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Study on Behaviour of Hydrogen Generation due to Radiolysis during the Transport of Damaged Fuel from Fukushima Daiichi Nuclear Power Station

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Abstract

In the transport of intact spent fuel discharged from an ordinarily operated nuclear power station, the amount of hydrogen generated by radiolysis was reported well within the safe range. The water in the spent fuel pools of the Fukushima Daiichi Nuclear Power Station (hereinafter referred to as "1FSFP") contains seawater constituents, because the 1FSFP were cooled by seawater during the accident. Hence, in the transport of damaged spent fuel from the 1FSFP, the hydrogen generation affected by such pool water conditions and leachate from the damaged fuel may exceed the permissible range. To evaluate the radiolysis behaviour properly, S/NRA/R conducted experiments with the objectives;

1. Measurement of equilibrium concentration of hydrogen generated by radiolysis of water with seawater and iodine ions or other ionic constituent,
2. Measurement of G values for hydrogen generation under the above water conditions, and
3. Verification of evaluation model for radiolysis behaviour based on the above results.

The following parameters were selected for the experiments in consideration of transport conditions including 1FSFP water:

- Test water: pure water with artificial seawater (hereinafter referred as "simulated water"), pure water with bromine ions and pure water with iodine ions
- Test water temperature: room temperature and 150 ºC
- Exposure dose rate: up to 10^3 Gy/h
- Exposure period: up to 100 h

The results indicate that the effect on the hydrogen generation by iodine among the test materials was the largest. Moreover, when the iodine ions of a particular concentration coexist under presence of seawater, iodine ions were found to have a dominant effect on the hydrogen generation.

The experimental results will be used as a technical basis for future safety evaluation of the transport of damaged fuel from 1FSFP.

Introduction

In the transport of intact spent fuel discharged from an ordinarily operated nuclear power station, the amount of hydrogen generated by radiolysis was reported well within the safe range [1]. On the other hand, some of spent fuel assemblies in the 1FSFP might be damaged by building debris and equipment dropped onto them. A wet type package (i.e., the package cavity is filled with pool water) is expected to be used in the case of the transport of the damaged fuel from the reactor building to the Common Pool (spent fuel storage installation separately established but commonly used for Units 1 to 6). An amount of hydrogen expected to be generated by radiolysis during the transport under the conditions with the leachate from the damaged fuel and quality of the 1FSFP water, i.e., with seawater constituents, may exceed the level predicted by the previously accumulated data. Therefore, there is a need to assess whether hydrogen generation stays within permissible level to confirm the safety of such transport.

For the proper evaluation of the amount of hydrogen, it is necessary to clarify the radiolysis mechanism of the pool water. In order to apply existing radiolysis models of water [2, 3, 4 and 5] to the case of 1F damaged fuel transport, the following additional data have to be complemented:

- G values for the simulated water containing iodine ions, pure water with bromine ions and pure water with iodine ions.
- Temperature dependency of reaction rate constants for elementary reaction of the simulated water and pure water with iodine ions.
- Effects of water temperature rise in the packaging during transport on hydrogen generation (up to about150 ºC [6]).

Experiments

The measurements of the G values and the equilibrium hydrogen concentration generated by radiolysis of water were carried out for different sets of the parameters of ion concentrations, water temperature and radiation dose.

<u>Test equipment and test conditions</u>

The test apparatus is mainly constituted by γ source (^{60}Co), capsule (300 cm^3), pressure transmitter and data logger as shown in Figure 1.

The test conditions are summarized in Table 1.

<u>Measurement results of equilibrium hydrogen concentration</u>

The test water with the presence of bromine ions, that with iodine ions and the simulated water with iodine ions were irradiated under room temperature and 150ºC. In each test the pressure change was

measured to calculate the equilibrium concentration of hydrogen depending on absorbed dose using Eq.1. The results are shown in Table 2.

$$C_{H_2} = \frac{P_g}{k_H M_{H_2O}}$$
Eq. 1

C_{H_2}: Equilibrium concentration of hydrogen (mol/g)

P_g : Hydrogen pressure (Pa)

k_H : Henry Constant (Pa)

M_{H_2O} : Molar mass of water (g/mol)

Major findings from these tests are as follows.

- The effect of the chlorine ions, although they are contained in simulated water with high concentration, on the hydrogen generation was small.

- The bromine ions are known to be the major component acting on the hydrogen generation in the radiolysis of seawater [7]. Its effects under room temperature and 150ºC were confirmed in these tests. The bromine ions had an intermediate effects on hydrogen generation between the iodine ions (described later) and the chlorine ions.

- When the simulated water contained iodine ions, iodine ions had dominant effects on hydrogen generation in the low absorbed dose area irrespective to simulated seawater concentrations (see Fig. 2). On the other hand, when the absorbed dose was high to some extent, the influence of chlorine ions concentration could not be ignored.

- Therefore, the effects on the hydrogen generation of the halogens becomes smaller in the order of iodine, bromine and chlorine (seawater).

- Concerning the effects of temperature on the hydrogen generation, the higher temperature resulted in the faster achievement of an equilibrium concentration of hydrogen. Without iodine ions, the pressure did not increase significantly from the saturated vapor pressure at 150 ºC (see Fig. 3).

Measured G values

The measured the G values of hydrogen generation are shown in Table 3. The major findings are as follows.

- With increase in various ion concentrations of the test water at room temperature, G values tended to increase. On the other hand, concerning the simulated water and pure water with iodine ions at 150 ºC, there was a tendency where the G values with increase in their concentrations. However, no clear relationship between the concentrations and G values was observed in the case of pure water with bromine ions.

Analysis

Outline of analysis code

A water quality analysis code "SIMFONY" [8] based on the radiolysis reaction mechanism of water was used in the analysis. In this analysis, at first, the hydrogen generation by the radiolysis of water (as a liquid single-phase) was calculated, then the hydrogen concentrations in the gas phase and liquid phase were obtained using Henry's law and the ideal gas equation with an assumption that the hydrogen concentration in the liquid phase would be gas-liquid equilibrium to that in the gas phase. A basic formula in SIMFONY (expression representing the time variation of the concentration of the chemical species "i" in the liquid single-phase under irradiation) is below.

$$\frac{dC_i}{dt} = \xi(g_i^\gamma Q^\gamma + g_i^n Q^n) + \sum_l^N \sum_m^N k_{lm} C_l C_m - C_i \sum_s^N k_s C_s \qquad \text{Eq. 2}$$

I : Generic term of chemical species

C_i : Concentration of chemical species "i" in liquid phase (moldm^{-3})

ξ : Unit conversion factor

g_i^γ and g_i^n : G values of gamma-ray and neutron, respectively (number(100eV)$^{-1}$)

Q^γ and Q^n : Absorbed dose rates of gamma-ray and neutron, respectively (Wdm^{-3})

N : Number of chemical species involved in the radiolysis reaction of pure water

k_{lm} : Chemical reaction rate constant of the reaction between chemical species "l" and "m" (M^{-1}s^{-1})

Analysis result

The correlation between the equilibrium hydrogen concentrations obtained by the analysis and the tests are shown in Fig. 4. Analysis results are considered to reproduce the experimental results well. Since the variations of the data are within the range of -50% to + 100%. The cause of slightly large difference in the low concentration area observed is understood as the accumulation of measurement errors coming from small changes in pressure.

Study on the radiolysis and reactions of a halide

When the seawater components coexist, certain components have been found to affect radiolysis and recombination reactions of water. Consequently, the amount of hydrogen generation increases if the major components of seawater, i.e., chlorine ions and bromine ions, present in high concentration. For example, The G value of the hydrogen in the 5M-NaCl solution is 0.6 [2], which is larger than that of pure water, 0.45.

This is understood as the recombination reaction is inhibited by the reactions of chlorine ions and bromine ions contained in seawater as shown in the following equations.

$$X^- + \cdot OH \quad \rightarrow \quad XOH^- \qquad\qquad\qquad \text{Eq. 3}$$

$$\text{XOH}^- \rightarrow \text{X}^- + \cdot\text{OH} \hspace{4cm} \text{Eq. 4}$$
$$\text{XOH}^- + \text{H}^+ \rightarrow \text{X} + \text{H}_2\text{O} \hspace{3.5cm} \text{Eq. 5}$$

Equation. 3 and 4 are an equilibrium reaction. As the reaction rate constants [2] of chlorine ions and bromine ions are shown below, the consumption of OH radicals does not proceed efficiently because the chlorine ions have larger reaction rate constant in the reverse reaction. On the other hand, the reaction to consume OH radicals proceeds effectively [3 and 6] because the bromine ions reaction rate constant of the reverse reaction is smaller than that of the forward reaction. Thus, the hydrogen generation increases when is seawater present, since the OH radicals, which are the initiators of the recombination reaction to water, are consumed by bromine ions.

$$\cdot\text{OH} + \text{Cl}^- \rightarrow \text{ClOH}^- \hspace{2cm} k_f = 4.3 \times 10^{11}$$
$$\text{ClOH}^- \rightarrow \cdot\text{OH} + \text{Cl}^- \hspace{2cm} k_b = 6.1 \times 10^{11}$$

and

$$\cdot\text{OH} + \text{Br}^- \rightarrow \text{BrOH}^- \hspace{2cm} k_f = 5.0 \times 10^{11}$$
$$\text{BrOH}^- \rightarrow \cdot\text{OH} + \text{Br}^- \hspace{2cm} k_b = 3.0 \times 10^{9}$$

In addition, iodine chemical reaction has been investigated from the point of view of the radioactive iodine re-release or flammable gas generation at the time of severe accident [5, 10 and 11]. According to Wren and Ball [5], iodine reaction rates are given as follows. The ratio $R = k_f / k_b$ (the forward reaction rate / the reverse reaction rate for halide ions and OH radicals) is shown in Table 4, where the rate R increases in the order of iodine ion > bromine ion > chlorine ion. For this reason, the iodine ion is considered to affect dominantly on the hydrogen generation.

$$\cdot\text{OH} + \text{I}^- \rightarrow \text{IOH}^- \hspace{2cm} k_f = 1.0 \times 10^{10}$$
$$\text{IOH}^- \rightarrow \cdot\text{OH} + \text{I}^- \hspace{2cm} k_b = 1.13 \times 10^{6}$$

Conclusions

Uncertainties in the chemical reaction mechanism and its rate constants have been reduced by determining the equilibrium concentrations of hydrogen generated by radiolysis under various conditions to cover the transport of damaged spent fuel in a wet type package. Also, G values of pure water with bromine ions and those of pure water with iodine ions, which were the key to explicate radiolysis reactions under the specific conditions, have been measured. By combining these new findings on the hydrogen generation behaviour and previous knowledge [2, 3, 5, 8 and 12] on the reactivity of the halide ions (elementary reactions and reaction rate constants), the amount of hydrogen generated during transport of the damaged spent fuel can be better evaluated using the radiolysis reaction model (Equation 2).

For the management of hydrogen generation at the time of transport, it is necessary to consider the

concentration of iodine ions leaching from damaged fuel since iodine ions have a dominant effect on the hydrogen generation including coexist seawater.

Acknowledgment

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Table 1 Test conditions

Items	Conditions
Capsule internal volume (cm^3)	300
Dose rate(Gy/h)	～10^3
Test temperature	Room temp.,150 ºC
Test time (h)	～100※

※There were the cases where the test time exceeded 100h to check the equilibrium pressure

Table 2 Measurement results of equilibrium concentration of hydrogen

No	Temp. (ºC)	Simulated water (Cl⁻) (M(=mol/L))	Iodine (M(=mol/L))	Bromine (M(=mol/L))	Hydrogen Concentration (ppb)
1	Room	1.4×10^{-3}			110
2	Room	2.8×10^{-3}			150
3	Room	1.4×10^{-2}			210
4	Room	1.4×10^{-3}	1.0×10^{-4}		7000
5	Room	2.8×10^{-3}	1.0×10^{-4}		5000
6	Room	1.4×10^{-2}	1.0×10^{-4}		2600
7	Room		1.0×10^{-4}		6000
8	Room		1.0×10^{-5}		520
9	Room		1.0×10^{-6}		80
10	Room			1.0×10^{-4}	650
11	Room			1.0×10^{-5}	80
12	Room			1.0×10^{-6}	20
13	150	1.4×10^{-3}			＜120※
14	150	2.8×10^{-3}			＜120※
15	150	1.4×10^{-2}			＜120※
16	150	1.4×10^{-3}	1.0×10^{-4}		5000
17	150	2.8×10^{-3}	1.0×10^{-4}		4500
18	150	1.4×10^{-2}	1.0×10^{-4}		4000
19	150		1.0×10^{-4}		4700
20	150		1.0×10^{-5}		410
21	150		1.0×10^{-6}		370
22	150			1.0×10^{-4}	350
23	150			1.0×10^{-5}	＜120※
24	150			1.0×10^{-6}	＜120※
25	Room	Reference data (pure water)			50
26	150				＜120※

※Measured by high range pressure gaouge.

Table 3 G-value calculation results concerning hydrogen generation

No	Ratio (vapour/liquid)	Test Water			G value (number/100eV)	
		Simulated water(Cl⁻) $(M(=mol/L))$	Iodine $(M(=mol/L))$	Bromine $(M(=mol/L))$	Room	150°C
1	0.2	$1.4×10^{-3}$			0.02	—
2	0.5	$1.4×10^{-3}$			0.02	0.04
3	1.0	$1.4×10^{-3}$			0.00	0.11
4	0.2	$2.8×10^{-3}$			0.03	—
5	0.5	$2.8×10^{-3}$			0.07	0.01
6	1.0	$2.8×10^{-3}$			0.12	0.09
7	2.0	$2.8×10^{-3}$			0.17	—
8	0.2	$1.4×10^{-2}$			0.04	0.01
9	0.5	$1.4×10^{-2}$			0.12	0.02
10	1.0	$1.4×10^{-2}$			0.26	0.28
11	2.0	$1.4×10^{-2}$			0.32	0.60
12	0.2		$1.0×10^{-6}$		0.06	—
13	0.5		$1.0×10^{-6}$		0.14	0.02
14	1.0		$1.0×10^{-6}$		0.17	0.35
15	2.0		$1.0×10^{-6}$		0.05	—
16	0.2		$1.0×10^{-5}$		0.21	0.05
17	0.5		$1.0×10^{-5}$		0.28	0.42
18	1.0		$1.0×10^{-5}$		0.46	0.42
19	2.0		$1.0×10^{-5}$		0.37	0.07
20	0.2		$1.0×10^{-4}$		0.54	1.04
21	0.5		$1.0×10^{-4}$		0.41	0.78
22	1.0		$1.0×10^{-4}$		0.57	0.75
23	2.0		$1.0×10^{-4}$		0.54	0.30
24	0.2			$1.0×10^{-6}$	0.02	—
25	0.5			$1.0×10^{-6}$	0.03	0.38
26	1.0			$1.0×10^{-6}$	0.04	0.22
27	2.0			$1.0×10^{-6}$	0.05	—
28	0.2			$1.0×10^{-5}$	0.02	—
29	0.5			$1.0×10^{-5}$	0.03	NA
30	1.0			$1.0×10^{-5}$	0.03	0.26
31	2.0			$1.0×10^{-5}$	0.04	—
32	0.2			$1.0×10^{-4}$	0.12	0.04
33	0.5			$1.0×10^{-4}$	0.15	0.06
34	1.0			$1.0×10^{-4}$	0.27	0.02
35	2.0			$1.0×10^{-4}$	0.39	0.55

Table 4 Comparison of the reaction rate ratios between the halide ions and the OH radical

Halogen Ion	R $(=k_f/k_b)$	Hydrogen Generation
Cl^-	0.7	
Br^-	200	↓ Increase
I^-	9000	
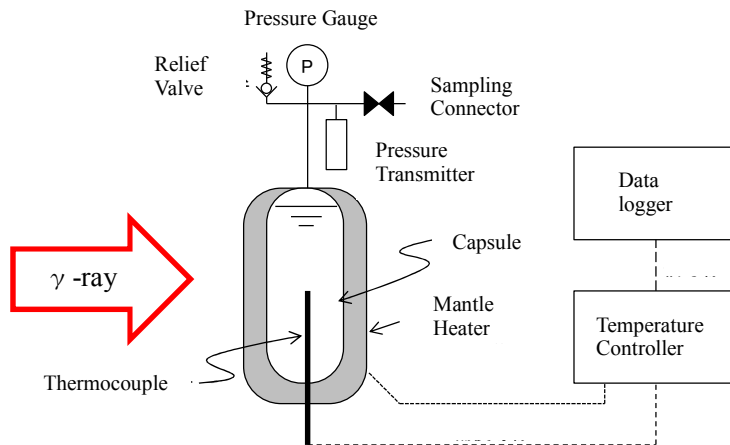
Fig.1 The Experimental apparatus

◆ simulated water ($1.4*10^{-3}$M) with iodine ions (10^{-4}M)

■ simulated water ($2.8*10^{-3}$M) with iodine ions (10^{-4}M)

▲ simulated water ($1.4*10^{-2}$M) with iodine ions (10^{-4}M)
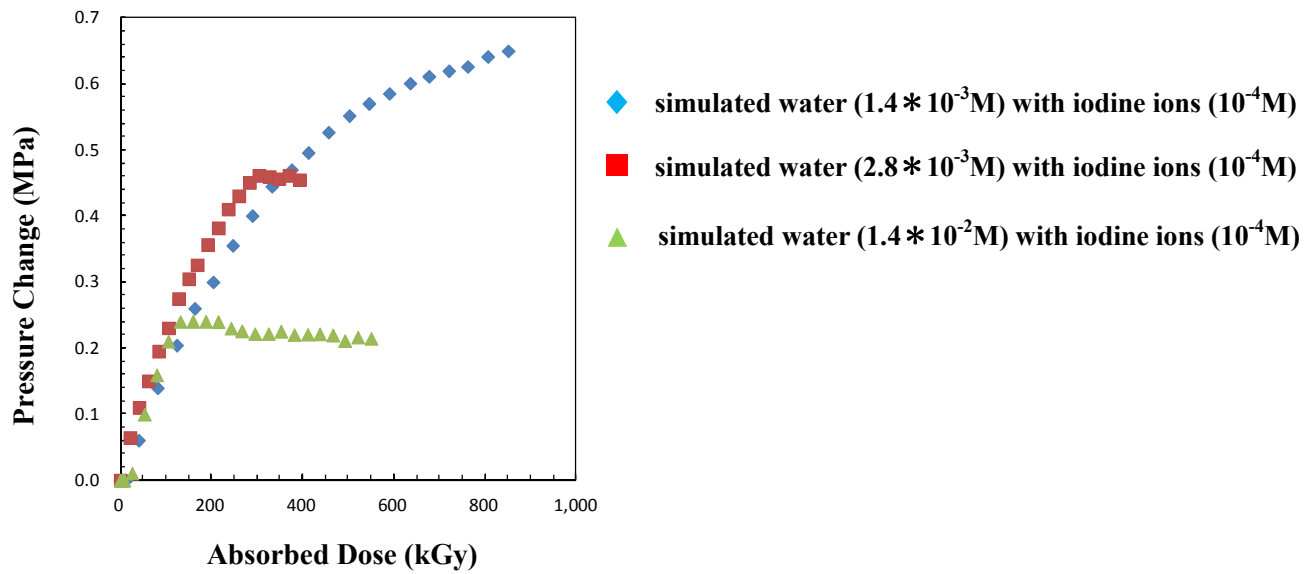
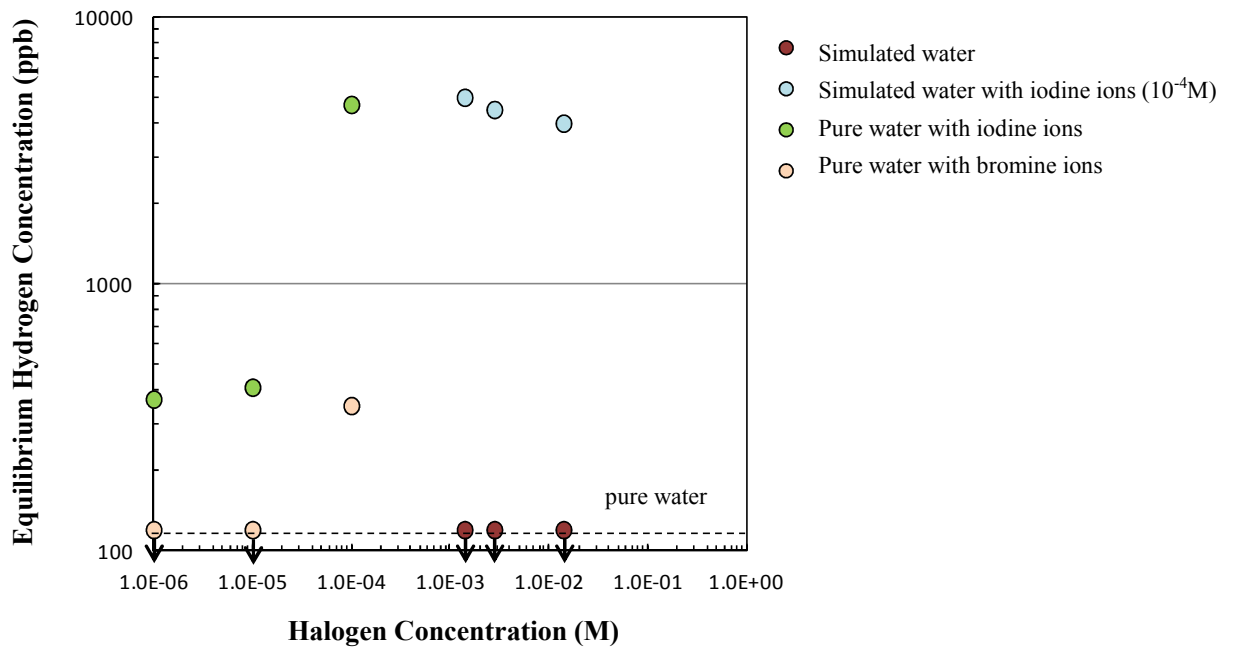Fig.2 Hydrogen generation in simulated water with iodine ions (Room temp.)

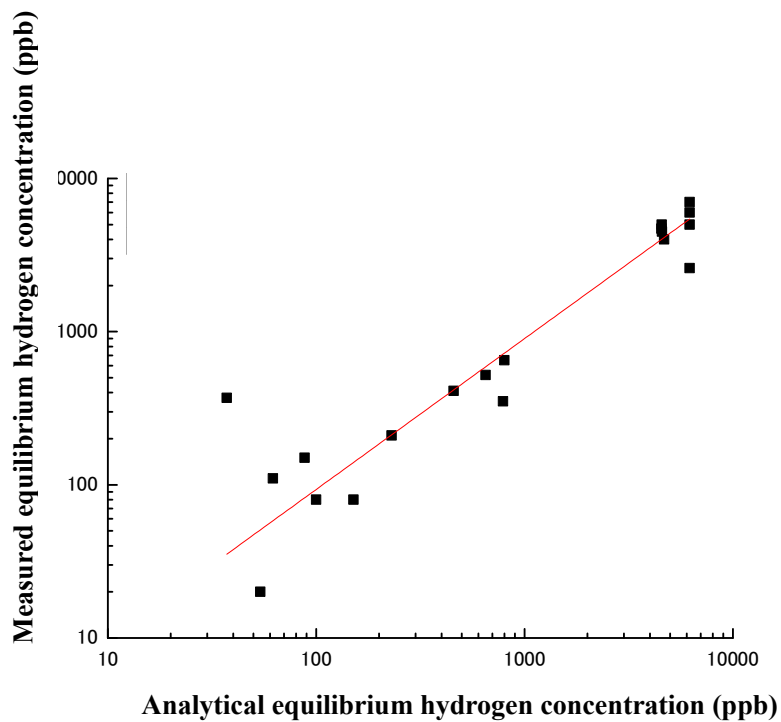Fig.3 Equilibrium hydrogen concentrations for various parameters (150℃)

Fig.4 Correlation between analytical and experimental equilibrium hydrogen concentrations（Room temperature and 150℃）