

## Effect of Iodate Ion on the Iodine Retention in Pool under Irradiation

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### 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 severe accidents. Nuclear fuel has large inventories of various isotopes of iodine, and released iodine from the fuel makes complex chemical forms under 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 in the containment [1-3]. This will be dissolved in the water by the discharge of coolant and a safety spray system, and be re-vaporized into the iodine by the oxidization or radiolysis process.

There exist two basic approaches, that is, mechanistic and empirical models, to modeling on the generation of volatile iodine, I<sub>2</sub>, from non-volatile iodide, I<sup>-</sup>, in the aqueous phase by radiolytic oxidation. The empirical models are practically used in the severe accident codes such as IODE, ASTEC, IMPAR *etc.* The mechanistic modeling tries to represent the whole set of elementary radiochemical reactions (typically including hundreds of important reactions in water) and solves for the kinetics of these reactions using some ordinary differential equation solvers. 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 [4] and the LIRIC model (Library of Iodine reactions in containment) developed in AECL [5].

We prepared a pool scrubbing code using the current iodine retention models, and performed sensitivity studies on the iodine retention such as the pool temperature, vapor velocity in a bubble, and iodine concentration [6]. We also issued a new correlation 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 using NaI solutions under gamma irradiation [7].

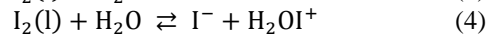
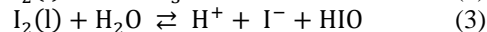
The important chemical parameters in an aqueous solution at equilibrium on the iodine chemistry are pH, chemical species, temperature, and total iodine concentration. The concentrations of chemical species at a given temperature, pH, and total iodine concentration are obtained by considering the main

chemical reactions. This means that the reaction set highly affects the equilibrium chemical species concentrations. There are severe studied iodine solutions in high alkaline solutions and low concentration. That is, Truesdale et. al [8] found that the disproportionation rate of hypiodous acid into iodide (I<sup>-</sup>) and iodate (IO<sub>3</sub><sup>-</sup>) has a peak value at pH 9.0, and Lin [9] showed that IO<sub>3</sub><sup>-</sup> production increases at lower iodine concentration. Iodate is a stable and nonvolatile species but it may be reduced and thus may contribute to I<sub>2</sub> production whenever the system condition is changed by pH or iodine concentration. IO<sub>3</sub><sup>-</sup> species become significant in the total iodine concentration of 10<sup>-6</sup> to 10<sup>-4</sup> M, pH of 5 to 11, especially higher than 7.0 [10].

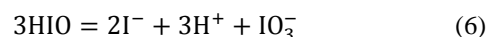
In the MELCOR code [4], only five reactions, and four iodine species, that is, I<sub>2</sub>, I<sub>3</sub><sup>-</sup>, HIO, and H<sub>2</sub>OI<sup>+</sup> in water are considered for iodine pool scrubbing calculations. We additionally consider the IO<sub>3</sub><sup>-</sup> species and HIO reaction, and the iodine partition coefficients are compared with and without IO<sub>3</sub><sup>-</sup> considered.

### 2. Method

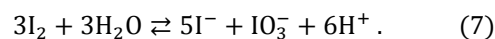
Considering the equilibrium concentration of inorganic iodine species inside the water phase in the MELCOR code [4], a limited set of the following chemical reactions is used, as shown in equations (1) through (5).



Hypiodous acid, HIO, is generally not stable because of disproportionation, and an additional reaction is considered as shown in Eq.(6).



The equilibrium constant of Eq. (6) has not been measured directly. The net reaction for the hydrolysis of iodine is then,



At equilibrium, the relationship between reactants and products in Eq.(1)~(5) and(7) are given by:

$$[I_{2(aq)}]_{eq} = K_1 [I_{2(g)}]_{eq} \quad (8)$$

$$[I_3^-]_{eq} = K_2 [I_{2(aq)}]_{eq} [I^-]_{eq} \quad (9)$$

$$[H^+]_{eq} [I^-]_{eq} [HIO]_{eq} = K_3 [I_{2(aq)}]_{eq} \quad (10)$$

$$[H_2OI^+]_{eq} [I^-]_{eq} = K_4 [I_{2(aq)}]_{eq} \quad (11)$$

$$[H^+]_{eq} [OH^-]_{eq} = K_5 \quad (12)$$

$$[IO_3^-] [I^-]^5 [H^+]^6 = K_6 [I_{2(aq)}]^3 \quad (13)$$

The equilibrium constants in equations (8) to (13) are determined at 25°C as follows [10]:

$$K_1 = 1.3882 \times 10^{-3} e^{\frac{3279.3}{T_{pool}}} \quad (14)$$

$$K_2 = 7.760 e^{\frac{1370}{T_{pool}}} \quad (15)$$

$$K_3 = 1.0423 \times 10^{-3} e^{\frac{7148}{T_{pool}}} \quad (16)$$

$$K_4 = 4.2271 \times 10^{-9} e^{\frac{1748}{T_{pool}}} \quad (17)$$

$$K_5 = 1.56531 \times 10^{-13} \exp\left(\frac{5462.8}{T_{pool}} - \frac{1.87376 \times 10^6}{T_{pool}^2}\right) \quad (18)$$

$$K_6 = 4.0 \times 10^{-48} \quad (19)$$

Assuming that a total of iodine concentration in an aqueous solution during the rising time of the bubbles (the vent depth divided by the average swarm velocity) is constant, equation (20) can be driven.

$$\Sigma [I_{2(aq)}] = 0.5[I^-] + 1.5[I_3^-] + [I_{2(aq)}] + 0.5[HIO] + 0.5[H_2OI^+] + 0.5[IO_3^-] = \text{const} \quad (20)$$

Equation (21) is obtained with the electric charge balance between the reactants and products.

$$([I^-] - [I^-]_p) + [I_3^-] - [H_2OI^+] - [H^+]^* - 5[IO_3^-] = 0 \quad (21)$$

$[H^+]^*$ , which is a product by reaction (3), must be equal to  $[HIO]$ . Therefore, Eq.(21) can be rewritten as follows.

$$([I^-] - [I^-]_p) + [I_3^-] - [H_2OI^+] - [HIO] - 5[IO_3^-] = 0 \quad (22)$$

Eq.(22) can be written by using Eqs (9), (11), (10), (13), and  $[I^-]_p = 0$  as follows:

$$[I^-] + K_2 [I_{2(aq)}] [I^-] - K_4 \frac{[I_{2(aq)}]}{[I^-]} - K_3 \frac{[I_{2(aq)}]}{[H^+] [I^-]} - 5K_6 \frac{[I_{2(aq)}]^3}{[I^-]^5 [H^+]^6} = 0 \quad (23)$$

For the given  $\Sigma [I_{2(aq)}]$  and  $[H^+]$  based on pH, two unknowns,  $[I^-]$  and  $[I_{2(aq)}]$  in equations (20) and (23), can be obtained using the Newton-Raphson method for nonlinear systems[11].

### 3. Results

The values of partition coefficient, which is defined as the ratio of total iodine in an aqueous solution to the gaseous phase, are calculated by solving equations (20) and (23).

Table 1 and Figure 1 show the calculated partition coefficients without and with  $IO_3^-$  species according to the pH and total iodine concentration in solution at 25°C. As shown in Table 1 and Figure 1, the partition coefficients increase drastically as pH and total iodine concentration in pool increase under all condition. The partition coefficients with  $IO_3^-$  are higher than without  $IO_3^-$  when pH is higher than 3.0 as the concentration of iodine decreases. This is why the  $[I_{2(aq)}]$  decreases in high pH condition if  $IO_3^-$  species is considered. If the pH is less than 3.0, the partition coefficient is not changed according to the aqueous iodine concentration. This result is similar to the Eggleton's results [12].

Table 1: Partition coefficient without and with  $IO_3^-$  species according to the pH and iodine concentration at 25°C

| pH  | Total Iodine Conc. (M) | Partition Coefficient |               |
|-----|------------------------|-----------------------|---------------|
|     |                        | w/t $IO_3^-$          | with $IO_3^-$ |
| 1.0 | $10^{-4}$              | 83.06                 | 83.13         |
| 3.0 | $10^{-4}$              | 83.20                 | 83.21         |
| 5.0 | $10^{-4}$              | 84.89                 | 88.5          |
| 7.0 | $10^{-4}$              | 103.37                | 9872.47       |
| 1.0 | $10^{-6}$              | 83.35                 | 83.35         |
| 3.0 | $10^{-6}$              | 84.73                 | 84.79         |
| 5.0 | $10^{-6}$              | 101.54                | 236.70        |
| 7.0 | $10^{-6}$              | 208.17                | -             |
| 1.0 | $10^{-8}$              | 86.414                | 86.4          |
| 3.0 | $10^{-8}$              | 101.82                | 102.45        |
| 5.0 | $10^{-8}$              | 489.07                | 10036.2       |
| 7.0 | $10^{-8}$              | 33868.9               | -             |

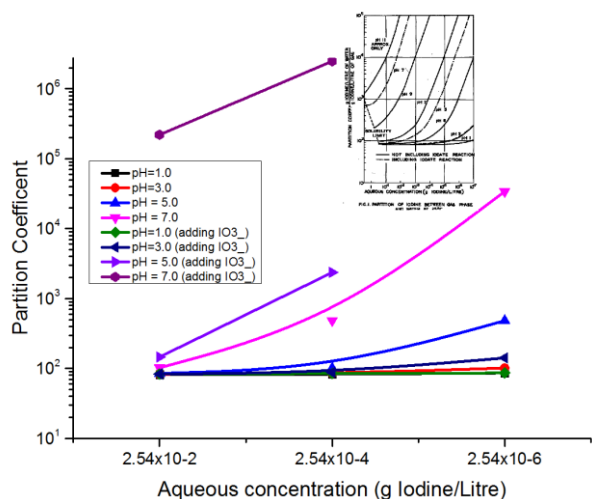


Fig. 1. Partition coefficient of iodine with and without  $\text{IO}_3^-$  according to the total iodine concentration and pH in solution

#### 4. Conclusion

An additional species,  $\text{IO}_3^-$ , and HIO reaction including  $\text{I}_2$ ,  $\text{I}_3^-$ , HIO, and  $\text{H}_2\text{OI}^+$  as aqueous iodine was considered and formulated. The partition coefficient increases drastically as pH increases if  $\text{IO}_3^-$  reaction was considered. It is also noted that the effect of the iodide reaction is insignificant at pH less than 3 but becomes increasingly important as the pH is raised.

#### ACKNOWLEDGMENTS

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