

## Kinetic behaviors of $e_{aq}^-$ and $\bullet OH$ radical in water radiolysis

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### 1. Introduction

Under severe accident in nuclear power plants, radioiodine is one of the most hazardous fission products because it can be released as volatile species causing a significant harmful impact on people's health. Therefore, precise understanding of iodine behavior is an important factor for the safety assessment of nuclear reactor.

Iodine in the aqueous solution changes its volatile molecule through chemical complexation with free radicals which are formed in water radiolysis. In particular, aqueous electrons ( $e_{aq}^-$ ) and hydroxyl radicals ( $\bullet OH$ ) play an essential role in iodine behavior [1]. Aqueous electrons react with oxygen and thus produce  $\bullet O_2^-$  radical which is a strong reductant of molecular iodine. On the other hand, the rate of iodide oxidation depends on the concentration of  $\bullet OH$  that oxidize  $I^-$  to  $I_2$  which eventually combines to form  $I_2$  (volatile species).

Korea Institute of Nuclear Safety (KINS) has been developing the Radio-Active Iodine chemistry Model (RAIM) which simulates iodine behavior in the containment [2]. However, it does not reflect the water radiolysis reaction in detail that has been just applied based on the IMOD (Iodine Model for containment codes) methodology. This paper presents the methods to compute the concentration of water radiolysis products and suggests the application of computing methods by comprehending the behavior of  $e_{aq}^-$  and  $\bullet OH$ .

### 2. Methods

#### 2.1 Kinetic reaction of water radiolysis

Kinetic reactions of free radicals by water radiolysis can be divided into two parts. The first part is water-radiolysis production. By irradiation in water, radicals such as  $e^-$ ,  $\bullet H$ ,  $\bullet OH$ ,  $H_2$ ,  $H_2O_2$  and  $H^+$  are produced within  $10^{-7}$  sec. The production rate is determined according to the product of G value and dose rate, where the G value is the number of molecules formed per 100 eV. Buxton et al. [3] reported the G-value at gamma radiation through the experiments (Table I).

Table I. G-value of radicals by water radiolysis [3]

Species	$e^-$	$\bullet H$	$\bullet OH$	$H_2$	$H_2O_2$	$H^+$
G-value (No. of molecule 100 eV)	2.6	0.6	2.7	0.45	0.7	2.6

The second part is related to subsequent reactions occurred by water radiolysis products. Reactants consist of water radiolysis products ( $e^-$ ,  $\bullet H$ ,  $\bullet OH$ ,  $H_2$ ,  $H_2O_2$ ,  $H^+$ ),

secondary products ( $\bullet O_2^-$ ,  $\bullet O$ ,  $\bullet HO_2$ ,  $HO_2^-$ ), and substances ( $H^+$ ,  $OH^-$ ,  $O_2$ ) dissolved in the existing. Wren et al. [4] compiled the kinetic reactions and the rate constants of water radiolysis (Table II).

Table II. Reactions and rate constants (25°C and 1atm) [4]

#	Kinetic reaction	Rate constant (L mol <sup>-1</sup> s <sup>-1</sup> )
1	$e^- + H_2O \rightarrow \bullet H + OH^-$	$1.9 \times 10$
2	$2e^- + 2H_2O \rightarrow 2OH^- + H_2$	$5.5 \times 10^9$
3	$e^- + \bullet H + H_2O \rightarrow OH^- + H_2$	$2.5 \times 10^{10}$
4	$e^- + H^+ \rightarrow \bullet H$	$2.3 \times 10^{10}$
5	$e^- + \bullet OH \rightarrow OH^-$	$3.0 \times 10^{10}$
6	$e^- + O_2 \rightarrow \bullet O_2^-$	$1.8 \times 10^{10}$
7	$e^- + H_2O_2 \rightarrow \bullet OH + OH^-$	$1.4 \times 10^{10}$
8	$e^- + \bullet O_2^- + H_2O \rightarrow OH^- + HO_2^-$	$1.3 \times 10^{10}$
9	$e^- + HO_2^- \rightarrow \bullet O^- + OH^-$	$3.5 \times 10^9$
10	$e^- + \bullet O^- + H_2O \rightarrow 2OH^-$	$2.2 \times 10^{10}$
11	$\bullet H + \bullet OH \rightarrow H_2O$	$7.0 \times 10^9$
12	$\bullet H + \bullet H \rightarrow H_2$	$7.75 \times 10^9$
13	$\bullet H + O_2 \rightarrow \bullet HO_2$	$2.1 \times 10^{10}$
14	$\bullet H + \bullet HO_2 \rightarrow H_2O_2$	$1.0 \times 10^9$
15	$\bullet H + H_2O_2 \rightarrow \bullet OH + H_2O$	$9.0 \times 10^7$
16	$\bullet H + \bullet O_2^- \rightarrow HO_2^-$	$2.0 \times 10^{10}$
17	$\bullet OH + \bullet O_2^- \rightarrow O_2 + OH^-$	$8.0 \times 10^9$
18	$2\bullet OH \rightarrow H_2O_2$	$5.5 \times 10^9$
19	$\bullet OH + \bullet O_2^- \rightarrow \bullet HO_2 + OH^-$	$7.5 \times 10^9$
20	$\bullet OH + H_2O_2 \rightarrow \bullet HO_2 + H_2O$	$4.2 \times 10^7$
21	$\bullet OH + H_2 \rightarrow \bullet H + H_2O$	$4.2 \times 10^7$
22	$\bullet OH + \bullet HO_2 \rightarrow O_2 + H_2O$	$6.0 \times 10^9$
23	$\bullet O^- + \bullet OH \rightarrow HO_2^-$	$2.0 \times 10^{10}$
24	$H_2O_2 + \bullet O^- \rightarrow \bullet O_2^- + H_2O$	$2.0 \times 10^8$
25	$H_2 + \bullet O^- \rightarrow \bullet H + OH^-$	$8.0 \times 10^7$
26	$\bullet O^- + HO_2^- \rightarrow OH^- + \bullet O_2^-$	$4.0 \times 10^8$
27	$\bullet O^- + O_2 \rightarrow \bullet O$	$3.0 \times 10^9$
28	$\bullet O_3^- \rightarrow \bullet O^- + O_2$	$3.0 \times 10^2$
29	$\bullet O_3^- + H_2O_2 \rightarrow \bullet O_2^- + O_2 + H_2O$	$1.6 \times 10^6$
30	$\bullet O_3^- + HO_2^- \rightarrow \bullet O_2^- + O_2 + OH^-$	$8.9 \times 10^5$
31	$\bullet O_3^- + H_2 \rightarrow O_2 + \bullet H + OH^-$	$2.5 \times 10^5$
32	$\bullet HO_2 + \bullet O_2^- \rightarrow O_2 + \bullet HO_2$	$8.9 \times 10^7$
33	$\bullet HO_2 + \bullet HO_2 \rightarrow H_2O_2 + O_2$	$2.0 \times 10^6$

34	$\text{H}_2\text{O}_2 \rightarrow \text{H}^\cdot + \text{HO}_2^\cdot$	$3.56 \times 10^{-2}$
35	$\text{H}^\cdot + \text{HO}_2^\cdot \rightarrow \text{H}_2\text{O}_2$	$2.0 \times 10^{10}$
36	$\cdot\text{HO}_2 \rightarrow \text{H}^\cdot + \cdot\text{O}_2$	$8.0 \times 10^5$
37	$\text{H}^\cdot + \cdot\text{O}_2 \rightarrow \cdot\text{HO}_2$	$4.5 \times 10^{10}$
38	$\cdot\text{OH} + \text{OH}^- \rightarrow \cdot\text{O}^- + \text{H}_2\text{O}$	$1.2 \times 10^{10}$
39	$\cdot\text{O}^- + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{OH}^-$	$1.7 \times 10^6$
40	$\text{H}_2\text{O} \rightarrow \text{H}^\cdot + \text{OH}^\cdot$	$1.43 \times 10^{11}$

## 2.2 Methods computing concentration rate of radicals

The concentration of radicals regarding various kinetic reactions (Table I and II) were calculated using a MATLAB code. The code algorithm is shown in Fig. 1. The initial condition was controlled as the acidity of water was maintained at pH 7, the  $\text{O}_2$  concentration was  $2.5 \times 10^{-4}$  mol/L, and dose rate was  $2 \text{ kGy} \cdot \text{h}^{-1}$ . The initial concentration of elements except  $\text{H}^\cdot$ ,  $\text{OH}^\cdot$ , and  $\text{O}_2$  was 0 mol/L. The initial parameters utilized in the present paper has been employed as same as the experimental data from Wren et al. [1] due to the validation of code. And the experiment was conducted under representative conditions.

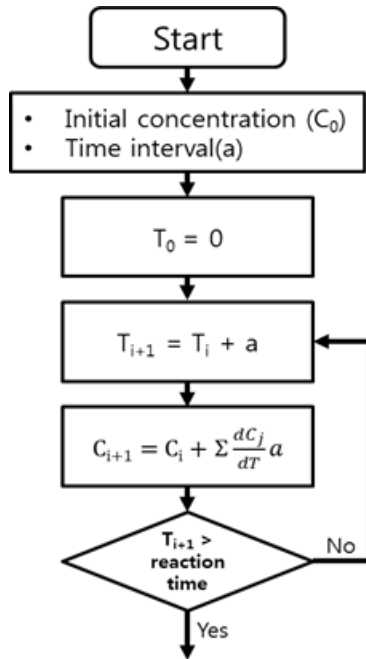


Fig. 1. Code algorithm for computing the concentration of water radiolysis products

The concentration variation of an element in a step was the accumulation of multiplication with kinetic reaction and interval time (a). The sum of concentration variation and precursor concentration became the concentration of elements in the step. For example, when the reaction occurred according to the chemical equation (1) (Table I), the variation of electrons could be computed in this way:

$$-\frac{d[e^-]}{dt} = \frac{d[\text{H}^\cdot]}{dt} = \frac{d[\text{OH}^\cdot]}{dt} = k_1[e^-] \quad (41)$$

$$\frac{d[e^-]}{dt} \cdot a = k_1[e^-] \cdot a = d[e^-] \quad (42)$$

$$[e^-]_{i+1} = [e^-]_i + \sum d[e^-] \quad (43)$$

For the case of computational time interval larger than  $10^{-7}$  sec, the uncertainty of the final result diverges with increasing time interval. However, with time interval shorter than  $10^{-7}$  sec, almost identical results were calculated at steady state regardless of time interval (Fig. 2.), except for the trivial differences in the beginning of reactions. Therefore, the time interval was controlled as  $10^{-7}$  sec.

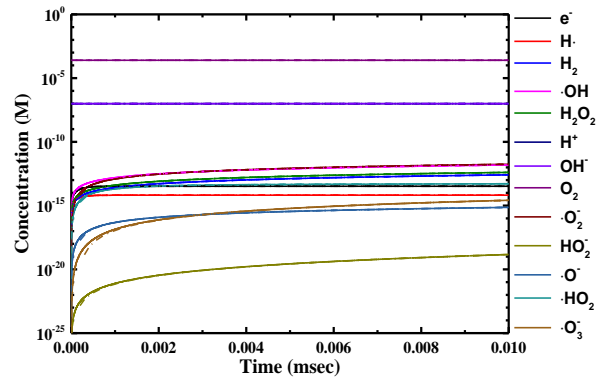


Fig. 2. Concentration of radicals at various time interval (—:  $10^{-10}$ , ---:  $10^{-9}$ , .....:  $10^{-8}$ , -.-.-:  $10^{-7}$ )

## 3. Results and Discussion

### 3.1 Behavior of water radiolysis products

In order to validate the developed code, the temporal behavior of water radiolysis products was compared with experimental data [1] which indicated the concentration of  $\text{H}_2\text{O}_2$  and  $e^-$  at steady state. The products reached the steady state after 1 hour reaction, and the results corresponded to the experiment data (Fig. 3). The concentration of  $\text{H}_2\text{O}_2$  and  $e^-$  from the computational result were  $1.1 \times 10^{-4}$  mol/L and  $8.2 \times 10^{-14}$  mol/L which were in the same order of experimental results ( $1.4 \times 10^{-4}$  mol/L and  $5.0 \times 10^{-14}$  mol/L). As a consequence, the calculation code can be reliable for the analysis of water radiolysis products.

As shown in Fig. 3, the concentration of  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  were dominant in the products so that they would be principal to impact other radiolysis products. On the other hand,  $\cdot\text{O}$ ,  $e^-$ , and  $\cdot\text{H}$  whose concentration were less than  $10^{-12}$  mol/L considered negligible. Following the results, kinetic reaction could be comprehended.

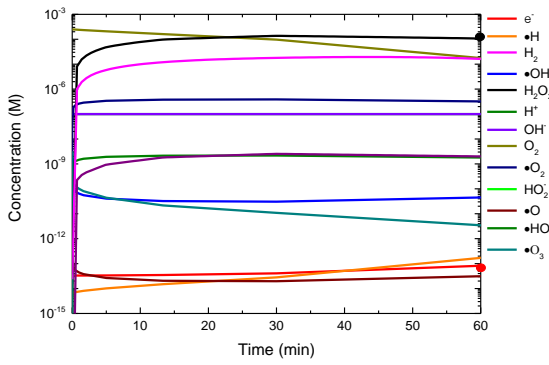
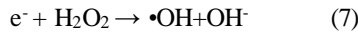
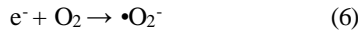


Fig. 3. Concentration of water radiolysis products (The line represents calculation results and the solid symbols denote the experimental results)

### 3.2 Aqueous electrons

To apply the result to the RAIM code, understanding the contribution of kinetic reaction is important. Fig. 4 shows the contribution of kinetic reaction to aqueous electrons. Aqueous electrons were only produced by water radiolysis directly. According to the equation (6) and (7), the concentration of solvated electrons, predominantly decreased.



Large amount of  $O_2$  and  $H_2O_2$  existed in water, as shown in Fig. 3, and both influenced the consumption rate of solvated electrons. The contribution ratios of  $O_2$  and  $H_2O_2$  were 82 % and 17 %, respectively (Fig. 5). Consequently, the concentration of electrons can be expressed by the above three kinetic equation in RAIM.

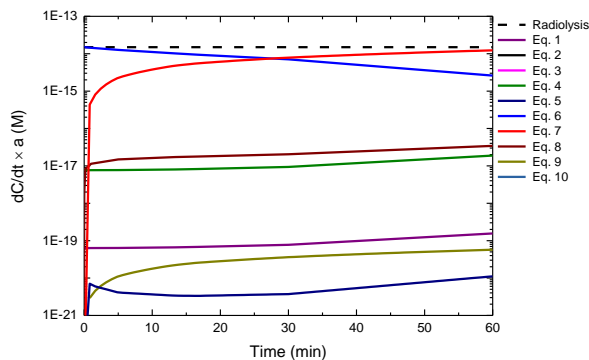


Fig. 4. Contribution of kinetic reaction of electron concentration [ $e^-$ ] (The dashed line represents production rate and solid line denotes consumption rate.)

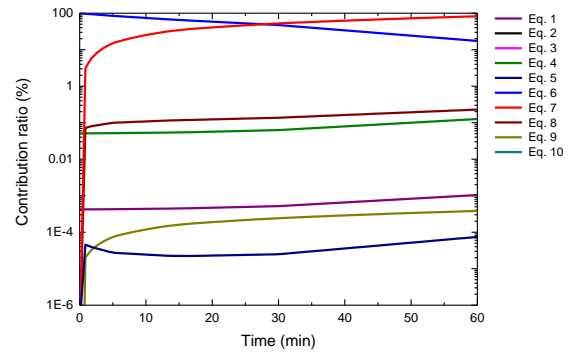


Fig. 5. Contribution ratio of various kinetic reactions in  $e^-$  consumption

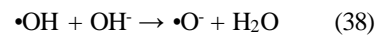
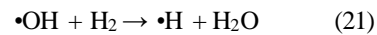
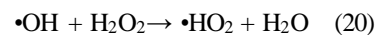
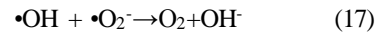
### 3.3 Hydroxyl radicals

As shown in Fig. 6, various kinetic reactions controlled the concentration of hydroxyl radical. In case of production rate, the primary reactions were direct water radiolysis and reactions as expressed in equations (7) and (15).



Sum of these reaction occupied 99 % in the production reaction for  $\bullet OH$  radicals (Fig. 7). The equation (7) affected not only aqueous electrons but also hydroxyl radicals. In addition,  $H_2O_2$  reacted in both reaction equations (7) and (15) were important factor for the production rate of  $\bullet OH$  radicals.

On the other hand, the consumption rate of hydroxyl radicals was related to the ten different kinetic reactions. The four kinetic reactions (17), (20), (21) and (38) mainly influenced the consumption rate.



Elements to decrease hydroxyl radical were mainly  $\bullet O_2^-$ ,  $H_2O_2$ ,  $H_2$  and  $OH^-$  in the order. All four elements were more than  $10^{-9}$  mol/L, and particularly the rate constant of equations (17) and (38) is over  $10^9$  L/mol/s. The contribution ratio of equations (20), (17), (38), and (21) were 39, 34, 16, and 9 %, respectively (Fig. 8). Therefore, the four kinetic reactions controlled the consumption rate of hydroxyl radicals in water radiolysis.

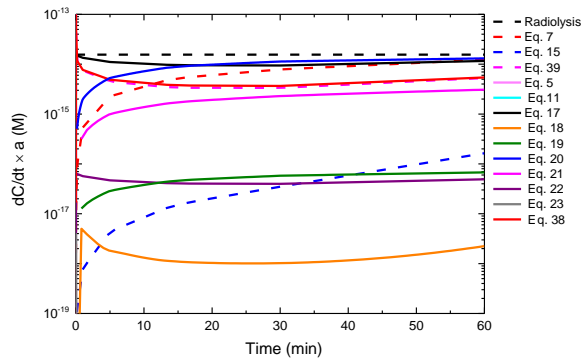


Fig. 6. Contribution of kinetic reaction of hydroxyl radical concentration [ $\bullet\text{OH}$ ] (The dashed line represents production rate and solid line denotes consumption rate.)

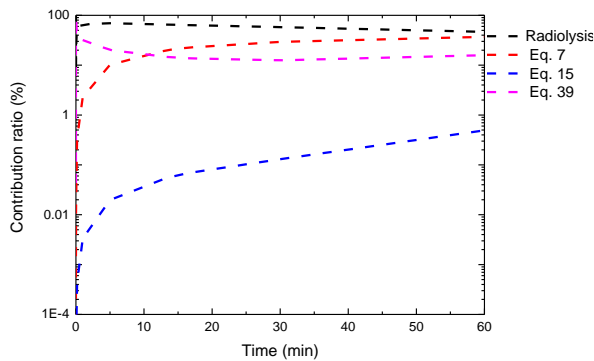


Fig. 7. Contribution ratios of various kinetic reactions in the  $\bullet\text{OH}$  production

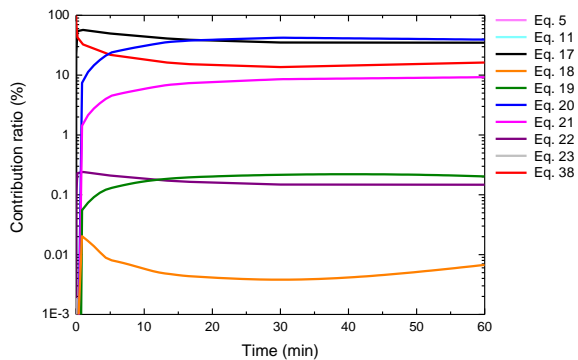


Fig. 8. Contribution ratio of various kinetic reaction in the  $\bullet\text{OH}$  consumption

#### 4. Conclusions

The calculation code to compute the concentration of water radiolysis products has been developed and validated. Based on the code, the reaction kinetics of aqueous electrons and hydroxyl radicals was investigated.

The contribution ratios of kinetic reactions calculated in the present work for various radical production reactions revealed the origination of radicals and provided information about major kinetic reactions in water radiolysis. Therefore, the calculation code developed in the present work can be applied to RAIM for the simplified calculation of water radiolysis products.

#### ACKNOWLEDGMENT

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