [H⁺] concentrations at each time step were interpolated using the measured pH values, as shown in Tables II and III, and the interpolation method was applied based on the known pH values. Fig. 5 shows that the calculated pHs are reasonably matched with the experiment data.

A code can be prepared using the C++ language to obtain the tri-iodide concentration change in NaI solution according to the irradiation time.
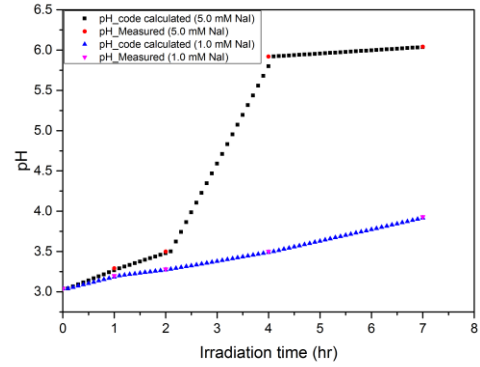
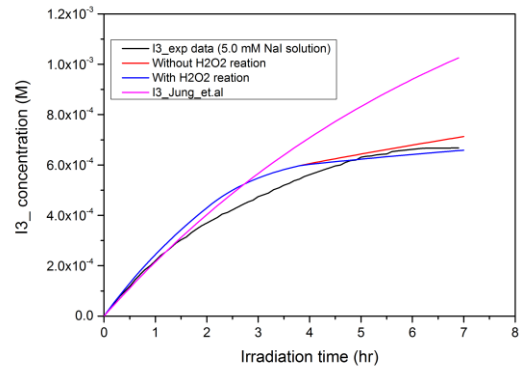Fig. 5. pH values in 1.0 and 5.0 mM NaI solution

Fig. 6. I_3^- concentration according to the irradiation time at 2.0 kGyh^{-1} in a 5.0 mM NaI solution

Figure 6 shows the formation of [I_3^-] concentration according to the irradiation time at 2.0 kGyh^{-1} in a 5.0 mM NaI solution. As shown in Fig.6, the formation of [I_3^-] concentrations can be compared with and without considering of the H_2O_2 reaction. In an initial 5.0mM

NaI solution, the pH was changed higher than 5.6 at 4 hour under 2.0 kGyh^{-1} gamma dose rate. For the 5.0 mM NaI solution as shown in Fig. 6, the formation of [I$_3^-$] concentration increases during the first several hours. However, the increasing rate of I$_3^-$ concentration decreases after 4 h. This is can be explained as the H+ consumed through the oxidation of iodide ion reactions, and thus the solution was then changed to a high pH. In this case, the oxidation reaction is somewhat of lesser importance, and the reduction reaction of I$_3^-$ by equation (12) is more important. Comparing the results from the experiment measurements with the calculated results from Jung *et al.* [3], the new reaction model in this paper is quite reasonable based on the measured data under the irradiation time.

Figure 7 shows the iodide oxidation behavior at various initial concentrations of NaI in solutions under a constant gamma dose of 2.0kGyh^{-1} during a 7 h irradiation time. As shown in Fig.7, the I$_3^-$ concentration also increases as the initial concentration of NaI increases. The radiolysis product (oxidizing hydroxyl) OH increases during the irradiation period, and H$^+$ and I$^-$ are consumed to generate I$_3^-$ in equation (10), and finally, the I$_3^-$ concentration and pH are increased. After 7 h, the I$_3^-$ concentration reaches a steady state because most of I$^-$ was consumed by iodide oxidation reactions in the case of an initial 1.0 mM NaI solution as shown in Fig. 7.

Figure 8 shows I$_3^-$ concentration according to the gamma dose rate in 1.0 and 5.0 mM NaI solution. As shown in Fig. 8, the I$_3^-$ concentration in the initial 1.0 and 5mM NaI soluion increases with an increase in dose rate when the irradiation time is a constant of 1 h. The values of the I$_2$ concentration in the solution are converted to into I$_3^-$ for an easy comparison in Fig. 8. As the gamma dose increases from 0.0 to 10.0 kGy, the concentration of I$_3^-$ increases and the pH in the solution also increases from 3.0 to 6.0. As shown in Fig. 8, the calculated concentration of I$_3^-$ agrees well with the measurement values from the experiment in 5.0mM NaI solution. However, the calculated concentration of I$_3^-$ are lower than the experimental one in 1.0mM NaI solution. That seems why not only I$_3^-$ but also I$_2$ concentration was included in the experimental data, but the correlation considered only I$_3^-$ concentration. Some I$_2$ molecules in 1.0mM NaI solution were observed by UV-VIS spectrum.

Figure 9 shows the I$_3^-$ concentration according to the irradiation time in a 5.0 mM NaI solution under x kGy h^{-1} for 1 h, and 2kGy h^{-1} for x h. As shown in Fig. 9, the dose rates were changed from 0 to 10 kGy.h^{-1} with a constant irradiation time of 1 h, and the irradiation times were changed with a constant gamma dose rate of 2.0 kGy h^{-1}. Even though the calculated I$_3^-$ concentrations at 0 to 10.0 kGy for 1 h dose rates are somewhat lower than at 2kGy h^{-1} for x h, the calculated results are reasonable when comparing Fig. 9 with Fig. 4.

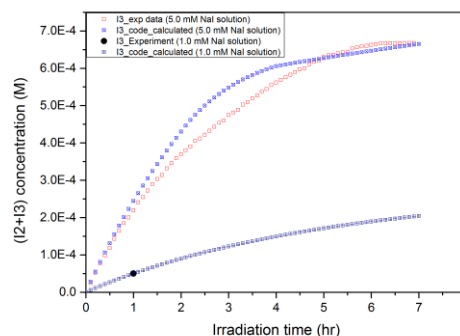

Fig. 7. I$_3^-$ concentration as a function of irradiation time in various NaI concentration solutions at a 2.0 kGyh^{-1} gamma dose rate
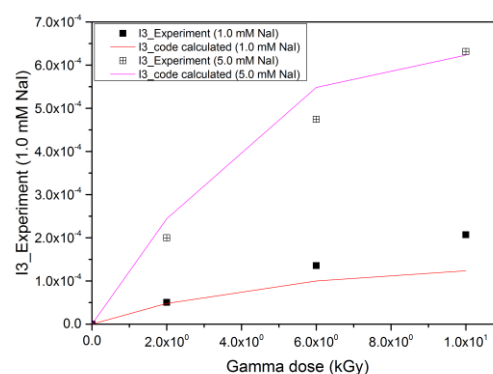

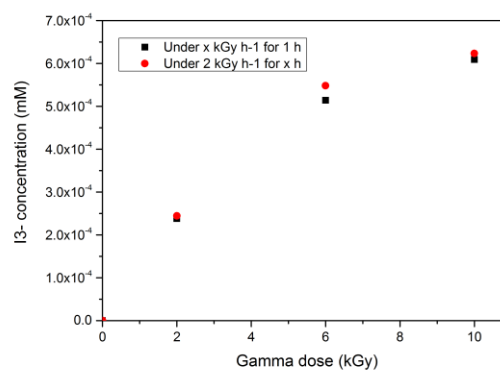Fig. 8. I$_3^-$ concentration according to the gamma dose rate in 1.0 and 5.0 mM NaI solution

Fig. 9. I$_3^-$ concentration according to irradiation time in 5.0 mM NaI solution under x kGy h^{-1} for 1 hour, and 2 kGy h^{-1} for x hours

5. Conclusion

A new correlation for the oxidation of iodide ions under gamma irradiation conditions was suggested. It was also verified using experiment data with the NaI solutions at an initial concentration of 10^{-4} to 10^{-5} M, pH value of 3.0 to 6.0, and gamma dose rates of 0.4 to 10.0 kGyh^{-1}, and irradiation time of 1 to 7 h. The predicted values based on the new correlation are quite reasonable when compared with the irradiation experiment data.

ACKNOWLEDGMENTS

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