論文の内容の要旨

論文題目　Simulation study of high temperature water radiolysis relevant to PWRs

（**PWR** に関わる高温水の放射線分解シミュレーションの研究）

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1. Introduction

Water radiolysis is a subject on chemical reactions occurred in aqueous solutions induced by irradiation with ionizing radiation. The water radiolysis can be divided into 3 steps; physical (~1fs), physico-chemical (~1fs to ~100fs), and chemical steps (~100fs to ~100ns). Briefly, the water molecules that exposed to the radiations are excited or ionized. After ionization, energetic electron so called "secondary electron" is ejected and may have sufficient excess energy to ionize other water molecules. The secondary electron is slowing down to the energy lower than ionization potential and loses its energy further by the collision with water molecules. Finally, it is thermalized and then trapped by surrounding water molecules. This electron is called "aqueous electron (e^{-}_{aq})" or "hydrated electron". On the contrary, excitation of water molecules induced the fragmentation into H atom and OH radical. Water decomposition products are distributed non-homogeneously and localized in a few nm region, so called "spurs", at ~1ps after the deposition of radiation energy. The amount of products at this stage is called initial yield (in the unit of molecule/100eV). The decomposition products diffuse and undergo non-homogeneous chemical reactions (spurs reactions) simultaneously, leading to the formation of the molecular products. The amount of the products, when the products attain the homogeneous distribution, is called as the primary yields of water radiolysis. The primary yields strongly depend on type and energy deposition density of radiation (linear energy transfer, LET; ev/nm). The high LET radiation is known to produce dense spurs that can form the cylindrical track along its trajectory. In the track more frequent reactions take place among radical species and larger molecular products such are formed.

In light water reactors (LWRs), water is used as a coolant and as a moderator. Thus water is unavoidably exposed to different types of radiation: fast neutrons and γ-rays, at the core. The formation of H_2O_2 and O_2 from water radiolysis has been proved in the boiling water reactors (BWRs), and forms the oxidizing environment, which is a key factor of the corrosion problem. The hydrogen water chemistry has been applied by addition the hydrogen gas to the coolant to obstruct the formation of these oxidizing species in BWRs. In pressurized water reactors (PWRs), the system becomes more complex due to the addition of the soluble neutron poison, boron-10 as H_3BO_3, to control the surplus chain reaction. Boron-10 captures thermal neutron and undergoes the $^{10}B(n, \alpha)^7Li$ reaction, which produce α-particle and recoiled lithium ion. This leads to the evolution of H_2 gas because of high LET particles. Similar to BWRs, the hydrogen addition has been applied to PWRs. At present, 25-40 cc H_2/kg H_2O (STP) should be added to the primary coolant of PWRs as an operation condition. However, recent study suggests that this amount of H_2 addition might bring detrimental effects to corrosion of structural materials.

In this work, the computer simulation model has been applied to the study of water radiolysis in PWRs to compensate for the complicated experimental measurement in the extreme condition. In order to improve the reliability and accuracy of the simulation, I have selected several research subjects as follows.

(1) *Calculation of G-values of water decomposition products in the* $^{10}B(n, \alpha)^7Li$ *reaction*
(2) *Mechanism of* H_2 *suppression in the α- radiolysis by* H_2 *addition*
(3) *Inter comparison of G-values and reaction sets for simulation of high temperature water radiolysis*
(4) *Acceptable reduction of* H_2 *addition in PWRs*

Above research subjects would be useful and valuable for the study of the radiolysis of water at elevated temperature and the determination of required amount of H_2 addition in the primary coolant circuit of PWRs.

2. Monte Carlo calculation of water radiolysis by $^{10}B(n, \alpha)^7Li$ reaction

Very little attention has been paid to the water radiolysis induced by the $^{10}B(n, \alpha)^7Li$ reaction because of low energy and short range (< 10µm) in water of helium and lithium ions, which make the evaluation difficult. In fact, the complete set of water decomposition yields induced by the $^{10}B(n, \alpha)^7Li$ reaction has not been determined yet.

Table 1: The yields of primary products of water radiolysis for each components at 300°C

	ɣ-rays	Fast-neutron	$^{10}B(n,\alpha)^7Li$
e^-_{aq}	2.5	0.57	0.02
$H^\cdot$	1.3	1.09	0.12
$^\cdot OH$	4.4	2.46	0.78
H^+	2.5	0.58	0.02
H_2	0.6	1.02	1.26
H_2O_2	0.3	0.56	0.77
O_2	0	0.01	0.07
HO_2	0	0.02	0.02
$-H_2O$	5	3.65	2.50

(Unit: molecules/100eV)

To evaluate the water radiolysis induced by the $^{10}B(n, \alpha)^7Li$ reaction, the Monte Carlo simulation code "IONLYS-IRT" has been employed. In brief, the IONLYS program models all the events of the "physical" and "physicochemical" stages of radiation action up to 1 ps. The spatial distribution of reactants at the end of the physicochemical stage, which is provided as an output of the IONLYS program, is used as the starting point for the "nonhomogeneous chemical stage" in the IRT program. The "independent reaction times" (IRT) method relies on the approximation that the reaction time of each pair of reactants is independent of the presence of other reactants in the system. The effect of multiple ionization, which is used to explain the production of HO_2/O_2^- in high LET radiation was also incorporated in the physicochemical stage of our program. The calculation was done separately for 0.37 MeV/amu helium and 1.2 MeV/amu lithium ions with an average LET of 196 and 225 keV/µm, respectively. The overall yields for the radiolysis by the $^{10}B(n,\alpha)^7Li$ reaction were calculated by summing the yields of each ion after being weighted by its fraction of total energy.

Under room temperature condition, the yields at 1µs in neutral water were estimated as shown in Table 1, and used as the initial data in the FACSIMILE simulation to reproduce the water radiolysis in homogeneous system and compare with the experimental data. The results from FACSIMILE simulation show a good agreement with the experiment.

The calculation was also extended to 300 °C for modelling of water radiolysis in primary coolant of PWRs as shown in Table 1.

3. Simulation of high temperature water radiolysis for PWR

A chemical kinetic simulation code FACSIMILE (MCPA SOFTWARE, UK) was employed to simulate and reproduce the homogeneous stage water radiolysis. Three key parameters for the simulations are the primary yields of the water decomposition products, the set of reactions and corresponding rate constants, and the dose rate.

3.1 Inhibition of α-radiolysis by H_2 addition

It was found that the continuous formation of H_2, O_2, and H_2O_2 observed during α-radiolysis of water could be suppressed by the addition of H_2 above a threshold hydrogen concentration (THC). Using the FACSIMILE simulation code, water radiolysis was reproduced in order to determine the THC and to clarify the mechanism at room temperature. Using the reaction set and rate constants of Ershov and Gordeev together with the primary yields for water decomposition products generated using 12 MeV α-particles, the THC was found to be 165 µM. Further simulation results clearly showed that the value of THC is strongly dependent on the reaction set and rate constants. In addition, a possible mechanism involving a chain reaction governed by (1) $OH + H_2 \rightarrow H + H_2O$ and (2) $H + H_2O_2 \rightarrow OH + H_2O$ was proposed as shown in Figure 1. The addition of H_2 above THC intervenes the reaction of OH with H_2O_2 and conveys the reaction to the production of H atom through reaction (1). The lower formation of HO_2 from reaction (2) leads to lower amount of O_2, which is the secondary product. This keeps the ratio of

H_2O_2 to O_2 high enough to prolong the competition reaction to reaction (3). The same inhibition effect was found when high temperature simulations at 300 °C were done, but the concentration range of all species and THC were much smaller as compared with the values obtained at room temperature. The importance of the rate constant of the reverse reaction of OH + H_2 → H + H_2O was also investigated.

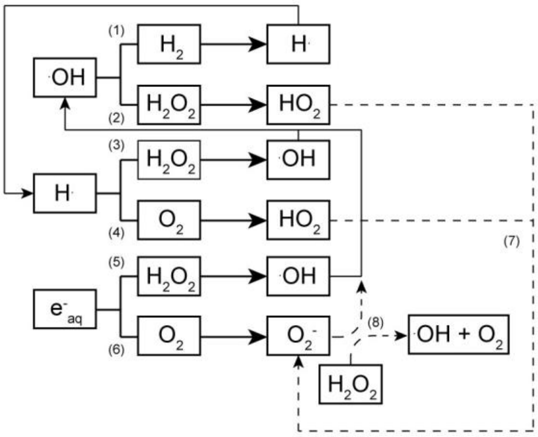

Figure 1: The chain reaction mechanism based on the competition reaction of radical towards molecular products. The first and second columns from the left are th initial species while the third column is the product excluding the recombination of water.

3.2 Inter-comparison of reaction sets for simulation

It is found that the simulation with different reaction sets and rate constants may cause a variation in the calculation results. Although several sets of chemical reaction for water radiolysis at elevated temperature have been reported, the comparison of the variation has not been done yet. To clarify this difference, we have picked up several sets of initial data for 285°C for application of our FACSIMILE simulation to calculate the radiolysis of water in BWRs.

The simulation has been done using the primary yields of γ-rays reported with the dose rate of 1kGy/s. Six reaction sets, A - F, and corresponding rate constants were employed for comparison. The simulation results are shown in Figure 2. The clear difference was observed, especially for $[O_2]$ between the results from simulations using reaction sets A-C and D-F, shown in the black line. Further investigation found that the rate constant of the reverse reaction of ·OH + H_2 → H· + H_2O for reaction set A-C is kept as 0 $M^{-1}s^{-1}$, while it is ~10^3 $M^{-1}s^{-1}$ for reaction set D-F. If this rate constant is fixed at 0 $M^{-1}s^{-1}$ for all sets, the variation of all species was reduced within one order between each set. The similar result was found, when the rate constant for all sets were fixed to be 6.2×10^3 $M^{-1}s^{-1}$, which is the highest rate constant among all sets.

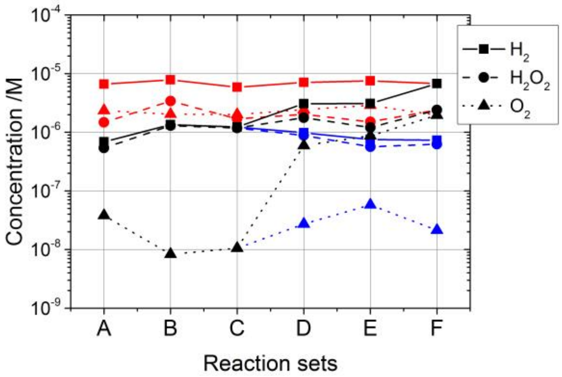

Figure 2: The concentration of molecular products from the simulation with different reaction sets (**Black**: ordinary rate constant, **Blue** and **Red**: k(H+H_2O) = 0 $M^{-1}s^{-1}$ and 6.2×10^3 $M^{-1}s^{-1}$ for all set)

3.3 Reduction of $[H_2]_{addition}$ in PWR

It is important to add enough amount of H_2 to suppress the formation of oxidizing species from the water radiolysis. However, the present addition of 25-40cc H_2 /kg H_2O (STP) in the primary coolant was suggested to be a cause of detrimental effect to the structural material in PWRs. The FACSIMILE simulation has been employed to determine the optimizing concentration for H_2 addition.

To reproduce the water radiolysis behavior inside the core of PWRs, the following parameters were taken; the reaction set and rate constant reported in AECL report 2009, the yields of primary products of water radiolysis by the mixed radiation of γ-rays, fast-neutron, and the radiolysis by the $^{10}B(n, \alpha)^7Li$ reaction, with the dose rates of 1.3, 4.0, and 0.8kGy/s for each component, respectively. The yields of water decomposition products for individual values are shown in Table 1. At 300 °C the results clearly showed that the steady state of all species was attained under γ-radiolysis as well as fast neutron, while continuous increase of the molecular species; H_2, H_2O_2, O_2, was found only in the radiolysis induced by the $^{10}B(n, \alpha)^7Li$ reaction. However, the result of mixed radiation did not show any continuous increasing

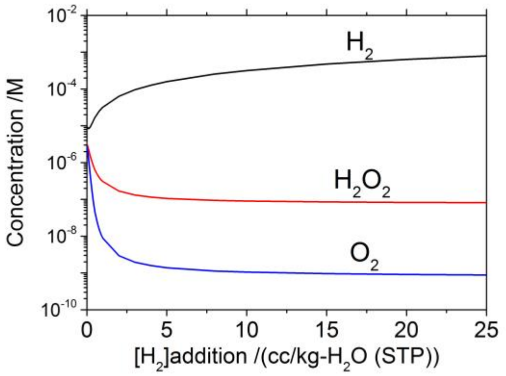

Figure 3: The concentrations of molecular products from water radiolysis as a function of H_2 addition

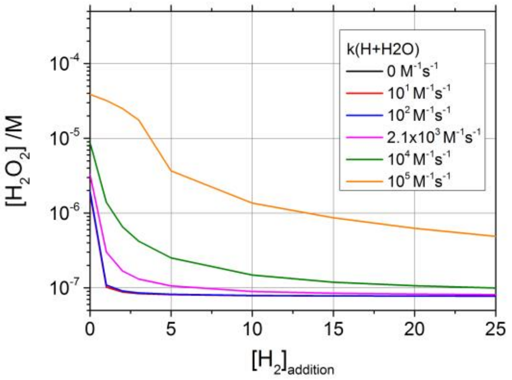

Figure 4: The calculated $[H_2O_2]$ as a function of $[H_2]_{addition}$ at different k($H + H_2O$)

behavior. This might due to the higher ratio of fast neutron and γ-rays, which suppress formation rate of molecular products. Although the steady state was achieved for all products, the concentrations of oxidizing species were high. When hydrogen was added, the suppression of oxidizing species; H_2O_2 and O_2, was clearly observed. The leveling off of $[H_2O_2]$ was attained even at a low concentration of 10 cc/kg-H_2O (STP), as shown in Figure 3.

In the primary coolant of PWRs, the radiation intensity depends on the position in the reactor. The dose rate normally increases when water is moving from the down comer to the core and decreases as leaving the core region. To simply imitate this change, we have assumed that the dose rate in our system can be expressed by a sine-function. In pure water without H_2 addition, the concentrations of molecular products tended to slowly, but not completely, follow the dose rate change. The presence of molecular products was still observed even after the dose rate drops to zero. In contrast, by introducing H_2 to the system, the reactions became faster and the concentrations of all species followed quickly to the dose rate, and may drop dramatically when dose rate reaches zero. This implies that the measurement in the sampling line far from the core region may not correctly represent the concentration of the component in the core of the reactors.

The rate constant of the $H + H_2O$ reaction was found to play an essential role in the water radiolysis, especially to the formation of the molecular products as mentioned in previous section. However, the rate constant of $H + H_2O \rightarrow OH + H_2$ reaction at 300°C is still on debate between ~10^3-10^4 $M^{-1}s^{-1}$. By varying this rate constant in this range, we found that the concentration of H_2O_2 is changed dramatically at the low $[H_2]_{addition}$, as shown in Figure 4.

4. Conclusion and future subject

Computer simulation model has been employed to develop and evaluate the basic data for the water radiolysis relevant to PWRs. In this work, the temperature dependence *G* values of the water decomposition products from the radiolysis induced by the $^{10}B(n, \alpha)^7Li$ reaction have been evaluated for the first time using the Monte Carlo simulation. The mechanism of H_2 suppression by H_2 addition has also been clarify and the reaction of $H + H_2O \rightarrow OH + H_2$ was found to play a key role in the determination of acceptable level of H_2 addition in PWRs. For more precise estimation, more information on the reverse reaction of $H_2 + OH \rightarrow H_2O + H$ is inevitably necessary.