

## Progress modelling of aqueous electrons and hydroxyl radicals in RAIM code

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### 1. Introduction

An accurate assessment regarding release of radioactive iodine in the environment under severe accidents of nuclear power plants is important to realistically evaluate the consequence of such accidents. Therefore, some research groups have developed the codes which simulate the iodine behavior in the containment vessel [1, 2]. Korea Institute of Nuclear Safety also has been developing the code called Radio-Active Iodine chemistry Model (RAIM).

The recent study [3] indicated that the RAIM had the potential for improvement of simulating the iodine behavior influenced by water radiolysis products such as aqueous electrons and hydroxyl radicals. In the existing RAIM modelling, it was considered that aqueous electrons only interacted with oxygen as a consumption reaction, but the reaction with hydrogen peroxide also could be major contributor to the iodine behavior as well as the consumption reaction of aqueous electrons. In case of hydroxyl radicals, RAIM took no notice of the pH impact. In other words, it dealt with the consumption reaction constants but not as a variable of pH.

In this communication, the procedures to develop the model related to aqueous electrons and hydroxyl radicals in RAIM will be addressed. And the upgraded RAIM (RAIM-1, 2, 3) codes were applied to OECD-BIP P10T2 test which showed the effect of pH on the iodine behavior [4] and compared with the existing RAIM1.8.3 code.

### 2. Methods

#### 2.1 Progress of aqueous electrons model

The calculation code which simulated the concentration of water radiolysis products was developed in the previous research [3]. The calculation was based on the G-value (Table 1), kinetic reactions and rate constants (Table 2) relating to water radiolysis in a pure water. In detail, the concentrations of species was obtained through accumulation of production rates and consumption rates which were multiplications of the concentrations, rate constants of related kinetic reaction and interval time (a) [3]. Through the calculation code, the concentrations of water radiolysis product were determined in the specific condition and the effect of each reactions could be understood.

Table 1. G-value of radicals by water radiolysis [5]

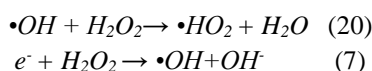
| Species                                  | e <sup>-</sup> | •H  | •OH | H <sub>2</sub> | H <sub>2</sub> O <sub>2</sub> | H <sup>+</sup> |
|--|----------------|-----|-----|----------------|-------------------------------|----------------|
| G-value<br>(No. of molecule)<br>(100 eV) | 2.6            | 0.6 | 2.7 | 0.45           | 0.7                           | 2.6            |

Table 2. Reactions and rate constants (25°C and 1atm) [6]

| #  | Kinetic reaction  | Rate constant<br>(L mol <sup>-1</sup> s <sup>-1</sup> ) |
|----|---|---|
| 1  | e <sup>-</sup> +H <sub>2</sub> O→•H+OH <sup>-</sup>   | 1.9 × 10  |
| 2  | 2e <sup>-</sup> +2H <sub>2</sub> O→2OH <sup>-</sup> +H <sub>2</sub>   | 5.5 × 10 <sup>9</sup>                                   |
| 3  | e <sup>-</sup> +•H+H <sub>2</sub> O→OH <sup>-</sup> +H <sub>2</sub>   | 2.5 × 10 <sup>10</sup>                                  |
| 4  | e <sup>-</sup> +H <sup>+</sup> →•H  | 2.3 × 10 <sup>10</sup>                                  |
| 5  | e <sup>-</sup> +•OH→OH <sup>-</sup>   | 3.0 × 10 <sup>10</sup>                                  |
| 6  | e <sup>-</sup> +O <sub>2</sub> →•O <sub>2</sub> <sup>-</sup>  | 1.8 × 10 <sup>10</sup>                                  |
| 7  | e <sup>-</sup> +H <sub>2</sub> O <sub>2</sub> →•OH+OH <sup>-</sup>  | 1.4 × 10 <sup>10</sup>                                  |
| 8  | e <sup>-</sup> +•O <sub>2</sub> <sup>-</sup> +H <sub>2</sub> O→OH <sup>-</sup> +HO <sub>2</sub> <sup>-</sup>                | 1.3 × 10 <sup>10</sup>                                  |
| 9  | e <sup>-</sup> +HO <sub>2</sub> <sup>-</sup> →•O <sup>-</sup> +OH <sup>-</sup>  | 3.5 × 10 <sup>9</sup>                                   |
| 10 | e <sup>-</sup> +•O <sup>-</sup> +H <sub>2</sub> O→2OH <sup>-</sup>  | 2.2 × 10 <sup>10</sup>                                  |
| 11 | •H+•OH→H <sub>2</sub> O   | 7.0 × 10 <sup>9</sup>                                   |
| 12 | •H+•H→H <sub>2</sub>  | 7.75 × 10 <sup>9</sup>                                  |
| 13 | •H+O <sub>2</sub> →•HO <sub>2</sub>   | 2.1 × 10 <sup>10</sup>                                  |
| 14 | •H+•HO <sub>2</sub> →H <sub>2</sub> O <sub>2</sub>  | 1.0 × 10 <sup>10</sup>                                  |
| 15 | •H+H <sub>2</sub> O <sub>2</sub> →•OH+H <sub>2</sub> O  | 9.0 × 10 <sup>7</sup>                                   |
| 16 | •H+•O <sub>2</sub> <sup>-</sup> →HO <sub>2</sub> <sup>-</sup>   | 2.0 × 10 <sup>10</sup>                                  |
| 17 | •OH+•O <sub>2</sub> <sup>-</sup> →O <sub>2</sub> +OH <sup>-</sup>   | 8.0 × 10 <sup>9</sup>                                   |
| 18 | 2•OH→H <sub>2</sub> O <sub>2</sub>  | 5.5 × 10 <sup>9</sup>                                   |
| 19 | •OH+•O <sub>2</sub> <sup>-</sup> →•HO <sub>2</sub> +OH <sup>-</sup>   | 7.5 × 10 <sup>9</sup>                                   |
| 20 | •OH+H <sub>2</sub> O <sub>2</sub> →•HO <sub>2</sub> +H <sub>2</sub> O   | 4.2 × 10 <sup>7</sup>                                   |
| 21 | •OH + H <sub>2</sub> →•H+H <sub>2</sub> O   | 4.2 × 10 <sup>7</sup>                                   |
| 22 | •OH+•HO <sub>2</sub> →O <sub>2</sub> +H <sub>2</sub> O  | 6.0 × 10 <sup>9</sup>                                   |
| 23 | •O <sup>-</sup> +•OH→HO <sub>2</sub> <sup>-</sup>   | 2.0 × 10 <sup>10</sup>                                  |
| 24 | H <sub>2</sub> O <sub>2</sub> +•O <sup>-</sup> →•O <sub>2</sub> <sup>-</sup> +H <sub>2</sub> O                              | 2.0 × 10 <sup>8</sup>                                   |
| 25 | H <sub>2</sub> +•O <sup>-</sup> →•H+OH <sup>-</sup>   | 8.0 × 10 <sup>7</sup>                                   |
| 26 | •O <sup>-</sup> +HO <sub>2</sub> <sup>-</sup> →OH <sup>-</sup> +•O <sub>2</sub> <sup>-</sup>                                | 4.0 × 10 <sup>8</sup>                                   |
| 27 | •O <sup>-</sup> +O <sub>2</sub> →•O <sub>3</sub> <sup>-</sup>   | 3.0 × 10 <sup>9</sup>                                   |
| 28 | •O <sub>3</sub> <sup>-</sup> →•O <sup>-</sup> +O <sub>2</sub>   | 3.0 × 10 <sup>2</sup>                                   |
| 29 | •O <sub>3</sub> <sup>-</sup> +H <sub>2</sub> O <sub>2</sub> →•O <sub>2</sub> <sup>-</sup> +O <sub>2</sub> +H <sub>2</sub> O | 1.6 × 10 <sup>6</sup>                                   |
| 30 | •O <sub>3</sub> <sup>-</sup> +HO <sub>2</sub> <sup>-</sup> →•O <sub>2</sub> <sup>-</sup> +O <sub>2</sub> +OH <sup>-</sup>   | 8.9 × 10 <sup>5</sup>                                   |
| 31 | •O <sub>3</sub> <sup>-</sup> +H <sub>2</sub> →O <sub>2</sub> +•H+OH <sup>-</sup>  | 2.5 × 10 <sup>5</sup>                                   |
| 32 | •HO <sub>2</sub> +•O <sub>2</sub> <sup>-</sup> →O <sub>2</sub> +HO <sub>2</sub> <sup>-</sup>                                | 8.9 × 10 <sup>7</sup>                                   |
| 33 | •HO <sub>2</sub> +•HO <sub>2</sub> →H <sub>2</sub> O <sub>2</sub> +O <sub>2</sub>   | 2.0 × 10 <sup>6</sup>                                   |
| 34 | H <sub>2</sub> O <sub>2</sub> →H <sup>+</sup> +HO <sub>2</sub> <sup>-</sup>   | 3.56 × 10 <sup>-2</sup>                                 |
| 35 | H <sup>+</sup> +HO <sub>2</sub> <sup>-</sup> →H <sub>2</sub> O <sub>2</sub>   | 2.0 × 10 <sup>10</sup>                                  |
| 36 | •HO <sub>2</sub> →H <sup>+</sup> +•O <sub>2</sub> <sup>-</sup>  | 8.0 × 10 <sup>5</sup>                                   |
| 37 | H <sup>+</sup> +•O <sub>2</sub> <sup>-</sup> →•HO <sub>2</sub>  | 4.5 × 10 <sup>10</sup>                                  |

|    |   |                       |
|----|---|-----------------------|
| 38 | $\bullet\text{OH} + \text{OH}^- \rightarrow \bullet\text{O}^- + \text{H}_2\text{O}$ | $1.2 \times 10^{10}$  |
| 39 | $\bullet\text{O}^- + \text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{OH}^-$ | $1.7 \times 10^6$     |
| 40 | $\text{H}_2\text{O} \rightarrow \text{H}^\bullet + \text{OH}^\bullet$               | $1.43 \times 10^{11}$ |

Using the same calculation code, the key kinetic reactions to determine the concentration of hydrogen peroxide which secondly influences the hydroxyl radicals were selected. Fig. 1 shows that each contribution of kinetic reactions for hydrogen peroxide and the main reactions were eq. 34 and 35. However, these two reactions were excluded from main reactions because the amount of two reactions were same and effect of each reaction canceled each other out. Except eq. 34 and 35, direct production reaction by water radiolysis was dominant. As regards consumption reactions, eq. 20 and 7 played important roles as ratios of effect are 51% and 48%, respectively (Fig. 2).



The two consumption reactions and radiolysis productions were utilized as the model to determine the concentration of hydrogen peroxide. And the variable of hydrogen peroxide was included in consumption reactions of aqueous electrons. In other words, the RAIM including the hydrogen peroxide model was developed and called as RAIM-1.

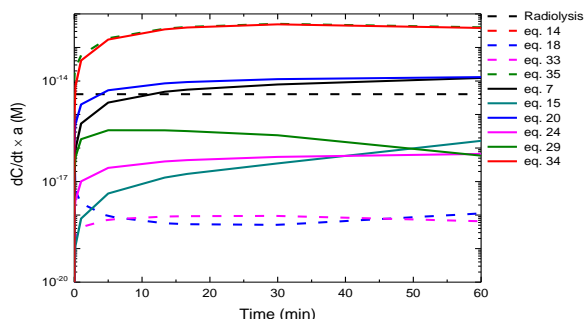


Fig. 1. Contribution of kinetic reaction of hydrogen peroxide (The dashed line represents production rate and solid line denotes consumption rate.)

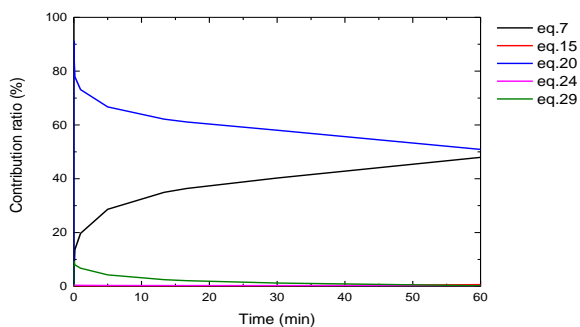
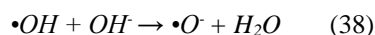
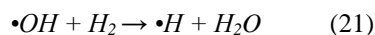
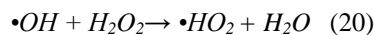
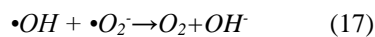


Fig. 2. Contribution ratio of various kinetic reactions in hydrogen peroxide consumption

## 2.2 Progress of hydroxyl radicals model

Various reactions such as eq. 17, 20, 21 and 38 influence consumption of hydroxyl radicals at high rate of contribution. Therefore, RAIM facilitated the sum of all reduction rate for consumption constant of hydroxyl radicals.



The total of reduction rate in various pH (4, 5, 6, 7, 8, 9 and 10) was calculated by the calculation code. Fig. 3 shows that the consumption constants of hydroxyl radicals were changed by pH condition and reached the steady state after nearly 30 minutes. And we could find the fit equation in accordance with the steady state constant which had the form of  $\exp(a+bx+cx^2)$ . Via fitting program ORIGIN9.1, the optimum numbers of a, b and c were figured out at 10.33, -1.64 and 0.2 in order and the coefficient of determination was 0.9999. This fitted equation reflecting the pH change applied on the RAIM-2 instead of the constant which was focused on the pH 7. In addition, RAIM-3 that contained both aqueous electron model and hydroxyl radical model was developed.

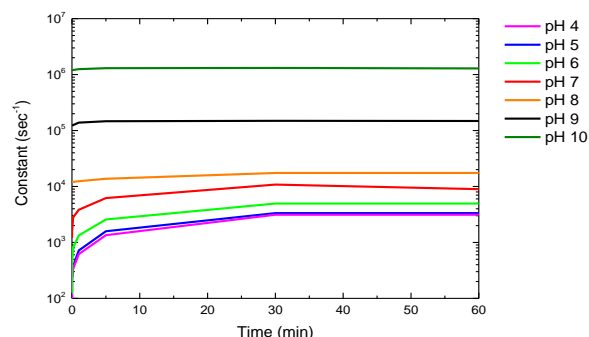


Fig. 3. Various hydroxyl peroxide consumption constant by change of pH

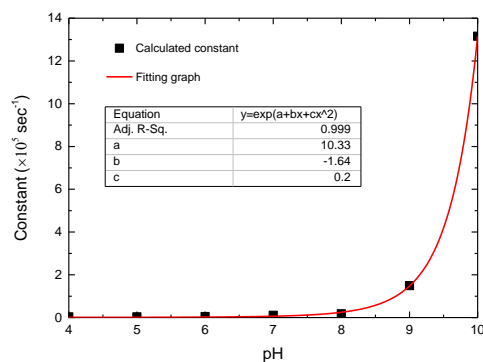


Fig. 4. Various hydroxyl peroxide consumption constant by change of pH and fitting equation

### 2.3 Application to P10T2 test

Using the experiment condition such as vessel volume, pH, temperature, initial concentration of iodine etc., RAIM code can simulate the iodine behavior of experiment test. For the simulation of RAIM codes, data of P10T2 test was employed. This experiment lasted for about 300 hours and, during the initial period, the pH was held at 10 for 45 hours. After that, the pH control was released and pH became about 7. The concentration of three species of iodine such as gaseous high volatile organic iodine (HVRI), gaseous low volatile organic iodine (LVRI) and inorganic gaseous iodine ( $I_2$ ) were checked on line. Results of experiment for three species were compared with those of existing code (RAIM1.8.3) and developed codes (RAIM-1, 2, 3) for evaluating an accuracy.

### 3. Results and Discussion

In principle, as pH increases, iodine becomes stable in form of anion so that the amount of gaseous iodine decreases. The experiment results of P10T2 also presented that when the pH is 10, the gaseous iodine is less than that at pH 7. Overall, the experiment and RAIM code results had the identical tendency (Fig.5, 6, 7).

Fig. 5, 6, and 7 indicate the pH effect to each concentration of HVRI, LVRI and  $I_2$  was obtained from the experiment and the codes which were existing RAIM and RAIM-1, 2, 3. At pH 7, the concentration of each iodine species ranged from  $10^{-9}$  M to  $10^{-10}$  M and all results from the experiment and the codes had the similar value. On the other hand, the results from the codes were larger than experiment results in one order at pH 10. It could mean that the existing constant focused on the condition of pH 7. Although the water radiolysis product model were improved to be variable of pH, the changes of result were not noticeable among the result of codes.

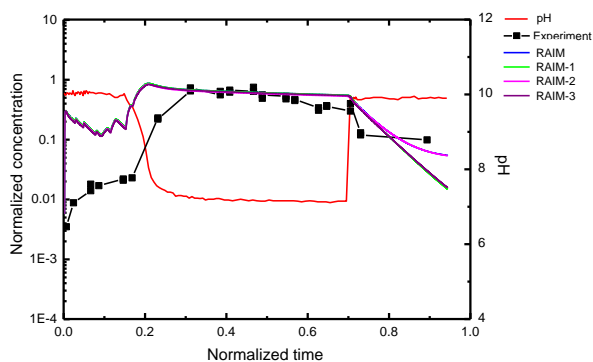


Fig. 5. HVRI concentration and its pH dependency

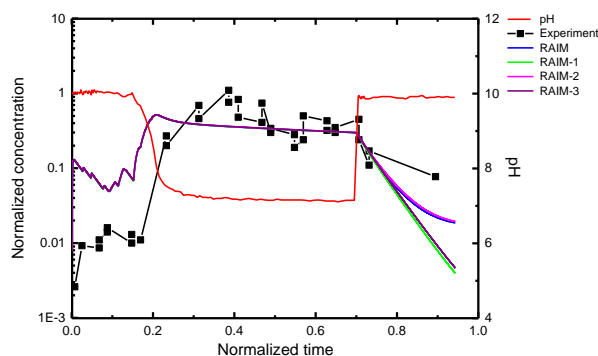


Fig. 6. LVRI concentration and its pH dependency

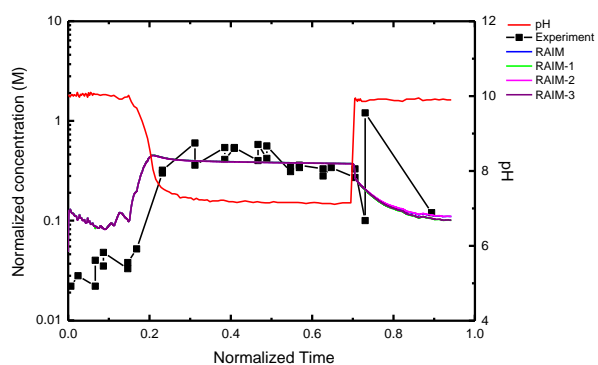


Fig. 7.  $I_2$  concentration and its pH dependency

For a comprehensive analysis, the difference between the experiment and the codes results were measured and averaged (Fig. 8, 9, 10). Over HVRI, the result of RAIM-1 was similar to the result of RAIM as shown in Fig. 8. Specifically, improvement of aqueous electron modelling could not in the least assist the enhancement of accuracy. In case of hydroxyl radicals, there were about 10% improvement in accuracy but the difference was same as about one order. Fig.9 shows that the upgrade for aqueous electrons increased the error in LVRI but integrated progress by aqueous electrons and hydroxyl radicals reduced the gap between the experiment and the codes as degree of 10%. Like HVRI, the accuracy of the codes for LVRI was not promoted. The differences between experiment and codes for  $I_2$  are the lowest among three iodine species as less than 100% (Fig. 10). However, the improvement through detailed modelling regarding aqueous electrons, hydroxyl radicals and both of them could not be discovered unlike other iodine species.

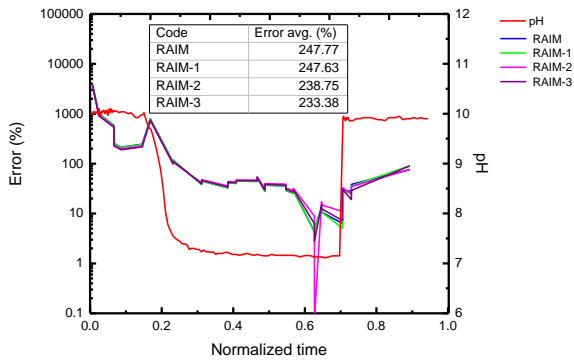


Fig. 8. Difference ratio between experiment result and RAIM results for HVRI concentration

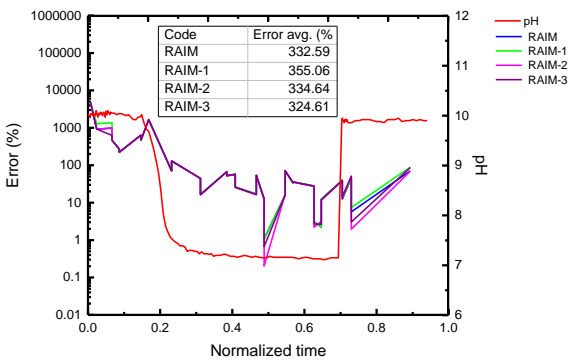


Fig. 9. Difference ratio between experiment result and RAIM results for LVRI concentration

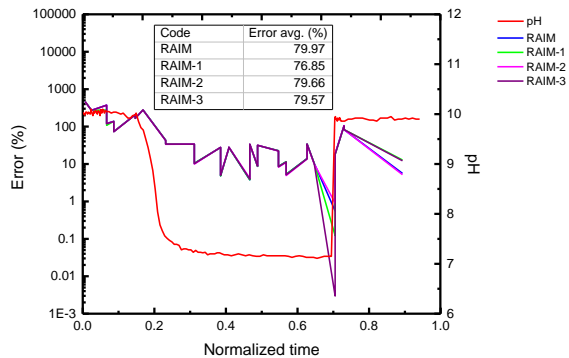


Fig. 10. Difference ratio between experiment result and RAIM results for I<sub>2</sub> concentration

#### 4. Conclusions

In this paper, the RAIM code was revised minutely with regards to aqueous electrons and hydroxyl radicals, and simulated the P10T2 test. Comparing with the existing RAIM, the improvement reduced the difference about 10%. However, the absolute difference values that is about one order at pH 10 could not be reduced by this approach. In other words, the impact of enhancement was insufficient. Therefore, instead of water radiolysis

products, other variables which may simulate the iodine behavior better at high pH need to be sought to improve RAIM.

#### ACKNOWLEDGMENT

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