Scientific paper

Hydrogen Production and the Stability of Hardened Cement Paste under Gamma Irradiation

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Abstract

Hardened cement pastes (HCP) with different water contents were irradiated with gamma rays under different temperatures and irradiation dose rates. The relationship between the quantity of hydrogen gas produced and the water content as well as the stability of HCP under gamma irradiation was evaluated. It is experimentally confirmed that hydrogen gas was mainly produced from the evaporable water. The G value of the hydrogen production assuming the radiation energy absorbed by the total water composed of chemically bound water (CBW) and evaporable water was ranging from 0.03 to 0.42. The G value of the hydrogen production for CBW was ranging from 0.03 to 0.07, which were an order of magnitude smaller than that of the bulk water (0.45).

Assuming that the radiation energy on evaporable water is used for the formation of hydrogen, it is experimentally confirmed that, in case of low dose rate, the G value tended to converge to a constant value when the evaporable water exceeded a certain value, while, in case of high dose rate, the G value increased as evaporable water increased. However, the G values of all cases grew with increasing evaporable water content and exceeded the G value of the bulk water (0.45). The CBW was not susceptible to gamma irradiation. Only 2 to 3% of the CBW was estimated to be decomposed by 200 MGy of gamma irradiation.

1. Introduction

Cement-based materials, such as concrete and mortar, are used as biological shield walls surrounding nuclear reactors in nuclear power plants, as containers for radioactive wastes, and as fillers between radioactive wastes and its containers. Although these materials are exposed to gamma radiation over a long period, a fundamental understanding of the interaction between gamma rays and cement-based materials has not yet been achieved.

Gamma radiation, an ionizing radiation, ionizes the irradiated substance by transferring either a portion of its contained energy via the Compton scattering process or its entire energy through a photoelectric process. A secondary electron generated by the ionization process possesses sufficient energy to excite and ionize the constituent atoms and molecules of the irradiated substance. The energy transferred by this secondary electron finally heats the irradiated substance, splits the constituent molecules, generates new molecules, and generates structural defects. Given that the energy of gamma rays radiated from a nuclear reactor ranges from 10 keV to 10 MeV (Maruyama et al. 2016), Compton scattering seems to be dominant in these interactions with the concrete surrounding a nuclear reactor.

Many studies on water radiolysis have been performed across the diverse fields of engineering and medical science. In nuclear power engineering, the behavior of water as a moderator has been well researched, and data on the influence of temperature, pH, the linear energy transfer (LET), solutes, and the interface effect have been gathered so that behavior under various irradiation conditions could be quantitatively simulated (Sanguanmith et al. 2011). Studies on the water present in cement-based materials are limited, and hydrogen gas production from these materials is not understood quantitatively. Further thorough investigations are therefore needed to confirm the soundness of these cement-based structural materials and to manage the hydrogen gas evolution more safely.

In water radiolysis, the processes that result after receiving energy are divided into three major stages: the physical process, the physicochemical process, and the chemical process. In the physical process, which takes place on the order of 10^-15 to 10^-15 seconds, water ionizes to either produce H2O^- and e^- or it becomes excited. In the subsequent physicochemical process, H2O^- reacts with the surrounding water molecules to produce H2O^+ and OH radicals, while electrons, e^-, hydrate with the...
surrounding water to transform into hydrated electrons, $e_{aq}^-$. The excited water then decomposes into OH radicals and H atoms. This process proceeds over the course of 10$^{-12}$ seconds. The energy transfer takes place discretely and H atoms. This process proceeds over the course of 10$^{-12}$ seconds. The energy transfer takes place discretely and H atoms.

When water containing fine nanoscale particles or water in the porous inorganic oxide is irradiated, a larger amount of hydrogen production is observed compared to that from the bulk water. Kumagai et al. (2013) studied the gamma irradiation of a mixture of mordenite, zeolite, and seawater. Cantarel et al. (2018) studied the gamma irradiation of a combination of zeolite and a geopolymer. Some studies (Le Caër 2011; Skotnicki and Bobrowski 2015) have reviewed different parameters in terms of their influence on the oxide surfaces on hydrogen production, including the LET, form of the adsorbed water, presence of oxygen, surface area, crystalline structure, size of particles, doping with other oxides, grafting, the catalytic decomposition of H$_2$O$_2$, band gap, and the dose rate.

Hardened cement paste (HCP) develops its strength by the hydration reaction between cement and water and functions as a binder of cement-based materials. HCP is a porous/colloidal material that possesses a wide range of void sizes ranging from nanometers to millimeters. The specific surface area of well-hydrated HCP exceeds 100 m$^2$/g (Litvan 1976; Feldman 1980; Thomas et al. 1999; Jennings 2000; Maruyama 2010). Therefore, this large surface area (at the solid-adsorbed water interface) should play an important role in the interaction between gamma rays and cement-based materials.

HCP may contain different forms of water with different restrictions, including chemically bound water (CBW) generated by the reaction of water with cement constituents [e.g., H$_2$O + CaO $\rightarrow$ Ca(OH)$_2$], interlayer water that resides between calcium-silicate-hydrates (C-S-H) sheets, and adsorbed water on the C-S-H gel (Powers 1960; Feldman and Sereda 1968; Feldman and Ramachandran 1971; Muller et al. 2013; Maruyama et al. 2019). Additionally, capillary water may exist in large pores. When HCP is subjected to radiation, the contained water decomposes, and hydrogen gas is produced via radiolysis. One safety concern is the extent to which CBW, that forms a part of C-S-H, decomposes. Another concern is the risk that the hydrogen gas produced by radiolysis may ignite or explode, and in the case of a closed system, the integrity of the packing structures might be lost due to the increase of the internal pressure. Noshita et al. (1994) reported that the yield of hydrogen gas generated from the HCP was proportional to the amount of free water. It was also noted that this value was a few times higher than the yield calculated using the G value of the bulk water and free water contents because of the effects of an organic additive, such as diethylene glycol, and electrons generated in the cementitious matrix. Kontani et al. (2013) reported that while CBW hardly decomposed, evaporable water decomposed more easily to produce hydrogen gas. Yin et al. (2019) reported that hydrogen production in C-S-H was enhanced compared to that in bulk water. They determined that this greater amount of hydrogen was produced from a greater specific surface area of C-S-H as a result of a low Ca/Si ratio. Chartier et al. (2018) examined the impact of the cement type and the aqueous solution added to the cement materials. They found that the status of the water had no major influence on hydrogen production and that hydrogen production was proportional to the total amount of water present in the materials. Although many reports have shown that hydrogen is produced during these reactions, oxygen has not been observed. Bouniol and Aspart (1998) explained that this is because peroxide is trapped in CaO$_2$·8H$_2$O.

In this study, HCP with different water contents were irradiated with gamma rays produced by Cobalt-60 under different temperatures and irradiation dose rates. The relationship between the quantity of hydrogen gas produced and the water content, as well as the stability of HCP under gamma irradiation was evaluated with reference to the above-mentioned findings on the radiolysis of water. A portion of the data referred to in the current study is summarized in a previous paper (Maruyama et al. 2017), while the undertaken experiments and newly obtained data are presented and discussed herein further.

### 2. Experimental

#### 2.1 Material and specimen

HCP specimens with a water to cement ratio of 0.3 were prepared with ordinary Portland cement and tap water. Table 1 shows the chemical composition of the ordinary Portland cement used. The density and Blaine specific surface area were 3.16 g/cm$^3$ and 3210 cm$^2$/g, respectively. A mortar mixer with a volume of 20 L was used to mix the cement paste. The cement was placed in the

### Table 1 Chemical composition of ordinary Portland cement.

| Chemical Composition (mass %) | SUM |
|------------------------------|-----|
| Ig  Sloss SiO$_2$ Al$_2$O$_3$ Fe$_2$O$_3$ CaO MgO SO$_3$ Na$_2$O K$_2$O TiO$_2$ P$_2$O$_5$ MnO SrO |
| 19.66 | 16.49 | 4.44 | 2.49 | 52.67 | 1.08 | 1.75 | 0.21 | 0.30 | 0.23 | 0.39 | 0.08 | 0.04 | 99.83 |

| Chemical Composition (mass %) | SUM |
|------------------------------|-----|
| Ig  Sloss SiO$_2$ Al$_2$O$_3$ Fe$_2$O$_3$ CaO MgO SO$_3$ Na$_2$O K$_2$O TiO$_2$ P$_2$O$_5$ MnO SrO |
| 19.66 | 16.49 | 4.44 | 2.49 | 52.67 | 1.08 | 1.75 | 0.21 | 0.30 | 0.23 | 0.39 | 0.08 | 0.04 | 99.83 |
mixer and mixed at low speed for 60 seconds with water added for the first 30 seconds. After that, the mixing was stopped for 30 seconds, during which the inside of the mixer was scraped off. Mixing was then carried out once more at a high speed for 90 seconds. No chemical admixture was added because there was a concern that gas would be produced by decomposition due to gamma irradiation. The mixed cement paste was placed in two steps into metal molds (summit mold) measuring 50 mm in diameter and 100 mm in height and molded by goading with a rod and a table vibrator during each step. After molding of the mixed cement paste, the upper parts of the molds were immediately covered with a vinyl sheet and the specimens were then placed in a plastic bag to seal them. The cement paste specimens were then cured in a temperature-controlled room at 20°C for four weeks.

After four weeks of curing, the specimens were demolded, their upper end surfaces polished, and their dimensions and masses measured. From the mass measurements and given a water to cement ratio of 0.3, it was determined that each specimen consisted of approximately 94.5 g of water and approximately 315 g of cement. After the measurement, the specimens were pre-dried in an oven to adjust the water content of the specimens. One group (24 specimens including backup specimens), which were fabricated to simulate the water content in service conditions, were dried at 40°C for two weeks. Another group (23 specimens including backup specimens), which were fabricated to simulate the case with no evaporative water, were dried at 120°C for a week. The group dried at 40°C is denoted as D40 and the group dried at 120°C is denoted as D120. To confirm the degree of drying, the dimensions and masses of the specimens were again measured. As shown in Fig. 1, the water content of D120 was 0.134 (g/g-cement) on average for 23 specimens and that of D40 was 0.239 (g/g-cement) on average for 24 specimens. The specimens shrunk by 3800 μ for D120 and by 2200 μ for D40 on average. After pre-drying, the specimens were sealed with aluminum packaging and stored until the irradiation test.

Eighteen specimens from each group were used for the gamma irradiation test, and another five or six specimens were used as references. The average compressive strength of three two-month-old specimens under sealed curing was 70.6 N/mm².

2.2 Gamma irradiation

A gamma irradiation test was carried out over the course of more than two months at the 60Co gamma irradiation facility of the Takasaki Advanced Radiation Research Institute (TARRI), which belonged to the Japan Atomic Energy Agency and is currently managed by the National Institutes for Quantum and Radiological Science and Technology. Three HCP specimens were enclosed in each of twelve stainless steel containers and irradiated, and the amounts of water released and gas produced were measured. The insides of the containers were filled with argon gas before the start of the irradiation test. This test involved the continuous measurement of hydrogen production under gamma irradiation for more than two months. During the irradiation test, argon gas flowed...
through the containers as a carrier gas at a flow rate of 100 ml/min (0°C, 1 atm.). Argon gas entered from the top of the containers and exited through the bottom together with the released water and gas produced from the HCP. The water and gas were then transported via a piping network to the measurement system. The argon gas flow rate was controlled by mass flow meters positioned between the argon gas cylinders and the containers. The argon gas cylinders and the measurement system were placed outside of the irradiation room and connected to the containers in the irradiation room using a stainless steel pipe with a 3.175 mm (1/8 inch) outer diameter through a hole in the shielding wall. A schematic of the gamma irradiation test system is shown in Fig. 2.

The target values of the gamma dose rate were set to three levels: 1, 5, and 10 kGy/h and the gamma dose rate was controlled by changing the distance between the radiation source and the specimens before irradiation as shown in Fig. 3. To measure the level of each dose rate, two specimens with aminograys, an alanine dosimeter (11 mm in diameter and 50 mm tall) developed by the Japan Atomic Energy Agency and Hitachi Cable (Kojima et al. 1993), were irradiated for an hour. Considering the attenuation that may occur due to the specimen itself, one dosimeter was attached in front of a specimen and the other dosimeter was attached behind another specimen. Measurements were made at the start and end of the irradiation test due to the attenuation of the radiation source that may occur during the irradiation test. The average values recorded at the start and end of the irradiation test by the front and back dosimeters were 7.05, 3.84, and 0.87 kGy/h for the first, second, and third rows, respectively.

The heating temperatures of the specimens during the irradiation test were set to either 60°C, 40°C, or 25°C. To heat the specimens inside the containers, the containers were wrapped with silicone rubber heaters and a heat-insulating material. Since the amount of heat required to keep the specimens at the target temperature value fluctuates depending on the gamma dose rate and the irradiation room temperature, the power of each heater was finely adjusted separately for each container. The temperatures of the specimens during irradiation were measured at five-minute intervals by T-type thermocouples attached to the sides of the middle specimens for each container. The temperature inside the irradiation room was also measured. The temperatures of the specimens and the irradiation room measured are shown in a prior paper (Maruyama et al. 2017). Since the irradiation room was constantly ventilated by air conditioning, the room temperature was almost the same as the outside ambient temperature, ranging from 10 to 20°C during the irradiation test. The specimen temperatures were controlled with an accuracy of approximately ±1°C, except for power outages, maintenance, and temporary stoppages of irradiation, which occurred 42 times and accounted for approximately 19 hours of the total duration of the irradiation test. The irradiation conditions for all twelve containers are shown in Table 2, and the twelve containers were irradiated simultaneously.

![Fig. 2 Schematic of the gamma ray irradiation testing system (Maruyama et al. 2017).](image)

![Fig. 3 Container arrangements (left: elevation view, right: plan view) (Maruyama et al. 2017).](image)
2.3 Measurements

The diameters, heights, and masses of the HCP specimens were measured using a digital caliper CD-20CPX and an electronic balance BL-620S with a precision of 0.01 mm and 0.01 g, respectively, before and after pre-drying and after finishing the irradiation test. The shrinkage strains of the HCP specimens were calculated using these measurements.

During the irradiation test, the released water and gas produced from the HCP specimens by heating and irradiation were transported to the measurement system by argon gas. The amounts of the released water and gas, including hydrogen, oxygen, nitrogen, and carbon dioxide, were measured continuously. The released water was first captured by water accumulators. The water accumulators were 250 ml glass containers filled with approximately 170 g of magnesium perchlorate. Water contained in the gas was absorbed when the gas passed through these containers. The weight increase of the accumulators indicated the amount of released water. In order to prevent the condensation of water in the upstream piping, the entire piping system from the containers to the water accumulators was wrapped with mantle heaters and ribbon heaters, and they were maintained at 45°C. The amount of released water was measured nine times during the irradiation test.

After the water was absorbed by the accumulators, the gas passed through a sample loop of 11.2 ml, after which the retained gas was introduced to a gas chromatograph and analyzed. The gas chromatograph analyses were sequentially performed for all containers. The time needed to analyze one container was approximately eight minutes, and the analysis of twelve containers took approximately one-hundred minutes. Gas from the containers that were not analyzed was released into the atmosphere after passing through the water accumulators. A GC-8AIT gas chromatograph made by Shimadzu Corporation was used for analysis of the gas. For the measurement, the detector was a thermal conductivity detector (TCD), the carrier gas was argon (with a purity of 99.999%), and the flow rates were 40 ml/min for H₂, O₂, and N₂, and 70 ml/min for CO₂.

After the gamma irradiation test, the amounts of evaporable water and CBW in the HCP specimens were measured. Measurements were taken for each of the two specimens in the six containers indicated by the circles in Table 2 along with the reference specimens of D40 and D120 that were stored in a sealed condition at 20°C after pre-drying. The specimens were dried at 105°C until the mass loss became constant, and the evaporable water content was calculated as the mass loss that occurred during the 105°C drying cycle. Following this, the specimens were further dried at 600°C until the mass loss became constant, and the CBW content was calculated as the mass loss that occurred during the 600°C drying cycle.

3. Experimental results

3.1 Water release

Figure 4 shows the water content of the HCP specimens during the irradiation test, which was calculated by subtracting the water collected by the water accumulators from the initial water content before irradiation. In each container with D40 specimens, the water content decreased sharply at the start of irradiation, gradually leveled out. A large amount of water was released from Container 1, 3, and 5 that were heated at 60°C, while that released from Container 11, heated at 25°C, was small. Therefore, it was found that at higher temperatures, more water was released. In comparison, for the containers that were heated at the same temperature, a difference in the dose rate was not observed. As D120 was pre-dried at 120°C before the irradiation test, the water released was found to be minimal during the irradiation test. According to the results of the mass measurement conducted just before the irradiation test, the mass of each specimen of D120 and D40 increased by approximately 0.3 to 0.4 g and 0.1 g, respectively, in comparison with their masses following the pre-drying process. It was determined that the specimens must have reabsorbed water from the atmosphere during their preparation before irradiation, such as during the specimen setting or during the measurement of their mass and dimensions. The finding that
the mass increase of D120, which was drier by pre-drying at a higher temperature, was larger than that of D40 supports this. The water released from Container 2, 4, and 6 of D120 during irradiation was more than the content of the reabsorbed water. This means that a small amount of evaporable water remained in the HCP after pre-drying.

3.2 Mass and dimension changes of the specimens
The mass losses and shrinkage strains of the HCP specimens following the irradiation test are shown in Figs. 5 and 6, respectively. These values denote the changes that occurred during the irradiation test. It was found that the higher the temperature was during irradiation, the larger the mass loss was for both D40 and D120. It was observed that the mass losses were almost consistent with the decrease in water contents, as shown in Fig. 4. As for D40, the higher the temperature during irradiation, the more the diameter and the height of the specimen were observed to have shrunk due to drying. Considering D120, the dimension changes were small, as these samples had already been pre-dried at a high temperature. The total shrinkage strains, which are the summation of the amount of change that occurred during pre-drying and the irradiation test, are shown in Fig. 7. The total shrinkage strain of D120, which was pre-dried at a high temperature and subsequently irradiated, and that of D40, which was dried under irradiation, were found to be nearly identical. The impact of gamma irradiation on the drying shrinkage was therefore not significant.

3.3 Hydrogen gas production
The hydrogen production rates are shown in Fig. 8. The hydrogen production rates of D40 reached an initial peak within a few hours to two days from the start of irradiation, and afterward dropped sharply. The rates gradually evened out and were almost constant at the end of the irradiation test. The three dose rates at each row are indicated in the figures by the dashed lines. The hydrogen
production rate at its peak value was highest with a higher dose rate. Among the containers exposed to the same dose rate, it was found that the higher the temperature that was used, the higher the hydrogen gas production peak. The rate of gas production for the containers at higher temperatures dropped more sharply following their peak values. This was because the containers heated at higher temperatures more easily released evaporable water from the HCP specimens.

The hydrogen production rates of the D120 specimens that were pre-dried at 120°C and had no evaporable water content was about one-tenth of those of the D40 specimens. As described earlier, it was possible that the D120 specimens re-absorbed and contained a small amount of evaporable water, and that this may be the main source of the observed hydrogen production. Unlike D40, it took about two to ten days for the D120 specimens to reach their peak hydrogen production values following the beginning of irradiation. In both D40 and D120, the lower the hydrogen production rate, the longer it took for these values to reach their maximum. We considered that...
this was because the hydrogen gas produced inside the HCP specimens was trapped in the microstructure of the HCP and required time to be released from the HCP. The actual hydrogen production rate before the peak might therefore be higher than the measured hydrogen production rate. As with D40, the peak production rate of the container with a higher dose rate was higher. A comparison of the containers with the same dose rate indicated that the higher the temperature, the higher the peak. Since the amount of water released from the D120 specimens during the irradiation test was small, the decreasing slopes of the hydrogen production rates after their peak values were more gradual than those of the D40 specimens. For both D40 and D120, the oxygen and nitrogen contents were less than the lower detection limit, and carbon dioxide was not detected.

The cumulative quantity of hydrogen produced by the D40 containers at the end of the irradiation test ranged from 5.5 mmol to 24.5 mmol, which corresponds to a mass of 0.01 g to 0.05 g, respectively, considering that the mass of 1 mol of H₂ is 2 g. These values are extremely minor as compared to the amount of water released (27.0 to 69.6 g), indicating that the decrease in the mass of the specimens during the irradiation test resulted almost entirely from the released water.

### 3.4 Evaporable and chemically bound water

The evaporable water and CBW contained in the HCP specimens after finishing the irradiation test, along with the contents of each of the sealed reference specimens stored at 20°C, are shown in Fig. 9. The quantity of CBW in all the measured specimens was almost constant, independent of the gamma dose rate and temperature. The higher the temperature, the more the evaporable water was found to decrease, however, differences in the evaporable water content was found independent of the dose rate. This result is consistent with the results of the water released and mass loss, as stated earlier.

### 3.5 G-values of the hydrogen production

The amount of hydrogen produced from HCP by radio-lysis depends on the water content and state of the water present in the HCP. The G values were calculated using the hydrogen production rate measured under the condition where the water content was continuously changing. The influences of the water content, dose rate, and temperature on the G value were also examined. The G value is defined as the number of chemical species produced or consumed when a substance absorbs the energy of 100 eV, as described in Equation (1). The G value of the hydrogen production can be expressed with Equation (2).

$$G = \frac{N}{E} \times 100 \left[ \frac{1}{100 \text{eV}} \right] \quad (1)$$

where $N$ is the number of chemical species produced or consumed and $E$ is the amount of energy absorbed [eV].

$$G = \frac{\frac{n \times 6.02 \times 10^{23}}{m \times D / (1.602 \times 10^{-19})} \times 100}{A \times \frac{n}{m \times D}} = \frac{A \times \frac{n}{m \times D}}{1/100 \text{eV}} \quad (2)$$

where $n$ is the hydrogen production rate [mol/h], $m$ is the mass of the substance absorbing the energy [g], $D$ is the gamma ray dose rate [kGy/h = J/g/h], and $A$: $9.648 \times 10^6$.

For the calculation of the G values, the energy absorbed by the total water in the HCP, the summation of the evaporable water and the CBW, was applied to the “m” in Equation (2). The G values plotted as a function of the irradiation time are shown in Fig. 10(a). The G values from before the hydrogen production rate reached a peak value are not plotted as during that period the evaluated hydrogen production rate might have been lower than the actual rate, as previously described.

The G values of the D40 containers at the start of irradiation were in the range of 0.28 to 0.42, and became larger as the temperature increased. However, the decrement rate of the G values of the D40 containers at higher temperatures increased, and at the end of irradiation, the G values with higher temperature became smaller. This was because the G values predominantly depended on the amount of the evaporable water. When comparing the D40 containers irradiated at the same temperature, the decrement rate of the G values increased for containers irradiated at higher dose rates. The G values of the D120 containers were within the range of 0.03 to 0.07, which were an order of magnitude smaller than that of the bulk water, 0.45 (Draganić and Dražanić 1971). The G value of each D120 container is shown in
Table 3. These G values were larger at higher irradiation temperature. The G values of D120 were almost constant throughout the irradiation test because the water contents of D120 specimens only changed minorly. As irradiation time passed and HCP dried, the evaporable water was lost and only the CBW remained, and therefore, G values of D40 approached to that of D120. The G values of D40 containers were also lower than that of the bulk water (0.45). This is because the G values here were calculated assuming that the radiation energy absorbed by the total water was entirely used for the formation of hydrogen.

The G values are shown as a function of the total water content in Fig. 10(b). Water contents lower than 0.134 g/g-cement corresponded to CBW, and this is indicated by the blue area in the figure. As indicated by the gray area in this figure, when the total water content increased, the G values increased. This supports that the evaporable water in the HCP is susceptible to radiolysis while the CBW is less likely to decompose. Considering the G values of D120, it was seen that the G value was small but not zero (0.03 to 0.07) when no evaporable water existed and only CBW was present. This means that the CBW should be decomposed, albeit slightly. In a comparison of containers whose dose rate was the same, the G value of the container at a higher temperature was larger. This trend can also be seen in another study (Elliot et al., 1993), where the yields of hydrogen obtained under gamma irradiation increased with increasing temperature up to 300°C. This is related to the diffusion and reactivity of decomposition products as they are highly dependent on temperature. Comparing the containers whose temperatures were the same, in the range of low water contents, the G value of the container with a lower dose rate was larger.

The G values of the hydrogen production of D40 that were calculated assuming that the radiation energy absorbed by only the evaporable water was used for the formation of hydrogen are shown in Fig. 11. In this calculation, “n” of Equation (2) was calculated by subtracting the hydrogen production rate estimated based on the G values of CBW from measured values. When the evaporable water, which is the main resource of hydrogen production, decreased, these G values approached to zero. In the range of water content observed in this test, in case of low dose rate, these G values tended to converge to a constant value when the evaporable water exceeded a certain value, while, in case of high dose rate, these G values increased as evaporable water increased. The different trend by the dose rate was observed. However, the G values of all cases grew with increasing

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**Table 3** G values of hydrogen production obtained from D120 assuming that the radiation energy absorbed by CBW was used for the formation of hydrogen.

| Container ID | Pre-drying Temp. (°C) | Irradiation Temp. (°C) | Gamma Dose Rate (kGy/h) | G value |
|--------------|------------------------|------------------------|-------------------------|---------|
| #2           | 7.05                   | 60                     | 0.04 - 0.06             |         |
| #4           | 3.84                   | 40                     | 0.04 - 0.06             |         |
| #6           | 0.87                   | 25                     | 0.04 - 0.05             |         |
| #8           | 3.84                   | 40                     | 0.05                    |         |
| #10          | 0.87                   | 25                     | 0.03 - 0.04             |         |
| #12          |                        |                        |                        |         |

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**Fig. 10** G values of hydrogen production assuming that the radiation energy absorbed by total water including CBW and evaporable water was used for the formation of hydrogen as function of (a) the irradiation time and (b) the total water content. The blue area in (b) shows the chemically bound water content (0.134 g/g-cement).
evaporable water content and exceeded the G value of the bulk water (0.45). Considering that water inside HCP in this range of water content should be adsorption water or condensed water residing in nano-scale space, the effect of energy transfer from solid phase is deduced.

4. Discussion

In this gamma irradiation test, the release of evaporable water and production of hydrogen gas from HCP were observed. The hydrogen production from the HCP that contained only CBW was very small. It is notable that hydrogen production of D120 might result from the water reabsorbed from the atmosphere. Using a G value of 0.07, the highest value determined for D120, it was calculated that 2 to 3% of the CBW was decomposed when the HCP was subjected to 200 MGy of gamma irradiation, which is a reference value for the aging management of nuclear reactor buildings in Japan (AIJ 2015; KEPCO 2016; Maruyama et al. 2017). This reference value was determined based on the figures shown by Hilsdorf et al. (1978). Gamma irradiation causes the Si-OH bond and Ca-OH bond in the HCP to ionize and form Si-O-Si, Si-O-Ca, and Ca-O-Ca bonds (Gartner et al. 2017), and this evolution is similar to that caused by elevated temperatures and drying (Cong and Kirkpatrick 1995).

Concerning the physical properties of the HCP, the compressive strength of the HCP does not change in the range of 100 to 200°C (US-NRC 2010). Therefore, the alterations resulting from these processes will not cause a change in the physical properties of the HCP any more than those caused by heating and/or drying. In addition, in circumstances where water exists around and inside the C-S-H, the influences described above may not occur because any changes are negated via dissolution and precipitation in a high-energy state. It may therefore be concluded that the impact of gamma irradiation on the physical properties of the HCP is almost the same as that induced by heat and/or drying, and a significant impact does not seem possible.

The G values of the hydrogen production assuming that the radiation energy absorbed by only the evaporable water was used for the formation of hydrogen were larger than that of the bulk water when the evaporable water exceeded a certain value. Yin et al. (2019) also reported that hydrogen production from C-S-H under gamma irradiation was enhanced as compared to that from the bulk water and that more hydrogen was produced with a higher specific surface area. One of the reasons for the enhancement of G value is deduced to be a result of the interface effect. That is, the energy absorbed by the solid phase in the HCP was transferred to the evaporable water through the interface between the solid phase and water, thereby indirectly inducing the radiolysis of water. Some of the energy absorbed by the evaporable water was transferred to the solid phase though. HCP has a high specific surface area with a nanoscale microstructure and therefore may be subjected to the interface effect. For confirmation of the interface effect, G values in a wider range of water content should be examined. If the interface effect exists, the trend of G values as shown in Fig. 12 is expected. When there is no evaporable water, the G value is zero because the resource of hydrogen production is nothing [see (i) in Fig. 12]. In the range below a certain amount of the evaporable water, G value grows over that of the bulk water due to the interface effect [(ii) in Fig. 12]. In the range above a certain amount of the evaporable water, G value approaches to that of the bulk water with increasing evaporable water

![Fig. 11 G values of hydrogen production obtained from D40 assuming that the radiation energy absorbed by only evaporable water was used for the formation of hydrogen as function of the total water content. The blue area shows the chemically bound water content (0.134 g/g-cement).](image-url)
because the interface effect dilutes ([iii] in Fig. 12).

Recently, with the use of $^1$H-NMR relaxometry, the evaporable water content in sealed HCP whose water to cement ratio was less than 0.48 was determined to be gel pore water or interlayer water and not capillary water (Muller et al. 2013). Therefore, in general, the evaporable water content in the concrete of a reactor building is considered to exist in either gel pores or interlayer spaces. Recent studies (Valori et al. 2010; Maruyama et al. 2019) have elucidated that both gel pores and interlayer spaces are confined by C-S-H sheets, and that the gel pores may be transformed into interlayer spaces in accordance with the drying process. From this point of view, the evaporable water is generally confined by C-S-H sheets and water molecules within this structure are approximately 1.0 nm (a distance of approximately four water molecules) from the surface. In the present study, drying at 40°C, which is less than 30% RH at 20°C, is the state in which the existing water molecules were adsorbed as the first monolayer (Badmann et al. 1981). Therefore, this trend may be extrapolated towards water molecules covering the entire surface of the C-S-H, which may exist at 30% RH and 20°C. In the future, to elucidate the impact of the solid phase-water interface, the water molecules in the second and further adsorbed water layers within the gel pores and interlayer spaces should be confirmed experimentally.

5. Conclusion

A $^{60}$Co Gamma irradiation test of HCP with different water contents was conducted under different temperatures and irradiation dose rates for more than two months. The following findings were obtained:

(1) When the HCP was dried at 40°C or 120°C as a pretreatment, the influence of subsequent gamma irradiation on the drying shrinkage was not significant.

(2) During the gamma irradiation, hydrogen was produced from the HCP dried above 40°C, while the production of oxygen, nitrogen, and carbon dioxide were not observed.

(3) Hydrogen gas was determined to be mainly produced from evaporable water. The G value of the hydrogen production assuming the radiation energy absorbed by the total water composed of CBW and evaporable water was ranging from 0.03 to 0.42.

(4) When it is assumed that the radiation energy absorbed by only evaporable water was used for the formation of hydrogen, in case of low dose rate, the G value tended to converge to a constant value when the evaporable water exceeded a certain value, while, in case of high dose rate, the G value increased as evaporable water increased. However, the G values of all cases grew with increasing evaporable water content and exceeded the G value of the bulk water (0.45).

(5) The G values were larger as the temperature of HCP during irradiation were higher.

(6) The G value of the hydrogen production for CBW was ranging from 0.03 to 0.07, which were an order of magnitude smaller than that of the bulk water (0.45). The CBW was not susceptible to gamma irradiation. Only 2 to 3% of the CBW was estimated to be decomposed by 200 MGy of gamma irradiation. The changes in the physical properties of HCP under gamma irradiation can be induced mostly by heating and drying during the irradiation.

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