Rapid Communication

Effect of Gamma Ray Irradiation on Deoxygenation by Hydrazine in Artificial Seawater

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At the spent nuclear fuel pools in the Fukushima Daiichi Nuclear Power Plant, hydrazine has been added to reduce dissolved oxygen in the pool water containing salts. The reduction behavior of dissolved oxygen in seawater with hydrazine in the presence of radiation is unknown. The effect of gamma ray irradiation on deoxygenation by hydrazine in artificial seawater was investigated at room temperature. We placed the artificial seawater with a small amount of hydrazine under gamma ray irradiation at dose rates of 0.3–7.5 kGy/h. The concentration of dissolved oxygen in the solutions was measured before and after the irradiation. The concentration of dissolved oxygen hardly decreased in the absence of gamma radiation in a few hours, whereas it markedly decreased in the presence of gamma radiation. The concentration of dissolved oxygen decreased with irradiation time. At this moment, hydrazine concentration decreased more than twice the dissolved oxygen concentration. This shows that some gamma radiolysis products of hydrazine act as deoxidizers. The concentration of dissolved oxygen in artificial seawater could be decreased by the addition of a small amount of hydrazine in the presence of gamma radiation at room temperature.

KEYWORDS: ***gamma ray, irradiation, solution, hydrazine, radiolysis, dissolved oxygen***

I. Introduction

In the Great East Japan Earthquake, a station blackout occurred following the earthquake and subsequent tsunami at the Fukushima Daiichi Nuclear Power Plant. Consequently, seawater was injected into the spent fuel pool of Unit 2 through Unit 4 for the purpose of cooling the spent fuel, with freshwater injection switched to later. Currently, to inhibit the corrosion of materials in the spent fuel pool, water containing hydrazine (N_2H_4) is injected into the spent fuel pool. This is done to reduce the oxidizer, the dissolved oxygen (DO), contained in the water in the pool.

As of September 2011, the values listed in **Table 1** were disclosed as the water quality of the pool for Unit 4 of the Fukushima Daiichi Nuclear Power Plant [1)]. The concentration of chloride ions (Cl^-) was 997 ppm. The N_2H_4 concentration was 59 ppm. The DO concentration

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Table 1 Concentration and activity of key aqueous solutes in the Unit 4 spent fuel pool in the Fukushima Daiichi Nuclear Power Plant

Date time	Cl^- ppm	N_2H_4 ppm	Cs-137 Bq/L	Cs-134 Bq/L	I-131 Bq/L
2011.9.2 15 : 00	997	59	3.1×10^4	2.2×10^4	ND

ND: Not detected.

Table 2 Chemical composition of artificial seawater (mol/dm^3)

Na^+	Mg^{2+}	Ca^{2+}	K^+	Sr^{2+}	Cl^-	$SO_4{}^{2-}$	$HCO_3{}^-$	Br^-	$BO_3{}^{3-}$	F^-
0.478	0.0547	0.0104	0.0102	0.00016	0.560	0.0288	0.0024	0.00084	0.00045	0.00007

is unknown because data are not provided. The spent fuel is stored in the spent fuel pool and the spent fuel radiates various radioactive products such as gamma rays. In the thermal power plant, and elsewhere, N_2H_4 is used as a deoxidizer for high temperature water, but the deoxidization effect is known to be limited in pure water at room temperature 2). When exposed to radiation, it is reported that N_2H_4 is degraded and the DO concentration is reduced by the reaction of its degradation products with DO 3-6, 8, 9). However, those are the results acquired with pure water, and the reaction behavior of DO and N_2H_4 is unclear in a system that contains seawater components, as in this case.

Hence, in this research, the influence of gamma rays on the reaction behavior of DO and N_2H_4 (deoxygenation) in artificial seawater was studied by irradiating pure water and artificial seawater containing an infinitesimal amount of N_2H_4 at room temperature with gamma rays, and then determining the quantity of DO and N_2H_4 in aqueous solution. In this paper, the comparison and study results are reported on the influences of gamma rays on the reaction behavior of DO and N_2H_4 in seawater and pure water.

II. Experimental Methodology

1. Testing Solution

Solutions of pure water and the artificial seawater Aquamarine (Yashima Pure Chemicals Co., Ltd.), with the addition of 10^{-3} mol/dm^3 of N_2H_4, were used for the test. The main components of artificial seawater are listed in **Table 2**. The chloride ion concentration was 0.560 mol/dm^3 (approximately 18,900 ppm). Special grade hydrazine 1 hydrate (purity 98.0%) was used as N_2H_4. The pH of pure water and artificial seawater at 25°C with the addition of 10^{-3} mol/dm^3 of N_2H_4 was 9.3.

2. Gamma Ray Irradiation Test

The gamma ray irradiation test was conducted in Irradiation Room 2 in Cobalt Building 1 of the Takasaki Advanced Radiation Research Institute of the Japan Atomic Energy Agency. The irradiation with gamma rays was started by pulling up the cobalt (Co-60) radiation source from the pool of the irradiation room and was stopped by pulling it down to the bottom of the pool. The average energy of emitted gamma rays from the cobalt radiation source was 1.25 MeV. The absorption dose rate was controlled by varying the distance of the sample and the

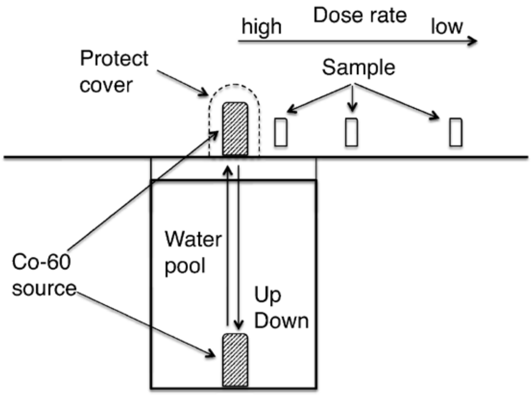

Figure 1 Schematic layout of Co-60 gamma-ray source and samples

Co-60 radiation source, and the absorbed dose quantity by varying the duration of irradiation. **Figure 1** shows a schematic of the positional relationship of the Co-60 radiation source and the samples. In this test, the gamma rays irradiated the samples at room temperature within the absorption dose rate range of 0.3–7.5 kGy/h. The dose rates were within the dose rate distribution ($1–10^6$ Gy/h) of the spent fuel pool of the Fukushima Daiichi Nuclear Power Plant as analyzed and evaluated by us [10)].

The samples for irradiation were pure water and artificial seawater with added N_2H_4, contained in a 25 mL test tube with no air gap and tightly plugged. The absorption dose rate at the position of irradiation was evaluated using an alanine dose meter (Aminogray: Hitachi Cable, Ltd.) The measurement range of the Aminogray was $10–10^5$ Gy.

3. Measurement of DO and N_2H_4 Concentrations

The concentrations of DO and N_2H_4 were measured before and after irradiation with gamma rays. The indigo carmine method was mainly used to determine the DO. The measurement range of this method was $3–34 \times 10^{-5}$ mol/dm^3 (1.0–11.0 ppm). When the determined value was one ppm and lower, a fluorescent DO concentration meter with a measurement range of $0–156 \times 10^{-5}$ mol/dm^3 (0–50.0 ppm) was used. For the determination of N_2H_4, the p-dimethylaminobenzaldehyde method was used. For adjusting the concentration within the measurement range when using this method, the sample was diluted with pure water. The measurement range was $2–234 \times 10^{-7}$ mol/dm^3 (0.005–0.750 ppm).

III. Results and Discussion

1. Deoxygenation Behavior in Pure Water without Irradiation

After tightly plugging a test tube containing 25 mL of pure water and N_2H_4, the temperature was maintained at a specified level for eight hours using an aluminum block constant-temperature tank (at 20, 30, 40, 50 and 65°C). As a point of information, the initial DO concentration of the test fluid was in a supersaturation status higher than atmospheric concentration. The DO concentrations measured at specified times are shown in **Figure 2**. The DO concentration showed a slight decrease after eight hours at 20°C. The decrease at 30°C was several ppm. At

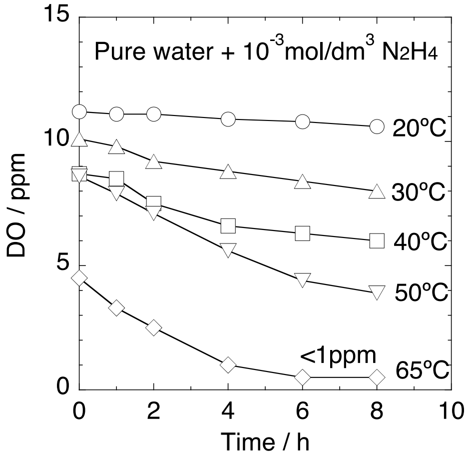

Figure 2 Decreases in dissolved oxygen in pure water with 10^{-3} mol/dm^3 hydrazine at different temperatures in the absence of gamma radiation

65°C, the DO concentration decreased to under one ppm in eight hours.

Thus, DO reduction by N_2H_4 was small at room temperatures of 20–30°C, but increased as the temperature rose.

2. Deoxygenation Behavior under Gamma Ray Irradiation

Pure water and artificial seawater, with the addition of N_2H_4, were irradiated with gamma rays at 7.5 kGy/h for one hour. As before, the initial DO concentration of the test fluid was in supersaturation, higher than air saturation. The DO concentration before and after irradiation is shown in **Figure 3**. For comparison, the DO concentration of a test fluid sample left for one hour with no irradiation (0 Gy/h) is indicated in the same chart. In the non-irradiated condition, the DO concentration after one hour was almost the same as before testing for both pure water and artificial seawater. After the gamma irradiation, both pure water and artificial seawater showed a DO concentration of one ppm or less. The reduction in DO concentration (deoxygenation) was clearly the result of the gamma irradiation. Incidentally, the DO concentration of artificial seawater before irradiation was lower than that in the pure water by approximately one ppm due to the salt content of the artificial seawater. The saturated DO concentration of a 3.5% NaCl solution, with a chloride ion concentration equivalent to the artificial seawater at 20°C, was 7.2 ppm[11)] and was lower than the saturated DO concentration of 9.1 ppm of pure water at the same temperature.

In this test, the temperature of the test water before and after the gamma irradiation was 25–30°C. Considering the temperature dependence of deoxygenation behavior in pure water shown in Figure 2, under the test conditions of this test, the influence of temperature on deoxygenation was small, while the influence of gamma irradiation was large.

3. Relation of Absorption Dose Rate and Deoxygenation Behavior

Pure water and artificial seawater, with the addition of N_2H_4, were irradiated with gamma rays at room temperature for one hour at different absorption dose rates within the range 0.3–7.5 kGy/h. The DO concentration after irradiation is shown in **Figure 4**. For comparison,

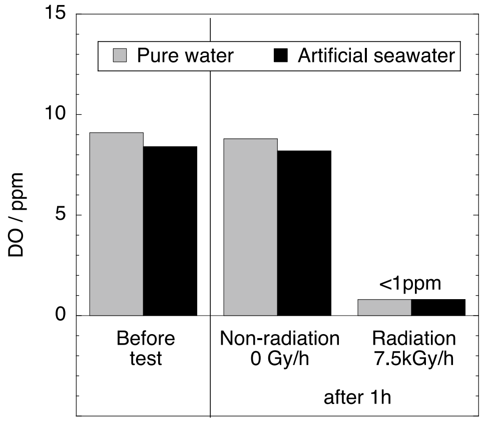

Figure 3 Concentrations of dissolved oxygen in pure water and artificial seawater containing 10^{-3} mol/dm^3 hydrazine at initial and after 1 hour without and with gamma ray irradiation at room temperature

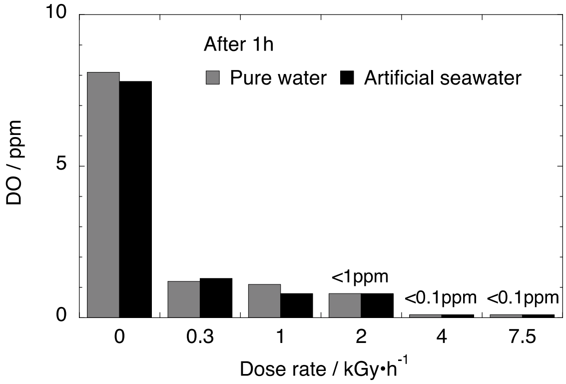

Figure 4 Comparison of concentration of dissolved oxygen with and without gamma ray irradiation at room temperature at different dose rates after 1 hour

the DO concentration of a test fluid sample left for one hour with no irradiation (0 Gy/h) is indicated in the same chart. For both pure water and artificial seawater, the DO concentration was one ppm or less for absorption dose rates of 2 kGy/h and above. The deoxygenation took place within the absorption dose rates in this test.

4. Time-Dependent Behavior of Dissolved Oxygen Concentration and Hydrazine Under Gamma Irradiation

Pure water and artificial seawater, with the addition of N_2H_4, were irradiated with gamma rays at 1 kGy/h at room temperature. The time-dependent DO and N_2H_4 concentrations are shown in **Figures 5** and **6**, respectively. For both pure water and artificial seawater, the DO concentration was one ppm or less as the duration of irradiation increased. Only 10 minutes was required for pure water, and 30 minutes for artificial seawater, in order to decrease to one ppm or less. The concentration of N_2H_4 continuously decreased with increasing duration of irradiation. Both pure water and artificial seawater showed a decrease from the initial concentration of 10^{-3} mol/dm^3 (approximately 33 ppm) to approximately 0.25×10^{-3} mol/dm^3 (approximately 8 ppm) from an irradiating duration of 60 minutes. Within the irradiating dose rate range (0.3–7.5 kGy/h) in this test, the N_2H_4 concentration showed a continuous decrease with increasing irradiating duration.

Usually, in the absence of irradiation, the chemical reaction of N_2H_4 and O_2 is expressed in Eq. (1) 2):

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \tag{1}$$

N_2H_4 and O_2 react with equivalent weights, where the chemical reaction of Eq. (1) progresses with equal concentrations because the molecular masses are equal. However, with irradiation by gamma rays at room temperature, the concentration of N_2H_4 and O_2 did not change with equivalent weights (1:1) as shown in Figures 5 and 6. With an irradiation duration of 60 minutes, the reduction in quantity of N_2H_4 was approximately 25 ppm while the reduction in quantity of DO was approximately 10 ppm.

Based on this, it is considered that N_2H_4 transferred to another chemical species (radiolysis product) and reacted with DO. Ershov et al 6). and Buxton et al 8). explain the deoxygenating reaction in pure water under the copresence of DO and N_2H_4 as follows, based on the measurement of pulse radiolysis:

$$\cdot N_2H_3 + O_2 \rightarrow O_2 \cdot^- + N_2H_2 + H^+ \tag{2}$$

Here, $\cdot N_2H_3$ is a radiolysis of N_2H_4 and is formed by the reaction with $OH\cdot$, a radiolysis of water 6, 8).

$$N_2H_4 + OH\cdot \rightarrow \cdot N_2H_3 + H_2O \tag{3}$$

On the other hand, for the radiolytic behavior of N_2H_4 in pure water with the absence of DO (DO = 0 ppm), several researchers 3, 7) suggest the reaction of Eq. (4):

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2 \tag{4}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{5}$$

Using a test fluid from which DO is completely removed by irradiating with gamma rays for 60 minutes, the determination of ammonium ions NH_4^+ was conducted using the indophenol blue method, and several ppm were detected. Because NH_4^+ is considered to be formed by the dissolution of NH_3 in water, it is further considered that deoxygenation progressed with the reaction of Eq. (2), and after deoxygenation, the reactions in Eq. (4) and Eq. (5) followed.

5. G-Values of Dissolved Oxygen and Hydrazine Under Gamma Irradiation

As shown in Figures 5 and 6, the concentration of DO and N_2H_4 decreased with increasing duration of gamma irradiation. Hence, the relation between gamma ray dose and the reduction in quantity of DO and N_2H_4 was quantified with regard to the G-value. From Figures 5 and 6, the *G*-values $G(-O_2)$ and $G(-N_2H_4)$, with regard to the reduction in DO and N_2H_4, were obtained at every measured time. $G(-O_2)$ and $G(-N_2H_4)$ were summarized with regard to measured time and absorption dose in **Table 3**. The values were $G(-O_2) = 18.0 \times 10^{-7}$ mol J^{-1} and $G(-N_2H_4) = 7.6 - 21.5 \times 10^{-7}$ mol J^{-1} for pure water of pH = 9.3, and $G(-O_2) = 5.8 - 11.0 \times 10^{-7}$ mol J^{-1} and $G(-N_2H_4) = 8.3 - 24.9 \times 10^{-7}$ mol J^{-1} for artificial seawater of pH = 9.3. $G(-N_2H_4)$ of seawater

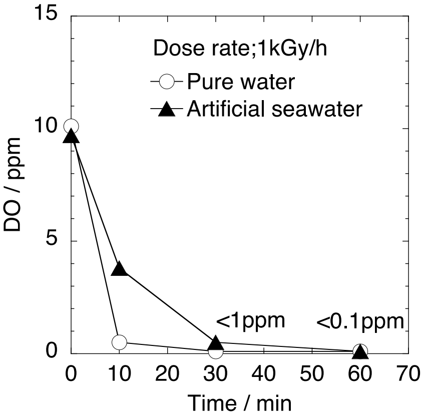

Figure 5 Changes of dissolved oxygen concentration for pure water and artificial seawater at room temperature at a dose rate of 1 kGy/h

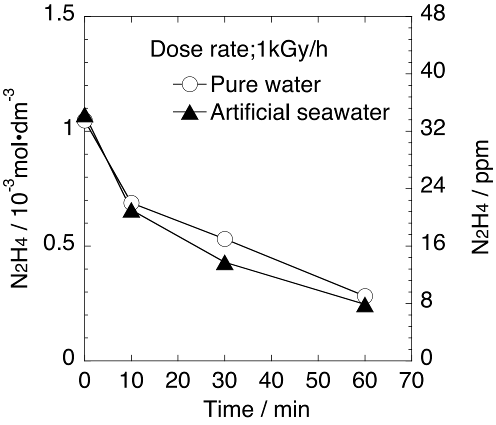

Figure 6 Change in hydrazine concentration in pure water and artificial seawater at room temperature at a dose rate of 1 kGy/h

Table 3 $G(-N_2H_4)$ and $G(-O_2)$ values in pure water (a) and artificial seawater (b) with 10^{-3} mol/dm^3 hydrazine at a dose rate of 1 kGy/h (unit: 10^{-7} mol J^{-1})

Time dose	(a) pure water		(b) artificial seawater	
	$G(-N_2H_4)$	$G(-O_2)$	$G(-N_2H_4)$	$G(-O_2)$
0–10 min 167 Gy	21.5	18.0	24.9	11.0
0–30 min 500 Gy	10.3 13[a]	—	12.9	5.8
0–60 min 1,000 Gy	7.6	—	8.3	—

[a] from Ref. 3), 5).

was almost the same as that of pure water, and $G(-O_2)$ was smaller.

The G-values obtained in this study were compared with those reported by other researchers. Lefort et al. [3] obtained $G(-N_2H_4)$ in pure water of $[N_2H_4] = 10^{-3}$ mol dm^{-3} and pH = 9.5 with an absorption dose rate of 0.293 Gy s^{-1} (1 kGy/h), and obtained the result of $G(-N_2H_4)$ =

13×10^{-7} mol J^{-1} with an absorption dose of 500 Gy. Furthermore, Ershov et al [5]. obtained $G(-N_2H_4)$ in pure water of $[N_2H_4] = 10^{-3}$ mol dm^{-3} and pH = 9.5 with an absorption dose rate of 0.113 Gy s^{-1} (approximately 400 Gy/h), and obtained a result of $G(-N_2H_4) = 13 \times 10^{-7}$ mol J^{-1} with an absorption dose of 500 Gy. The *G*-value in this study in pure water of 500 Gy was $G(-N_2H_4)=10.3\times10^{-7}$ mol J^{-1}, not a large difference from the previous reports. Incidentally, Buxton et al [9]. reported that a reason for large $G(-N_2H_4)$ values is that a chain reaction is involved in the reduction of N_2H_4.

Regarding the $G(-O_2)$ value, nothing was reported by Lefort et al. [3] or Ershov et al. [5].

6. Influence of Seawater Components Under Gamma Irradiation

The hydrated electron e^-_{aq} is known to react rapidly with O_2 [12]. On the other hand, the reaction of e^-_{aq} and N_2H_4 is slow [13]. The reaction and reaction rate constant *k* are indicated in Eqs. (6) and (7) respectively:

$$\begin{gathered} e^-_{aq} + O_2 \rightarrow O_2^- + H_2O \\ k_{(6)} = 1.9 \times 10^{10}\ dm^3 \cdot mol^{-1} \cdot s^{-1} \end{gathered} \tag{6}$$

$$\begin{gathered} e^-_{aq} + N_2H_4 \rightarrow H^+ + \cdot N_2H_4 + OH^- \\ k_{(7)} = 2.3 \times 10^{6}\ dm^3 \cdot mol^{-1} \cdot s^{-1} \end{gathered} \tag{7}$$

Based on these factors, there is a possibility of reduction in DO regardless of the presence of N_2H_4. Furthermore, because the reduction in DO was slower in artificial seawater than in pure water under gamma irradiation, it was hypothesized that a component of the artificial seawater was influencing the reduction of DO. This possibility was investigated.

First, an investigation was made to determine whether the DO is reduced regardless of the presence of N_2H_4 by irradiating pure water and artificial seawater with gamma rays without the addition of N_2H_4. The DO concentrations are shown in **Figure 7** where the gamma irradiation is for one hour at a dosage rate of 7.5 kGy/h. The data with the addition of N_2H_4 is also included in Figure 3 for the references.

The reduction in DO concentration was approximately one ppm for pure water. No reduction in DO concentration was observed in the artificial seawater. In contrast, under identical irradiation, the DO concentration was one ppm or less and the reduction exceeded seven ppm for both pure water and artificial seawater with the addition of N_2H_4. Based on these results, it has been shown that the DO concentration decreases with gamma irradiation without the addition of N_2H_4, but the effect of added N_2H_4 was stronger on the reduction of DO under irradiation with gamma rays. Furthermore, it was confirmed that the DO then decreased according to a mechanism different from that in pure water because a component of seawater is present in the artificial seawater.

Next, the influence of chloride ions, highly abundant in seawater, was studied. In pure water, the irradiation facilitated deoxygenation by N_2H_4 is considered to progress via the following reaction [8, 13]:

$$\begin{gathered} N_2H_4 + OH\cdot \rightarrow \cdot N_2H_3 + H_2O \\ k_{(8)} = 1.4 \times 10^{10}\ dm^3 \cdot mol^{-1} \cdot s^{-1} \end{gathered} \tag{8}$$

$$\begin{gathered} \cdot N_2H_3 + O_2 \rightarrow O_2\cdot^- + N_2H_2 + H^+ \\ k_{(9)} = 3.8 \times 10^{8}\ dm^3 \cdot mol^{-1} \cdot s^{-1} \end{gathered} \tag{9}$$

The chemical species that influences the reduction of DO is considered to be the hydroxyl radical OH•.

Because of the high chloride ion concentration in artificial seawater, it is presumed that the reaction in Eqs. (8) and (9) is blocked by the reaction of OH• and Cl^- according to the reaction of Eq. (10) 14).

$$Cl^- + OH\cdot \rightarrow ClOH^- \qquad (10)$$
$$k_{(10)} = 4.3 \times 10^9\ dm^3 \cdot mol^{-1} \cdot s^{-1}$$

In this experiment, gamma rays irradiated a 3.5% NaCl solution containing almost the same amount of chloride ions as the artificial seawater with added N_2H_4 and it was found that the speed of DO reduction was slow, similar to that in artificial seawater. This fact supports the influence of chloride ions on the progress of deoxygenation under the irradiation of gamma rays.

To clarify the mechanisms for deoxygenation by N_2H_4 in water systems that contain seawater components in a radioactive environment, further research is necessary to build a system for evaluating the influence of individual seawater components and evaluating their interrelated influences.

IV. Conclusions

Pure water and artificial seawater with the addition of an infinitesimal quantity of hydrazine, N_2H_4, at room temperature, were irradiated with gamma rays. In the absence of radiation, the DO concentration did not decrease in a short period of time for either pure water or artificial seawater. However, the DO concentration did decrease in a short period for both pure water and artificial seawater when irradiated with gamma rays. Because the N_2H_4 concentration decreased continuously after the removal of DO, it was further considered that the radiolysis products of N_2H_4 were involved in the reduction of DO (deoxygenation). Because the addition of N_2H_4 in the water containing seawater components removes the DO, a cause of corrosion, in a short period of time in a radioactive environment at room temperature, the addition of N_2H_4 to spent fuel pool water, under proper control of N_2H_4 concentration, is considered to be an effective countermeasure for inhibiting the corrosion of the metallic materials that make up the spent fuel pool.

References

1) http://www.tepco.co.jp/nu/fukushima-np/images/handouts_110903_04-j.pdf
2) S. Tubakizaki, M. Takada, H. Gotou, K. Hawatari et al., "Alternatives hydrazine in water treatment at thermal power plant," *Mitsubishi Heavy Industries Tech. Rev.*, 46(2), 43 (2009).
3) M. Lefort, M. Hassinsky, *J. Chim. Phys.*, 53, 527 (1956).
4) B. G. Ershov, T. L. Mikhailova, A. Yu. Emel'yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 5, 1192 (1985). [in Russian]
5) B. G. Ershov, T. L. Mikhailova, A. Yu. Emel'yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 11, 2450 (1988). [in Russian]
6) B. G. Ershov, T. L. Mikhailova, A. Yu. Emel'yanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2, 341 (1991). [in Russian]
7) G. V. Buxton, C. R. Stuart, "Radiation chemistry of aqueous solutions of hydrazine at elevated temperatures Part 1.- Oxygen-free solutions," *J. Chem. Soc., Faraday Trans.*, 92(9), 1519-1525 (1996).
8) G. V. Buxton, C. R. Stuart, "Radiation chemistry of aqueous solutions of hydrazine at elevated temperatures Part 2.- Solutions containing oxygen," *J. Chem. Soc., Faraday Trans.*, 93(8), 1535-1538 (1997).
9) G. V. Buxton, D. A. Lynch, "Radiation chemistry of aqueous solutions of hydrazine at elevated

temperatures Part 3. The chain reaction in oxygenated solutions irradiated with ^{60}Co γ- rays," *Phys. Chem. Chem. Phys*., 1, 3293-3296 (1999).

10) N. Sato, T. Motooka, C. Kato, M. Yamamoto, "Corrosion phenomena in spent nuclear fuel storage pool containing salinity -(1) determination of the corrosive environment by the water radiolysis calculation," *Proc. 2012 Annual Meeting of AESJ*, Mar. 27-29, 2012, Fukui, Japan, (2012). [in Japanese] [CD-ROM].

11) D.B.Radtke, A. F. White, J. V. Davis, F.D.Wilde, "National field manual for the collection of water-quality data-dissolved oxygen," *Techniques of Water-Resources Investigations, book 9*, U.S. Geological Survey, chap. A6 (1998).

12) A. J. Elliot, "A pulse radiolysis study of the temperature dependence of reactions involving H, OH and e^{-}_{aq} in aqueous solutions," *Radiat. Phys. Chem*., 34, 753-758 (1989).

13) E. Hayon, M. Simic, "Intermediates produced from the oneelectron oxidation of hydrazine. Evidence for the formation and decay of tetrazane and triazene." *J. Am. Chem. Soc*., 94, 42-47 (1972).

14) G. G. Jayson, B. J. Parsons, A. J. Swallow, "Some simple, highly reactive, inorganic chlorine derivatives in aqueous solution. Their formation using pulses of radiation and their role in the mechanism of the Fricke dosimeter." *J. Chem. Soc., Faraday Trans. 1*, 69, 1597-1607 (1973).