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ARTICLE

Effect of pH on water radiolysis enhanced by Zirconium oxide particles

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We have experimentally studied the effect of pH on the observed yield of Hydrogen (H₂) generation by Co-60 gamma radiolysis of water with zirconium oxide particles. The particles we used were a commercial monoclinic zirconia powder (m-ZrO₂) and an oxidation product of zircaloy-4. The oxidation product was crushed to the particle with a median particle diameter of 3 μ m and a specific surface area was 1.27 m²/g. The median particle diameter and specific surface area of m-ZrO₂ were 3 μ m and 19.6 m²/g. 10 wt% of the oxidation product or m-ZrO₂ was added to water whose pH was adjusted with KOH and H₂SO₄. The observed H₂ yield from the radiolysis of the solutions became high in a specific pH range. In addition, the contributions of only the oxides to the hydrogen generation, of both the m-ZrO₂ and the oxidation product of zircaloy-4 tended to increase in proportion to the pH value around pH7 and indicated the effect of enhancing hydrogen generation above pH7. From these facts and the measurements of particle distribution and zeta potential, we conclude that pH dependence on the water radiolysis that is enhanced by zirconium oxides is due to changes in the pH value of the mixture solution induced by the added particles, changes in charging conditions of the particles, and the differences in the dispersion state of the particles in the aqueous solution.

Keywords: hydrogen generation; water radiolysis; pH; Zirconium oxide particle; G-value

1. Introduction

Water radiolysis is a decomposition of water through a physical or chemical reaction phase caused by irradiating water with ionizing radiation such as gamma rays. The chemical species, such as ionized molecules, electrons, and exciting water molecules, produced by the radiation generate molecular hydrogen (H₂), hydroxyl radicals, and so on. Ref. [1] reported that the amount of H₂ generated by the water radiolysis is affected by the presence of several oxides. In particular, zirconium oxide and uranium oxide are classified as the best oxides that increase the amount of H₂ produced by radiolysis from surface-adsorbed water.

Waste from severe accidents at a nuclear reactor is expected to contain oxidation products of zirconium alloy, which is used as a fuel cladding material, and it is assumed to be present in water. Therefore, we investigated the effect of the zirconium alloy (Zircaloy-4) oxidation product on H₂ generation by Co-60 gamma-ray radiolysis in water [2]. The H₂ yield of water radiolysis is defined by the G-Value expressed in the amount of H₂ per Joule of absorbed dose. In our study, the observed H₂ yield, G(H₂) (mol/J), was calculated from the proportionality of the absorbed dose (Gy=J/kg) of the irradiated solution and H₂

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gas generation (mol/kg). We found the $G(H_2)$ was enhanced by added the oxidation product of zircaloy-4. The enhancement of H_2 production seems to depend on either the specific surface area or particle size of the oxidation products, but it was not certain which was dominant.

To clarify whether the particle size of the oxidation product affects H_2 generation, we crushed the oxidized zircaloy-4 into various-sized particles and investigated the effect of these particles on H_2 generation by water radiolysis. **Figure 1** shows that $G(H_2)$ increases significantly as the median particle diameter of the oxidation product is reduced [3].

We found the particle size of the oxidation product influences the H₂ generation. Especially the presence of particles that have a median particle diameter smaller than $60 \mu m$ the G(H₂) became larger than that of only distilled water. The size of particle was added at 10 wt% is also related to the total surface area of the particles in water. The G(H₂) per surface area calculated from the specific surface area of the oxidation products and the amount of the added particles were constant regardless of the particle size. We concluded that the enhancement of H₂ generation by the oxidation products was mainly due to the surface area of the added particles.

Regarding the effect of oxide particles dispersed in water on hydrogen evolution by water radiolysis, Ref. [4]

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2.0E-08 1.0E-08 0.0E+00 0 100 200 300 400 500 Median Particle Diameter (μm)

Oxidation Product

Distilled Water

Figure 1. The dependence of the $G(H_2)$ on the median particle diameter of the oxidation product [3].

reported using nanoparticles of TiO_2 and Al_2O_3 . It has indicated that the hydrogen yield was enhanced mainly by the effective surface area of the nanoparticles regardless of chemical species.

In our previous study [3], we compared the G(H₂) of 10 wt% solutions with the addition of commercial monoclinic zirconia powder (m-ZrO₂) or the oxidation product of zircaloy-4 with the same particle size.

The dashed line in Figure 2 indicates the $G(H_2)$ for distilled water (1.8×10^{-8} mol/J). The G(H₂) of water added the oxidation particles became greater than that of the only distilled water. If these enhancements depend on only the surface area of the added particles, we can't explain why G(H₂) was higher for the oxidation product with a smaller specific surface area than for m-ZrO₂. We considered that there is a factor other than the surface area of the particles that can enhance hydrogen generation. The pH of the distilled water we used was 5.7. The pH of the 10wt% solutions with m-ZrO₂ and the oxidation product were 5.4 and 6.2, respectively. We estimated that the change in pH of the solution to which the particles were added would affect hydrogen generation. To investigate the effect of the pH of the irradiated solution on the amount of hydrogen generated, we conducted the following experiments.

2. Material and methods

2.1. Chemicals and materials

All solutions used in this experiment were prepared using distilled water (SOGO Laboratory Glass Works Co., Ltd.). Potassium Hydroxide (Nacalai tesqueinc., KOH) and Sulfuric Acid (Nacalai tesqueinc., H₂SO₄) were used to adjust the pH of the solution. These chemicals used were Guaranteed Reagent (GR) grade.

A zircaloy-4 plate (New Metals and Chemicals Ltd.) which dimensions are 0.914 mm in thickness by 100 mm in width and 100 mm in length and a dry air (Shimakyu Co., Ltd.) which consists of O_2 21% and N_2 balance were used to make the oxidation product. The zircaloy-4 plate consists of Sn 1.44%, Fe 0.20%, Cr 0.10%, Al 0.01%, Si



Figure 2. Comparison of the G(H₂) of the commercial zirconia and the oxidation product of zircaloy-4 [3].

0.007% and Zr balance.

Commercial monoclinic zirconia powder (Wako Pure Chemical Industries, Ltd., m-ZrO₂) was used to compare with the oxidation product of zircaloy-4.

Potassium Dichromate (Nacalai tesqueinc., K₂Cr₂O₇) was used for a chemical dosimeter.

2.2. Oxidation of zircaloy-4

The zircaloy-4 plate was cut into pieces (10 \times 20 \times 0.914mm) before oxidation. 4 pieces of the zircaloy-4 were placed on a quartz boat in a quartz reaction tube which was set into a ceramic electric tubular furnace (Asahi-rika Co., Ltd. ARF-50KC). The room in the quartz reaction tube was replaced with the dry air. The furnace temperature was raised to 1100°C by a rate of 10°C/min. Then the zircaloy-4 pieces were heated at 1100°C for 4 hours under 0.5 L/min dry air condition. Thereafter, the furnace was cooled to room temperature over 5 hours. The dry air was flowing in the quartz reaction tube until the pieces were cooled around room temperature. The oxidized pieces were crushed using an agate mortar well and classified with a stainless-steel sieve which opening was 20 µm. The oxidation of zircaloy-4 was confirmed by X-ray Diffraction measurement.

2.3. Characterization of the oxidation products

Particle size distribution of the oxidized particle and m-ZrO₂ were measured using a laser scattering particle size distribution analyzer (HORIBA Ltd. LA-960) with a wet method. X-ray Diffraction (XRD) of the particle was analyzed by a powder diffractometer (Rigaku Co. Miniflex600) at 40kV and 15mA, using Cu-K α radiation. The phase composition was obtained with Rietveld analysis module of Integrated X-ray powder diffraction software (Rigaku Co. PDXL2). The specific surface area of the particle was calculated by Brunauer-Emmet-Teller (BET) method using adsorption isotherms with H₂O at 298.15K with BELSORP-max (BEL Japan Inc.).

4.0E-08

3.0E-08

Table 1. The features of the oxidation products.

Oxidation Product	Median Particle Diameter in a distilled water [µm]	Phase composition		Specific Surface
		Monoclinic ZrO ₂ [%]	Tetragonal ZrO ₂ [%]	Area [m ² /g]
Oxidation Product of Zircaloy-4	3	99	1	1.27
m-ZrO ₂	3	100	0	19.6

2.4. Water radiolysis

We prepared the solutions in which were adjusted the pH from pH2 to pH12 with KOH or H₂SO₄. The aqueous solution was contacted with the oxidation product of zircaloy-4 or m-ZrO₂ in a 4ml glass vial (Chromacol, Ltd. 4-SV). The amount of the particles was calculated to the weight fraction to be 10%. The height of the mixture solution was adjusted to 1cm in the vial. The mixture solution was not deaerated. The vial containing the mixture was stirred at 3000 rpm for 2 minutes using a vortex mixer (ELMI, V-3 SkyLine Vortex Mixer) after sealed with a septum. There were the aqueous phase and the air phase in the vial. As a control, the pH-adjusted water without particle was also prepared. The pH values of these solutions were measured by a pH meter (HORIBA Ltd. D-12).

These solutions were irradiated with a gamma-ray at an average dose rate of 4-5 kGy/h by a Co-60 source in the National Institutes for Quantum and Radiological Sciences and Technology. These solutions and chemical dosimeters (1mM $K_2Cr_2O_7/0.4M H_2SO_4$) were irradiated simultaneously for 30, 60, 90 and 120 minutes at room temperature. After the irradiation, these vials were stirred at 3000 rpm for 2 minutes using a vortex mixer.

The absorbed doses of the solutions were calculated from the measurement of absorbance of the chemical dosimeter at 350nm using a UV-Visible spectrometer (JASCO Co. V-550). H₂ gas concentrations of the air phase in the vials were measured with a gas chromatograph system (GL Sciences Inc. GC-3200W) equipped with a thermal detector (TCD) and a molecular sieve column using argon carrier gas. The detected H₂ peak was calibrated with the standard H₂ gases. The G(H₂) (mol/J) was calculated from the proportionality of absorbed dose (Gy=J/kg) and H₂ production (mol/kg) for all solutions.

2.5. Cluster size and Zeta potential measurement in the pH-adjusted solutions

Particle size distribution of the oxidation product of zircaloy-4 and m-ZrO₂ in the mixture solutions adjusted the pH was measured using a laser scattering particle size distribution analyzer (HORIBA Ltd. LA-960) with a batch cell. The pH of distilled water was adjusted between 1 and 14 with KOH or H₂SO₄. The particle was mixed with the solutions and stirred well. After stirring, the solution was poured into the batch cell, and measured the particle size distribution. Since the median diameter of particles may change under different solvent conditions even for the same solid particles, the median diameter in a pH-adjusted aqueous solution was defined as the cluster size. The cluster size was detected from the particle size distribution of the pH-adjusted mixed solution.



Figure 3. pH dependence of the observed hydrogen yield.

Zeta potential of both the oxidation product of zircaloy-4 and m-ZrO₂ measurements were performed in the pH 2-13 using an electrophoretic light scattering zeta potential analyzer (Malvern Panalytical Ltd. Zetasizer pro).

3. Results

The features of the oxidation product and the commercial zirconia powder are in **Table 1**. Both the oxidation product of zircaloy-4 and m-ZrO₂ consisted of almost monoclinic zirconium oxide. The oxidation product was crushed to the particle with a median particle diameter of 3 μ m in a distilled water and a specific surface area is 1.27 m²/g. The median particle diameter and specific surface area of m-ZrO₂ were 3 μ m in a distilled water and 19.6 m²/g.

Figure 3 shows the dependence of $G(H_2)$ on the pH of the solution. A dashed line was added to show that the $G(H_2)$ of only distilled water (pH=5.7) is 1.8×10^{-8} mol/J. Most of the $G(H_2)$ of the pH-adjusted water with the particles became greater than the $G(H_2)$ of the distilled water.

Focusing on the pH-adjusted water, it appears that the $G(H_2)$ and pH trends differ between below and above pH8. Ref. [5] reported that the hydrogen generation to a gas phase from water with a headspace by water radiolysis has a different trend depending on the pH of the water; at pH8 or below, the amount of hydrogen generated is still small, but at pH8 or above, that amount is increased due to the influence of oxygen species produced by water radiolysis. Therefore, the results for the pH-adjusted water in Figure 3 were divided into two groups, one below PH8 and the other above pH8, and two approximation straight lines were attached.

4. Discussion

By changing the pH of the solution, the radiolytic hydrogen yield of the pH-adjusted water to which the particle was added changed. The $G(H_2)$ values of the commercial zirconia or the oxidation product of zircaloy-4 in the distilled water of Figure 2 were slightly different from those at the same pH in Figure 3. This means that the reagents were added for pH adjustment might depress the hydrogen generation of water radiolysis. The G(H₂) of only the pH-adjusted water without particle addition varied with the pH. Ref. [6] reported that the primary yield of H₂ on water radiolysis is almost constant in the pH value between 3 and 11. Hence, we inferred that this change in $G(H_2)$ is due to the reaction that occurred while the initial chemical species produced by water radiolysis reached to the gas phase. It seems that the $G(H_2)$ of only pH-adjusted water were different trends below or above the pH8. So, the results for the pH-adjusted water in Figure 3 were divided into two groups, one below PH8 and the other above pH8, and two approximation straight lines were attached. These lines show that the change in $G(H_2)$ at pH8 or below was small, and at pH8 or higher, it rapidly increased as the pH increased. This trend in the $G(H_2)$ of the pH-adjusted water was consistent with the effect of pH on water radiolysis reported by Pamela et al. [5].

Therefore, we used the following method to evaluate the only particle contribution to radiolytic hydrogen generation.

Assuming that the energy of gamma rays irradiating water or a solid causes radiolysis of water and independently produces hydrogen, $G(H_2)$ can be expressed by the following equation.

$$G(H_2) = G_{water} \times f_w + G_{ox} \times f_{ox}$$

= $G_{water} + (G_{ox} - G_{water}) \times f_{ox}$ (1)

Where G_{ox} is the hydrogen generation term due to energy deposited to the oxide or oxidation product [7]. f_w and f_{ox} are the absorption fractions of water and solid, respectively, corresponding to the fraction of energy imparted to them ($f_w + f_{ox} = 1$). f_{ox} is calculated as follows.

$$f_{ox} = w_{ox} \times (\mu_{en}/\rho)_{ox}$$

$$\div [w_w \times (\mu_{en}/\rho)_w + w_{ox} \times (\mu_{en}/\rho)_{ox}] \quad (2)$$

Where $(\mu_{en}/\rho)_w$ and $(\mu_{en}/\rho)_{ox}$ are the mass energy impartation coefficient for a photon of 1.25 MeV and w_{ox} is the weight fraction of ZrO₂ [8].

 G_{ox} at each pH was obtained from $G(H_2)$ and G_{water} which was calculated from the approximate lines of the pH-adjusted water in Figure 3.

The relation between pH and G_{ox} is shown in **Figure 4**. To show the trend of G_{ox} changes around pH7, two approximate lines in the range of pH5 to pH9 were added to Figure 4. Around pH7, the G_{ox} of both the m-ZrO₂ and the oxidation product of zircaloy-4 tended to increase in proportion to the pH value. The dependence of G_{ox} on the



Figure 4. pH dependence of the Gox.

pH suggests that the concentration of H^+ or OH^- affects the enhancement of hydrogen generation by the particles. The points above the dashed-dotted line with $G_{ox} = 0$ mean that the presence of the powder has an enhancing effect on radiolytic hydrogen generation. The contribution of the particles to radiolytic hydrogen generation depends on the pH of the mixed solution, which had the effect of enhancing hydrogen generation above pH 7.

In the radiolysis of water at pH<8, hydrogen generated as a result of ionization or excitation of water molecules is decreased by reacting with hydroxyl radicals in the water. The hydroxyl radical in water reacts also with hydrogen peroxide and oxygen radicals, but the concentration of the hydroxyl radical is still high in the pH range of 5 to 8 as reported by Jiju et al. [9]. Thereby, the concentration of hydrogen reaching the gas phase is determined by the reaction of hydroxyl radicals with hydrogen in water.

Particles present in water release hydrated electrons through ionization or excitation due to interaction with gamma rays. The released hydrated electron reacts with oxygen to generate oxygen radicals, which are responsible for decreasing hydroxyl radicals in the water. Other hand, it has also been reported that these hydrated electrons generate hydrogen through a reaction with water molecules [10]. We speculated that the relationship between Gox and pH around pH7 is the result of the hydrated electrons released by particles being captured by hydrogen ions around the particles, suppressing the decrease in hydroxyl radicals. The reason why Gox had deviated from the approximate straight lines below pH3 and above pH11 is assumed to be due to the capture of hydrated electrons emitted from the particles or the reaction between the hydrated electrons and water molecules reaching a limit.

The G_{ox} values were almost below zero at pH<7. By the comparison with $G(H_2)$ values at the same pH in Figure 2 and Figure 3, the reagents added for pH adjustment might depress the G_{ox} .



Figure 5. Comparison between zeta potential for the $m-ZrO_2$ and the oxidation product of zircaloy-4.

We assumed that the difference in slope between the two approximate lines in Figure 4 was caused by the charged conditions of the particles. Many oxide particles are electrically charged in water. According to the report of Jens et al. [11], the zeta potential of ZrO₂ particles with a diameter of 0.7 micrometers changes depending on the pH, and the particles are not stable against flocculation in aqueous suspensions.

To investigate the charged state of particles near pH 7, we measured the zeta potential of particles in a pHadjusted solution. **Figure 5** shows the comparison between the zeta potential for the m-ZrO₂ and the oxidation product of zircaloy-4. A difference in the zeta potential transitions around pH7 was observed between m-ZrO₂ and the oxidation product of zircaloy-4, with m-ZrO₂ changing slightly more rapidly. By comparing these trends in Figure 5 with the G_{ox} trends in Figure 4, we conclude that the pH dependence of G_{ox} is also affected by the charged condition of the particle.

We reported that the enhancement of H_2 generation by the oxidation products was mainly due to the surface area of the added particles [3]. Hence, we hypothesized that the aggregation by the charged condition changes limiting the effective contact area between the particle surface and water. To investigate whether the conditions of the added particles are affected by the pH of the solution, we measured the cluster size of the particles in the pHadjusted solutions.

Figure 6 shows the cluster size of the zircaloy-4 oxidation product varied with the pH of the solution. It reached the smallest cluster size around pH7 and it was increased in acidic or alkaline solutions. We assumed that the particles were well dispersed in the solution because of the presence of small clusters in the solution.

In the m-ZrO₂ solution, there was no tendency for the clusters to pile up, but there was a tendency for the cluster size to decrease as the solution went from neutral to alkaline. It came to the smallest cluster size around pH13.



Figure 6. pH dependence of the cluster size.

Since these results contrast with the trend of the G_{ox} in Figure 4 which the G_{ox} was maximum above pH11 for m-ZrO₂ aqueous solution and around pH8 for zircaloy-4 oxidation product powder aqueous solution, the change in pH of the solution due to the added particles might affected the dispersion state of the particles, which changed their effective surface area and was reflected in the hydrogen generation of water radiolysis.

5. Conclusions

To investigate the effect of the oxidation product of zircaloy-4 on water radiolysis hydrogen generation, we conducted irradiation experiments of the mixture solutions of varying pH. The $G(H_2)$ of the pH-adjusted water with the oxide added became larger than the $G(H_2)$ of only distilled water and varied with pH. However, the $G(H_2)$ of the pH-adjusted water without the oxides varied too.

The G_{ox} , contributions of only the oxides to the hydrogen generation, of both the m-ZrO₂ and the oxidation product of zircaloy-4 tended to increase in proportion to the pH value around pH7. Especially, the G_{ox} indicated the effect of enhancing hydrogen generation above pH7. The results of zeta potential measurements in each pH solution showed that the pH dependence of G_{ox} is affected by the charged condition of the particle.

The G_{ox} of the oxidation product of zircaloy-4 showed a maximum around pH8 and m-ZrO₂ reached a maximum above pH11. The results of particle cluster size measurements in each pH solution showed that the G_{ox} tended to increase as the particle cluster size decreased.

From these results, we conclude that the enhancement of the hydrogen generation in water radiolysis by the addition of zirconium oxides is due to changes in the pH value of the mixture solution induced by the added particles, changes in charging conditions of the particles, and the differences in the dispersion state of the particles in the aqueous solution.

References

- N.G. Petrik, A.B. Alexandrov and A.I. Vall, Interfacial Energy Transfer during Gamma Radiolysis of Water on the Surface of ZrO₂ and Some Other Oxides, *The Journal of Physical Chemistry B*, 105 (2001), pp. 5935-5944.
- [2] Y. Matsumoto, T.-M.-D. Do, M. Inoue, R. Nagaishi and T. Ogawa, Hydrogen generation by water radiolysis with immersion of oxidation products of Zircaloy-4, *Journal of Nuclear Science and Technology*, 52 (2015), pp. 1303-1307.
- [3] Y. Matsumoto, T. Suzuki, T. Ogawa, M. Inoue and R. Nagaishi, The influence of various sized zircaloy-4 oxidation products on hydrogen generation of the water solution by Co-60 gamma radiolysis, *Mechanical Engineering Journal*, 7 (2020), 19-00562.
- [4] S. Seino, T. Yamamoto, R. Fujimoto, K. Hashimoto, M. Katsura, S. Okuda and K. Okitsu, Enhancement of Hydrogen Evolution Yield from Water Dispersing Nanoparticles Irradiated with Gamma-Ray, *Journal* of Nuclear Science and Technology, 38 (2001), pp. 633-636.
- [5] A. Pamela Yakabuskie, Jiju Joseph and J. Clara Wren, The effect of interfacial mass transfer on steady-state water radiolysis, *Radiation Physics and Chemistry*, 79 (2010), pp. 777-785.
- [6] C. Ferradini and JP. Jay-Gerin, The effect of pH on

water radiolysis: a still question. A mini review, *Research on Chemical Intermediates*, 26 (2000), pp. 549-565.

- [7] Y. Kumagai, A. Kimura, M. Taguchi, R. Nagaishi, I. Yamagishi and T. Kimura, Hydrogen production in gamma radiolysis of the mixture of mordenite and seawater, *Journal of Nuclear Science and Technology*, 50 (2013), pp. 130-138.
- [8] JH. Hubbell and SM. Seltzer, Tables of X-Ray Mass Attenuation Coefficients and Mass Energy-Absorption Coefficients from 1 keV to 20 MeV for Elements Z = 1 to 92 and 48 Additional Substances of Dosimetric Interest, National Institute of Standards and Technology (1995), p. 5632.
- [9] M. Jiju Joseph, C. Byung Seon, P. Yakabuskie and J. Clara Wren, A combined experimental and model analysis on the effect of pH and O₂(aq) on gradiolytically produced H₂ and H₂O₂, *Radiation Physics and Chemistry*, 77 (2008), pp. 1009-1020.
- [10]G. Imanova, Molecular hydrogen production by radiolysis of water on the surface of nano-ZrO₂ under the influence of gamma rays, *Synthesis and Sintering*, 2 (2022), pp. 9-13.
- [11] J. Cordelair and P. Greil, Application of the method of images on electrostatic phenomena in aqueous Al₂O₃ and ZrO₂ suspensions, *Journal of Colloid and Interface Science*, 265 (2003), pp. 359-371.