Hydrazine Radiolysis by Gamma-Ray in the N$_2$H$_4$–Cu$^+$–HNO$_3$ System

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Abstract: Radiolysis of chemical agents occurs during the decontamination of nuclear power plants. The γ-ray irradiation tests of the N$_2$H$_4$–Cu$^+$–HNO$_3$ solution, a decontamination agent, were performed to investigate the effect of Cu$^+$ ion and HNO$_3$ on N$_2$H$_4$ decomposition using a Co-60 high-dose irradiator. After the irradiation, the residues of N$_2$H$_4$ decomposition were analyzed by Ultraviolet-visible (UV) spectroscopy. NH$_4^+$ ions generated from N$_2$H$_4$ radiolysis were analyzed by ion chromatography. Based on the results, the decomposition mechanism of N$_2$H$_4$ in the N$_2$H$_4$–Cu$^+$–HNO$_3$ solution under γ-ray irradiation condition was derived. Cu$^+$ ions form Cu$^+$N$_2$H$_4$ complexes with N$_2$H$_4$, and then N$_2$H$_4$ is decomposed into intermediates. H$^+$ ions and H$^*$ radicals generated from the reaction between H$^+$ ion and e$_{aq}^-$ increased the N$_2$H$_4$ decomposition reaction. NO$_3^-$ ions promoted the N$_2$H$_4$ decomposition by providing additional reaction paths: (1) the reaction between NO$_3^-$ ions and N$_2$H$_4^+$, and (2) the reaction between NO$_5^+$ radical, which is the radiolysis product of NO$_3^-$ ion, and N$_2$H$_5^+$. Finally, the radiolytic decomposition mechanism of N$_2$H$_4$ obtained in the N$_2$H$_4$–Cu$^+$–HNO$_3$ was schematically suggested.

Keywords: radiolysis; γ-ray; irradiation; hydrazine; copper ion; nitrate ion

1. Introduction

Hydrazine (N$_2$H$_4$) is commercially used to produce plastics, medicines, and textile dyes and to reduce the corrosion of a boiler in a thermal power plant [1,2]. In the nuclear field, N$_2$H$_4$ is added to the primary feed water to maintain the hydrogen concentration and to remove dissolved oxygen [3]. In addition, N$_2$H$_4$ can be applied as a chemical decontamination solution to remove radioactive nuclides in an oxide layer of a primary system in the nuclear power plant [4]. The decontamination solution containing N$_2$H$_4$ is developed to reduce the damage of the base metal and the secondary radioactive wastes compared with the decontamination using organic acid [5,6]. They are composed of N$_2$H$_4$ and inorganic acids such as HNO$_3$ and H$_2$SO$_4$ [5–7]. Furthermore, the metal ions can be added into the decontamination solution containing N$_2$H$_4$ for improving the decontamination performance [8]. For this reason, a N$_2$H$_4$–Cu$^+$–HNO$_3$ decontamination solution was suggested as the effective chemical decontamination solution [7]. The decontamination solution, however, can be decomposed under the high radiation field [9]. The radiolysis of the decontamination solution occurs by radionuclides in the primary system, such as Co-60 and Co-58, during the application. The decomposition of major compositions of the decontamination solution affects the decontamination performance. Therefore, it is necessary to analyze the radiolysis of N$_2$H$_4$, which is the major component of the N$_2$H$_4$–Cu$^+$–HNO$_3$ decontamination solution, during irradiation.
In this regard, a number of research studies concerning decomposition of N$_2$H$_4$ solution have been carried out. It is known that the decomposition of N$_2$H$_4$ under irradiation conditions can occur through a reaction with radiolysis products of water. Various radicals and products, such as e$_{aq}^-$, *OH, and H$_2$O$_2^-$, are generated by the radiolysis of water [10]. The radiolysis products of water are represented in Equation (1) [11].

\[
\text{H}_2\text{O} \xrightarrow{\gamma-\text{radiation}} 0.27\text{e}_\text{aq}^-, 0.06 \text{H}^+, 0.26^*\text{OH}, 0.045\text{H}_2\text{O}_2, 0.08 \text{H}_2\text{O}_2, 0.27\text{H}_3\text{O}^+ \text{ (1)}
\]

The decomposition reaction mechanism of N$_2$H$_4$ in the aqueous solution by γ-ray irradiation can be found in the study of Buxton et al. [12]. They reported that radicals such as N$_2$H$_4^\bullet^+$, NH$_3^\bullet$ and N$_2$H$_5^\bullet$, generated from N$_2$H$_4$, are decomposed into N$_2$ and NH$_3$. It is also shown that the NH$_4^+$ ion was produced by a reaction between H$^+$ radical and N$_2$H$_5^\bullet$. Garaix et al. studied the decay mechanism of the NO$_3^\bullet$ radical generated by the radiolysis of NO$_3^-$ ions in the N$_2$H$_4$ solution using an electron beam [13]. They concluded that N$_2$H$_4$ exists mainly as N$_2$H$_5^\bullet$ or N$_2$H$_6^{2\bullet}$ in the acidic solution, both of which cause rapid consumption of NO$_3^\bullet$ radicals. Motooka et al. also reported that the deoxygenation reaction with radiolysis of N$_2$H$_4$ can be suppressed by salt in the water in the γ-radiation field [14]. In this way, the molecular structure of N$_2$H$_4$ after radiolysis and the decomposition mechanism of the N$_2$H$_4$ depend on the composition of the solution. However, there are few research studies about the N$_2$H$_4$ decomposition reaction in N$_2$H$_4$–Cu$^+$–HNO$_3$ solution. Therefore, it is necessary to study the decomposition reaction mechanism of the N$_2$H$_4$ in N$_2$H$_4$–Cu$^+$–HNO$_3$ solution during γ-ray irradiation to simulate the decontamination condition.

In this study, we evaluated the effects of Cu$^+$ ions and HNO$_3$ on N$_2$H$_4$ decomposition under the γ-radiation field. The study was performed by analyzing the concentration of remaining N$_2$H$_4$ and the concentration of the products in N$_2$H$_4$–Cu$^+$–HNO$_3$ solution after the irradiation. The decomposition mechanism of N$_2$H$_4$ in the solution containing Cu$^+$ ions and HNO$_3$ was also suggested.

2. Theoretical Background

2.1. Radiolysis of Hydrazine in Acidic Solution

Hydrazine generally exists in the form of N$_2$H$_5^+$ by its reaction with H$^+$ ions in an acidic solution, as given in Equation (2) [13,15,16]. At pH 1, N$_2$H$_6^{2\bullet}$ coexists with N$_2$H$_5^+$ through the reaction shown in Equation (3) [13,15,17]. Therefore, N$_2$H$_4$ exists in the forms of N$_2$H$_5^+$ and N$_2$H$_6^{2\bullet}$ in the N$_2$H$_4$–HNO$_3$ system before irradiation.

\[
\text{N}_2\text{H}_4 + \text{H}^+ \rightarrow \text{H}_2\text{N}_2\text{H}_3^+, \text{pK} \approx 7.9 \text{ (2)}
\]

\[
\text{N}_2\text{H}_5^+ + \text{H}^+ \leftrightarrow \text{N}_2\text{H}_6^{2\bullet}, \text{pK} \approx -1 \text{ (3)}
\]

In an acidic solution, the same as the condition of this study, e$_{aq}^-$, H$^+$, OH$^-$, and H$_2$O$_2$ are generated as products after water radiolysis. It is possible that e$_{aq}^-$ reacts with H$^+$ ions in the acidic solution and generates H$^+$ as in the following Equation (4) [18]. The reactions between the water radiolysis products and the chemical species of N$_2$H$_4$ lead to the decomposition of N$_2$H$_4$.

\[
e_{aq}^- + \text{H}^+ \rightarrow \text{H}^+, k = 2.2 \times 10^{10} \text{M}^{-1}\text{s}^{-1} \text{ (4)}
\]

The principal decomposition reactions and rate constants of the chemical species of N$_2$H$_4$ in the irradiation condition are listed in Equations (5)–(23). As shown in Equation (5), N$_2$H$_6^{2\bullet}$ reacts with OH$^*$ and produces N$_2$, the end product of N$_2$H$_4$ decomposition at pH 1 [19].

\[
\text{N}_2\text{H}_6^{2\bullet} + 4\text{OH}^* \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 2\text{H}^+ \text{ (5)}
\]

In addition, N$_2$H$_5^+$ is the main species form of N$_2$H$_4$ in the acidic solution. N$_2$H$_5^+$ reacts with the radiolysis products of water such as e$_{aq}^-$, H$^+$, or OH$^*$ as shown in
Equations (6)–(9) [12,20]. NH$_4^+$ ion, one of the end products of N$_2$H$_4$ decomposition, is produced by the reaction between N$_2$H$_5^+$ and H*, as indicated in Equation (7). The intermediates of N$_2$H$_5^+$ decomposition, N$_2$H$_4$, NH$_2^*$, and N$_2$H$_4^{**}$, are generated by the reactions in Equations (6), (8) and (9). These intermediates cause the consecutive decomposition reactions of N$_2$H$_4$. In particular, N$_2$H$_4$ can also be hydrolyzed into N$_2$H$_5^+$ and N$_2$H$_6^{2+}$ as shown in Equations (2) and (3).

The consecutive decomposition reactions of N$_2$H$_4$ with OH*, N$_2$H$_4^{**}$, and H$_2$O$_2$ are listed in Equations (10)–(12) [12,20,21]. N$_4$H$_8^+$ is formed by the reaction between N$_2$H$_4$ and N$_2$H$_4^{**}$, as indicated in Equation (10). *N$_2$H$_3$ is generated by the reaction between N$_2$H$_4$ and OH*, as shown in Equation (11). The intermediates, N$_4$H$_8^+$ and *N$_2$H$_3$, participate in the other consecutive decomposition reactions of N$_2$H$_4$. However, N$_2$ is produced as the end product by the reaction between N$_2$H$_4$ and H$_2$O$_2$ (Equation (12)).

NH$_2^*$ generated by the reaction in Equation (7) causes the reactions with N$_2$H$_5^+$ or N$_2$H$_4$, as represented in Equations (13) and (14) [12]. N$_2$H$_4^{**}$, *N$_2$H$_3$, and NH$_3$ are formed after the reactions shown in Equations (13) and (14). Among these products, N$_2$H$_4^{**}$ and *N$_2$H$_3$ cause the consecutive reactions because they are the reactive intermediates.

N$_2$H$_4^{**}$ produced by Equations (8), (9) and (13) participate in the consecutive reactions represented in Equations (15) and (16) [12]. As shown in Equation (15), N$_4$H$_8^{2+}$ is generated after the reaction of N$_2$H$_4^{**}$ with N$_2$H$_5^+$. As indicated in Equation (16), N$_4$H$_8^{2+}$ reacts with N$_2$H$_4^{**}$, and the reaction products are N$_4$H$_8^{2+}$ and N$_2$H$_5^+$. The N$_4$H$_8^{2+}$ is directly decomposed into N$_2$ and NH$_3$ in the ratio of 1 to 2. On the other hand, N$_2$H$_5^+$ is repeatedly decomposed into other forms, as represented in Equations (6)–(9), (13) and (15).

*N$_2$H$_3$ generated by Equations (11) and (14) is decomposed into various forms, as listed in Equations (17)–(22) [12]. The main end products of *N$_2$H$_3$ decomposition are N$_2$ and NH$_3$, as represented in Equations (19) and (20). The main intermediates, N$_2$H$_4$ and N$_2$H$_2$, are also generated from the decomposition reaction of *N$_2$H$_3$, as shown in Equations (17)–(22). N$_2$H$_4$ is hydrolyzed into N$_2$H$_5^+$ and N$_2$H$_6^{2+}$ in the acidic solution or causes consecutive decomposition reactions. N$_2$H$_2$ reacts with H* and *N$_2$H$_3$ is produced as shown in Equation (23).

As mentioned above, it is expected that various intermediates are generated during the decomposition of the chemical species of N$_2$H$_4$. Therefore, the intermediates can affect the reaction with Cu* ions or NO$_3^-$ ions in the N$_2$H$_4$–Cu*–HNO$_3$ system.

\[
N_2H_5^+ + e_{aq}^- \rightarrow H^* + N_2H_4, \quad k = 1.6 \times 10^8 \ \text{M}^{-1}\text{s}^{-1} \quad (6)
\]
\[
N_2H_5^+ + H^* \rightarrow NH_2^* + NH_4^+, \quad k = 1.0 \times 10^4 \ \text{M}^{-1}\text{s}^{-1} \quad (7)
\]
\[
N_2H_5^+ + H^* \rightarrow H_2 + N_2H_4^{**}, \quad k = 1.3 \times 10^5 \ \text{M}^{-1}\text{s}^{-1} \quad (8)
\]
\[
N_2H_5^+ + OH^* \rightarrow N_2H_4^{**} + H_2O, \quad k = 8.2 \times 10^7 \ \text{M}^{-1}\text{s}^{-1} \quad (9)
\]
\[
N_2H_4 + N_2H_4^{**} \leftrightarrow N_4H_8^{**}, \quad k_f = 6.0 \times 10^7 \ \text{M}^{-1}\text{s}^{-1}, \quad k_b = 4.0 \times 10^5 \ \text{M}^{-1}\text{s}^{-1} \quad (10)
\]
\[
N_2H_4 + OH^* \rightarrow *N_2H_3 + H_2O, \quad k = 5.4 \times 10^9 \ \text{M}^{-1}\text{s}^{-1} \quad (11)
\]
\[
N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O, \quad k = 2.4 \times 10^8 \ \text{M}^{-1}\text{s}^{-1} \quad (12)
\]
\[
NH_2^* + N_2H_5^+ \rightarrow N_2H_4^{**} + NH_3, \quad k = 1.0 \times 10^6 \ \text{M}^{-1}\text{s}^{-1} \quad (13)
\]
\[
NH_2^* + N_2H_4 \rightarrow *N_2H_3 + NH_3, \quad k = 1.0 \times 10^7 \ \text{M}^{-1}\text{s}^{-1} \quad (14)
\]
\[
N_2H_4^{**} + N_2H_5^+ \leftrightarrow N_4H_8^{2+}, \quad k_f = 6.0 \times 10^7 \ \text{M}^{-1}\text{s}^{-1}, \quad k_b = 4.0 \times 10^5 \ \text{M}^{-1}\text{s}^{-1} \quad (15)
\]
\[
N_2H_4^{**} + N_4H_8^{2+} \rightarrow N_4H_8^{2+} + N_2H_5^+ (N_4H_8^{2+} \rightarrow N_2 + 2NH_3), \quad k = 4.0 \times 10^8 \ \text{M}^{-1}\text{s}^{-1} \quad (16)
\]
\[
*N_2H_3 + e_{aq}^- + H_2O \rightarrow N_2H_4 + OH^-, \quad k = 7.0 \times 10^9 \ \text{M}^{-1}\text{s}^{-1} \quad (17)
\]
\[
*N_2H_3 + H^* \rightarrow N_2H_4, \quad k = 7.0 \times 10^9 \ \text{M}^{-1}\text{s}^{-1} \quad (18)
\]
2.2. Change of Copper Species during Irradiation

Copper ions in the solution would cause the decomposition of \( \text{N}_2\text{H}_4 \) during the irradiation. The redox reactions mainly occur between copper ions and radiolysis products of water such as \( \text{e}_{\text{aq}}^- \), \( \text{H}^+ \), and \( \text{OH}^- \), as listed in Equations (24)–(28) [22–25]. The equations show that copper ions coexist in the forms of \( \text{Cu}^0 \), \( \text{Cu}^+ \) ions and \( \text{Cu}^{2+} \) ions regardless of initial chemical species. In addition, Fenton reaction occurs in an acidic condition, as represented in Equation (29) [26,27]. The above reactions can affect the decomposition of \( \text{N}_2\text{H}_4 \) in the \( \text{N}_2\text{H}_4-\text{Cu}^+-\text{HNO}_3 \) system.

\[
\text{Cu}^+ + \text{e}_{\text{aq}}^- \rightarrow \text{Cu}^0
\]  
\[
\text{Cu}^+ + \text{H}^+ \rightarrow \text{Cu}^0 + \text{H}^+, k = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{Cu}^+ + \text{OH}^- \rightarrow \text{Cu}^{2+} + \text{OH}^-, k = (2 \pm 1) \times 10^{10} \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{Cu}^{2+} + \text{e}_{\text{aq}}^- \rightarrow \text{Cu}^+, k = 3.5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{Cu}^{2+} + \text{H}^+ \rightarrow \text{Cu}^+ + \text{H}^+, k < 1.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{H}_2\text{O}_2 + \text{Cu}^+ + \text{H}^+ \rightarrow \text{OH}^* + \text{H}_2\text{O} + \text{Cu}^{2+}
\]  

2.3. Radiolysis of Nitrate Ion

The principal reactions of \( \text{NO}_3^- \) ions during the irradiation are listed in Equations (30)–(38) [13,28–33]. The reactions can be classified by direct and indirect decomposition reactions. As shown in Equation (30), the \( \text{NO}_3^- \) ion is directly changed into \( \text{NO}_3^2- \) and electron due to the \( \gamma \)-ray irradiation [13,28]. The \( \text{NO}_3^- \) ion is also changed into \( \text{NO}_3^2- \) or \( \text{NO}_2^* \) through the reactions with \( \text{e}_{\text{aq}}^- \) or \( \text{H}^* \), as can be seen in Equations (31) and (32) [29,30]. The \( \text{NO}_3^2- \) reduces into \( \text{NO}_2^* \) in the water, as represented in Equation (33) [29,31]. During irradiation, \( \text{NO}_2^* \) reacts with the radiolysis products of water such as \( \text{e}_{\text{aq}}^- \), \( \text{H}^* \), and \( \text{OH}^* \), and \( \text{H}^+, \text{NO}_2^- \) ion, and \( \text{NO}_3^- \) ions are produced as listed in Equations (34)–(36) [32]. On the other hand, \( \text{NO}_2^* \) reacts with water and generates \( \text{NO}_2^- \) and \( \text{NO}_3^- \) ions, as shown in Equation (37) [13,33]. As represented in Equation (38), \( \text{NO}_2^- \) ions generated from the reaction in Equations (34), (35) and (37) are changed into \( \text{NO}_3^- \) ions and \( \text{NO}_2^* \) through the reaction with \( \text{NO}_3^* \) [13,33]. The generated \( \text{NO}_2^- \) ions are directly consumed, and \( \text{NO}_2^* \) and \( \text{NO}_3^- \) ions are regenerated by the reaction indicated in Equation (38). As mentioned above, \( \text{NO}_3^- \) ions and their radicals generated from the radiolysis of \( \text{NO}_3^- \) can also participate in the decomposition reaction of \( \text{N}_2\text{H}_4 \) in the \( \text{N}_2\text{H}_4-\text{Cu}^+-\text{HNO}_3 \) system.

\[
\text{NO}_3^- \xrightarrow{\text{radiation}} \text{NO}_3^- + \rightarrow \text{NO}_3^2- + \text{e}^-
\]  
\[
\text{NO}_3^- + \text{e}_{\text{aq}}^- \rightarrow \text{NO}_3^2- + \text{e}^-, k = 9.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{NO}_3^- + \text{H}^* \rightarrow \text{NO}_2^* + \text{OH}^-, k = 1.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{NO}_3^2- + \text{H}_2\text{O} \rightarrow \text{NO}_2^* + 2\text{OH}^-, k = 1.0 \times 10^3 \text{ M}^{-1}\text{s}^{-1}
\]  
\[
\text{NO}_2^* + \text{e}_{\text{aq}}^- \rightarrow \text{NO}_2^-, k = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}
\]
\[ \text{NO}_2^\bullet + \text{H}^\bullet \rightarrow \text{H}^+ + \text{NO}_2^- , \quad k = 1.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \]  
(35)

\[ \text{NO}_2^\bullet + \cdot\text{OH} \rightarrow \text{H}^+ + \text{NO}_3^- , \quad k = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \]  
(36)

\[ 2\text{NO}_2^\bullet + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+ , \quad k = 4.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1} \]  
(37)

\[ \text{NO}_3^\bullet + \text{NO}_2^- \rightarrow \text{NO}_2^\bullet + \text{NO}_3^- , \quad k = 4.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \]  
(38)

3. Results

3.1. Effect of Copper Ions on Hydrazine Decomposition

In order to investigate the effect of copper ions on the \( \text{N}_2\text{H}_4 \) decomposition, \( \gamma \)-ray was irradiated to the \( \text{N}_2\text{H}_4–\text{Cu}^+–\text{HNO}_3 \) solution and \( \text{N}_2\text{H}_4–\text{HNO}_3 \) solution at pH 3. The absorbed dose was varied from 0 to 20 kGy, and the \([\text{N}_2\text{H}_4]_0\) in the solutions was equal to \( 50 \times [\text{N}_2\text{H}_4]_0 \) in the solutions was equal to \( 50 \times 10^{-3} \text{ mol dm}^{-3} \). The pH of the solution was adjusted to 3 using \( \text{HNO}_3 \). Figure 1 shows the change in the concentration of \( \text{N}_2\text{H}_4 \) as a result of the \( \gamma \)-irradiation. The decomposed portion of \( \text{N}_2\text{H}_4 \) increased with the increase in the absorbed dose regardless of the presence of the Cu\(^+\) ions. This result indicates that the amount of radiolysis products of water participating in the \( \text{N}_2\text{H}_4 \) decomposition was enhanced when the absorbed dose was increased. At the same absorbed dose, the decomposed portion of \( \text{N}_2\text{H}_4 \) was higher when the copper ions existed than that when the copper ions were absent, as indicated in Figure 1. In particular, \( 12.48 \times 10^{-3} \text{ mol dm}^{-3} \) of \( \text{N}_2\text{H}_4 \) in the solution containing Cu\(^+\) ions was decomposed after the 20 kGy of \( \gamma \)-irradiation. When the Cu\(^+\) ions were absent in the solution, \( 9.05 \times 10^{-3} \text{ mol dm}^{-3} \) of \( \text{N}_2\text{H}_4 \) was decomposed. Moreover, the G-values for the \( \text{N}_2\text{H}_4 \) decomposition were calculated for 20 kGy of absorbed dose and listed in Table 1. G\((–\text{N}_2\text{H}_4)\), for the solution containing Cu\(^+\) ions, was higher than that of the solution not containing Cu\(^+\) ions.

![Figure 1](image-url)

Figure 1. Dependence of \( \text{N}_2\text{H}_4 \) decomposition on Cu\(^+\) ions after \( \gamma \)-irradiation on the solution of which \([\text{N}_2\text{H}_4]_0 = 50 \times 10^{-3} \text{ mol dm}^{-3} \) at pH 3.
Table 1. G(−N₂H₄) values in the N₂H₄–HNO₃ and N₂H₄–Cu⁺–HNO₃ solutions of which [N₂H₄]₀ = 50 × 10⁻³ mol dm⁻³ at 20 kGy of absorbed dose.

| Total Dose (kGy) | w/o Cu⁺ Ions | w/Cu⁺ Ions |
|------------------|--------------|------------|
| 20               | 4.52         | 6.24       |

There are several explanations for the effect of copper ions on the decomposition of N₂H₄: (1) a catalyzed reaction of H₂O₂ occurs [34], (2) copper ions lower the energy barrier of N–H bonds cleavage in the gas phase [35], and (3) the formation of Cu⁺N₂H₄ occurs [36,37]. The experimental condition of Zhong and Lim is similar to that of this study [36,37]. They suggested that Cu⁺N₂H₄ complex acts as a scavenger and it increases the decomposition reaction of N₂H₄. The predicted mechanism is given in Equations (39)–(41). N₂H₄ reacts with Cu⁺ ion and forms the Cu⁺N₂H₄ complex, as shown in Equation (39). This complex can react with H₂O₂ and produces N₂H₂, as indicated in Equation (40). The reaction between the Cu⁺N₂H₄ complex and N₂H₂ causes the generation of Cu⁺(N₂H₃)₂ that decomposes into Cu⁺ ion and N₂H₃, as represented in Equation (41).

\[
\text{Cu}^+ + \text{N}_2\text{H}_4 \leftrightarrow \text{Cu}^+\text{N}_2\text{H}_4 \tag{39}
\]

\[
\text{Cu}^+\text{N}_2\text{H}_4 + \text{H}_2\text{O}_2 \rightarrow \text{Cu}^+ + \text{N}_2\text{H}_2 + 2\text{H}_2\text{O}, \text{(slow)} \tag{40}
\]

\[
\text{Cu}^+\text{N}_2\text{H}_4 + \text{N}_2\text{H}_2 \leftrightarrow \text{Cu}^+(*\text{N}_2\text{H}_3)_{2\text{cage}} \rightarrow \text{Cu}^+ + 2^*\text{N}_2\text{H}_3, \text{(slow)} \tag{41}
\]

N₂H₄ was considered to be reproduced as the intermediate during radiolysis in this study; however, the hydrazine was hydrolyzed into N₂H₅⁺ or N₂H₃⁺⁺ in acidic conditions. The N₂H₄ could form the Cu⁺N₂H₄ complex with the Cu⁺ ion through the reaction, as indicated in Equation (39). As can be seen in Equations (40) and (41), it was possible that the Cu⁺N₂H₄ complex was separated into Cu⁺ ion, N₂H₂, and water after reacting with H₂O₂ generated from the radiolysis of water. The N₂H₄ could react with H⁺ and generate *N₂H₃ according to the Equation (23). Moreover, N₂H₂ could also cause a reaction with the Cu⁺N₂H₄ complex and form Cu⁺(N₂H₃⁺)₂. Cu⁺(N₂H₃⁺)₂ was directly decomposed into *N₂H₃ and Cu⁺ ion following the reaction in Equation (41). *N₂H₃ was decomposed into N₂ or NH₃ during the γ-ray irradiation, as listed in Equations (19) and (20). The Cu⁺ ion regenerated from the reactions shown in Equations (40) and (41) repeatedly formed the Cu⁺N₂H₄ complex and caused the decomposition reaction of N₂H₄ again. Therefore, these two reactions offered new decomposition reaction paths of N₂H₄ where the Cu⁺ ion acted as the catalyst.

The electrochemical characterization, under the same conditions as this experiment, was also performed by Yang et al. [38]. Figure 2 shows the cyclic voltammograms using an ITO (Indium–Tin Oxide) electrode in solutions of 3 mM N₂H₄, 0.3 mM Cu(NO₃)₂, 0.1 M NaNO₃, and 3 mM N₂H₄ + 0.3 mM Cu(NO₃)₂. All the test solutions were adjusted to pH 3 using HNO₃. The oxidation peak of the N₂H₄ near 0.3 V increased significantly with the addition of Cu(NO₃)₂. The peak is quite different from that of N₂H₄ alone or Cu(NO₃)₂ alone. This result implies that Cu⁺ ions make coordination compounds with N₂H₄, as listed in reaction Equation (39). Therefore, it is inferred that Cu⁺ ions affect the N₂H₄ decomposition by formation of the Cu⁺N₂H₄ complex in the N₂H₄–Cu⁺–HNO₃ system.

3.2. Effect of HNO₃ on Hydrazine Decomposition

HNO₃ affects the decomposition of N₂H₄ in two ways: (1) the effect of H⁺ ions and (2) the effect of NO₃⁻ ions. In order to investigate the effect of H⁺ ions and NO₃⁻ ions on N₂H₄ decomposition, the concentration of the chemical species of N₂H₄ was analyzed according to the pH change under the radiation field. The pH of each solution was adjusted to 1, 3, and 5 by adding HNO₃, respectively. Every sample solution included 50 × 10⁻³ mol dm⁻³ of N₂H₄ and 0.5 × 10⁻³ mol dm⁻³ of Cu⁺ ions. As a result, the concentration of chemical species of N₂H₄ decreased with a decreasing pH.
at the same absorbed dose, as shown in Figure 3. The concentrations of decomposed \( \text{N}_2\text{H}_4 \) were \( 29.96 \times 10^{-3} \text{ mol dm}^{-3} \) (pH = 1), \( 15.92 \times 10^{-3} \text{ mol dm}^{-3} \) (pH = 3), and \( 13.42 \times 10^{-3} \text{ mol dm}^{-3} \) (pH = 5) at 40 kGy, respectively. The decomposed portion of \( \text{N}_2\text{H}_4 \) significantly increased as the solution’s pH decreased from 3 to 1. At the same time, the G(–N\(_2\text{H}_4\)) at pH 1 was \( 7.49 \times 10^{-7} \text{ mol J}^{-1} \) for 40 kGy of absorbed dose, as shown in Table 2. The G(–N\(_2\text{H}_4\)) at pH 3 and 5 were \( 3.98 \times 10^{-7} \text{ mol J}^{-1} \) and \( 3.35 \times 10^{-7} \text{ mol J}^{-1} \) for 40 kGy of absorbed dose, respectively. Based on this result, it was confirmed that the G-values for the decomposition of \( \text{N}_2\text{H}_4 \) increased with the decreasing of the pH.

**Figure 2.** Cyclic voltammograms of 3 mM \( \text{N}_2\text{H}_4 \), 0.3 mM \( \text{Cu(NO}_3\text{)}_2 \), 0.1 M \( \text{NaNO}_3 \), and 3 mM \( \text{N}_2\text{H}_4 + 0.3 \text{ mM Cu(NO}_3\text{)}_2 \) solutions at scan rate of 20 mV/s. Adapted with permission from [38] Haesik Yang.

**Figure 3.** Concentration change of chemical species of \( \text{N}_2\text{H}_4 \) according to the absorbed dose under various pHs condition.
Therefore, the increase in HNO\(^{-}\) \(\text{pH } 1\) than at \(\text{pH } 3\) and \(\text{pH } 5\). The increase in H• \(\text{pH } 3\) and \(\text{pH } 5\), when the absorbed doses increased at the rates shown in Figure 3. This was posed directly through the reactions listed in Equations (10)–(12). On the other hand, it position. As mentioned above, the reaction between the H• and the intermediates of N\(_2\)H\(_4\) decomposition, such as N\(_2\)H\(_3^+\), N\(_2\)H\(_3^*\), and N\(_2\)H\(_2\), listed in Equations (7), (8), (18) and (23). When the reactions shown in Equations (7), (8) and (23) occurred, NH\(_4^+\) ions or the intermediates such as •NH\(_2\), N\(_2\)H\(_4^{•+}\), and N\(_2\)H\(_3^+\) were produced. As represented in Equation (18), N\(_2\)H\(_4\) is recovered through the reaction between •N\(_2\)H\(_3^+\) and H•. This N\(_2\)H\(_4\) could be decomposed after hydrolysis into N\(_2\)H\(_3^+\) or be decomposed directly through the reactions listed in Equations (10)–(12). On the other hand, it was possible to form the Cu•N\(_2\)H\(_4\) complex with copper ions and cause a decomposition reaction of N\(_2\)H\(_4\) using Equations (40) and (41). In particular, N\(_2\)H\(_4\) and •N\(_2\)H\(_3^+\) generated from the reactions shown in Equations (18) and (23) have a high reaction rate, which are 7.0 \(\times\) \(10^9\) M\(^{-1}\) s\(^{-1}\) and 3.0 \(\times\) \(10^9\) M\(^{-1}\) s\(^{-1}\), among the reactions concerned H•. The N\(_2\)H\(_4\) and •N\(_2\)H\(_3^+\) are mostly decomposed into N\(_2\) and NH\(_3\), as mentioned above.

Firstly, the above results can be explained by the effect of the H\(^+\) ion on N\(_2\)H\(_4\) decomposition. As mentioned above, the reaction between the H\(^+\) ion and e\(_{aq}^-\) caused the generation of H\(^•\), as represented in Equation (4). The increase in H\(^•\) promoted the reaction between H\(^•\) and the intermediates of N\(_2\)H\(_4\) decomposition, such as N\(_2\)H\(_3^+\), N\(_2\)H\(_3^*\), and N\(_2\)H\(_2\), listed in Equations (7), (8), (18) and (23). When the reactions shown in Equations (7), (8) and (23) occurred, NH\(_4^+\) ions or the intermediates such as •NH\(_2\), N\(_2\)H\(_4^{•+}\), and N\(_2\)H\(_3^+\) were produced. As represented in Equation (18), N\(_2\)H\(_4\) is recovered through the reaction between •N\(_2\)H\(_3^+\) and H•. This N\(_2\)H\(_4\) could be decomposed after hydrolysis into N\(_2\)H\(_3^+\) or be decomposed directly through the reactions listed in Equations (10)–(12). On the other hand, it was possible to form the Cu•N\(_2\)H\(_4\) complex with copper ions and cause a decomposition reaction of N\(_2\)H\(_4\) using Equations (40) and (41). In particular, N\(_2\)H\(_4\) and •N\(_2\)H\(_3^+\) generated from the reactions shown in Equations (18) and (23) have a high reaction rate, which are 7.0 \(\times\) \(10^9\) M\(^{-1}\) s\(^{-1}\) and 3.0 \(\times\) \(10^9\) M\(^{-1}\) s\(^{-1}\), among the reactions concerned H•. The N\(_2\)H\(_4\) and •N\(_2\)H\(_3^+\) are mostly decomposed into N\(_2\) and NH\(_3\), as mentioned above.

Secondly, the increase in the decomposition reaction of N\(_2\)H\(_4\) with the lowering of the pH of the N\(_2\)H\(_4\)–Cu\(^{2+}\)–HNO\(_3\) solution could also be explained by the effect of the NO\(_3^-\) ion. When the NO\(_3^-\) ion reacts with NH\(_4^+\), which is the chemical species of N\(_2\)H\(_4\), N\(_2\)H\(_2\) and •NO\(_2^-\) are produced due to the reaction, as represented in Equation (42) [39]. As listed in Equation (23), the N\(_2\)H\(_2\) reacts with H•, and •N\(_2\)H\(_3^+\) is generated. As mentioned above, •N\(_2\)H\(_3^+\) normally decomposes into N\(_2\) and NH\(_3\), leading to N\(_2\)H\(_4\) decomposition. •NO\(_2^-\) participates in the reaction with radiolysis products of water, and finally NO\(_3^-\) is formed by the reaction shown in Equations (34)–(38). On the other hand, NO\(_3^-\) generated during the radiolysis of NO\(_3^-\) ions also affects N\(_2\)H\(_4\) decomposition. When NO\(_3^+\) reacts with N\(_2\)H\(_3^+\), N\(_2\)H\(_4^{•+}\) and HNO\(_3\) are produced, as shown in Equation (43) [13,39]. N\(_2\)H\(_4^{•+}\) is consecutively decomposed not only by the reaction listed in Equations (15) and (16) but also by the reaction shown in Equation (42). NO\(_3^-\) ions recovered from the reaction shown in Equation (43) participate in the decomposition reaction of the chemical species of N\(_2\)H\(_4\). Therefore, the increase in HNO\(_3\) in the N\(_2\)H\(_4\)–Cu\(^{2+}\) solution accelerated the decomposition of N\(_2\)H\(_4\) by increasing the occurrence of reactions concerned with H• and adding new decomposition reaction paths, including that of the NO\(_3^-\) ion.

\[ \text{N}_2\text{H}_4^{•+} + \text{NO}_3^- \rightarrow \text{N}_2\text{H}_2 + \text{H}_2\text{O} + \cdot\text{NO}_2, \quad k = 2.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \]  
\[ \text{N}_2\text{H}_5^+ + \text{NO}_3^- \rightarrow \text{N}_2\text{H}_4^{•+} + \text{NO}_3^- + \text{H}^+, \quad k = 1.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1} \]  

Moreover, the decomposed portion of N\(_2\)H\(_4\) increased rapidly at pH 1 compared to at pH 3 and 5, when the absorbed doses increased at the rates shown in Figure 3. This was caused by H• and NO\(_3^-\) being generated by irradiation. Since the amount of HNO\(_3\) added at pH 1 was larger than at pH 3 and 5, the amount of H• and NO\(_3^-\) produced was larger at pH 1 than at pH 3 and 5. The increase in H• and NO\(_3^-\) promoted the decomposition of N\(_2\)H\(_4\) through the reactions, as mentioned above.

In order to investigate the anionic effect, the remaining concentration of N\(_2\)H\(_4\) in the NO\(_3^-\) ion system was compared with that of the SO\(_4^{2-}\) ion system at pH 3. Quantities of 10, 20, and 40 kGy of the absorbed doses were irradiated to each solution. The initial concentration of N\(_2\)H\(_4\) in each solution was 50 \(\times\) \(10^{-3}\) mol dm\(^{-3}\). As shown in Figure 4, the decomposed concentration of N\(_2\)H\(_4\) increased when the absorbed dose increased regardless of the type of acid added. At the same absorbed dose, three times higher concentrations of N\(_2\)H\(_4\) in the NO\(_3^-\) ion system were decomposed as compared to the
SO₄²⁻ ion system. As indicated in Table 3, the G-value for the decomposition of N₂H₄ at 40 kGy was 3.98 × 10⁻⁷ mol J⁻¹ when the acid added in the solution was HNO₃. G(–N₂H₄) was 1.25 × 10⁻⁷ mol J⁻¹ when the acid injected in the solution was H₂SO₄. From these results, we found that the NO₃⁻ ions facilitated the decomposition of N₂H₄ in the solution.

![Graph showing concentration change of chemical species of N₂H₄ according to the absorbed dose under different acid conditions.](image)

**Figure 4.** Concentration change of chemical species of N₂H₄ according to the absorbed dose under different acid conditions.

**Table 3.** G(–N₂H₄) values of N₂H₄–Cu⁺–HNO₃ and N₂H₄–Cu⁺–H₂SO₄ solutions of which [N₂H₄]₀ = 50 × 10⁻³ mol dm⁻³ at 40 kGy of absorbed dose.

| Total Dose (kGy) | G(–N₂H₄) Value (10⁻⁷ mol/J) |
|------------------|-----------------------------|
|                  | Containing HNO₃ | Containing H₂SO₄ |
| 40               | 3.98            | 1.25            |

3.3. Decomposition Mechanism of Hydrazine in N₂H₄–Cu⁺–HNO₃ System

The decomposition reactions of the N₂H₄ in N₂H₄–Cu⁺–HNO₃ system are schematically shown in Figure 5. N₂H₄ in the acidic solution is hydrolyzed and coexists as N₂H₅⁺ or N₂H₆²⁺. These species are decomposed into intermediates such as N₂H₄•⁺, N₂H₃, and NH₂• under irradiation conditions. N₂H₄ can decompose into NH₄⁺ ion, N₂, or NH₃. However, it was verified that the end products were mainly formed with N₂ or NH₃. In addition, N₂H₄ decomposition was promoted by the influence of the Cu⁺ ion, H⁺ ion, and NO₃⁻ ion in the N₂H₄–Cu⁺–HNO₃ system, as explained in Sections 3.1 and 3.2. As represented in green line in Figure 5, Cu⁺ ions form the Cu⁺N₂H₄ complex with N₂H₄. The Cu⁺N₂H₄ complex participates in the reactions, as shown in Equations (40) and (41). The complex decomposes into N₂H₃ and further decomposes into the end products through the consecutive reactions, as listed in Equations (17)–(22). The recovered Cu⁺ ion from the complex repeatedly forms an N₂H₄ complex that acts as a catalyst to accelerate the decomposition of N₂H₄. H⁺ was produced through the reaction between the H⁺ ion and eₐq⁻. Therefore, the decomposition reaction of N₂H₄ by H⁺ was promoted as the concent-

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(Note: The original text contains additional figures and equations, which are not shown here for brevity. The provided text is a condensed summary of the key points as per the instructions.)
tration of the H$^+$ ion increased. As shown in the orange line in Figure 5, NO$_3^-$ ions or NO$_3^*$ radicals accelerate the N$_2$H$_4$ decomposition by providing the additional reaction paths to change N$_2$H$_6^{2+}$ into N$_2$H$_4^{2+}$. They also cause N$_2$H$_4^{2+}$ to decompose into N$_2$H$_2$. NO$_3^-$ ion and NO$_3^*$ were regenerated by the radiolysis of NO$_2^*$ and NO$_5^*$, as shown in Equations (34)–(38), and they participated in the N$_2$H$_4$ radiolysis reaction again. Consequently, N$_2$H$_4$ decomposition was promoted in the N$_2$H$_4$–Cu$^+$–HNO$_3$ system through the mechanism shown in Figure 5.

Figure 5. Schematic diagram of radiolysis of N$_2$H$_4$ in N$_2$H$_4$–Cu$^+$–HNO$_3$ system.

In order to verify the effect of Cu$^+$ ions on the decomposition mechanism of N$_2$H$_4$ in the N$_2$H$_4$–HNO$_3$ solution, the fraction of N$_2$H$_4$ and end products were analyzed after irradiation with 20 kGy of the absorbed dose. The initial concentrations of N$_2$H$_4$ in the solution were 50 $\times$ 10$^{-3}$ mol dm$^{-3}$, and the pH of the solution was adjusted to 3. The results were compared with and without Cu$^+$ ions in the solution, as represented in Figure 6. Through the above reactions, it was verified that N$_2$H$_4$ in the N$_2$H$_4$–Cu$^+$–HNO$_3$ solution was finally decomposed into N$_2$, NH$_3$, and NH$_4^+$ ion under an irradiation condition by the reactions with radiolysis products of water or consecutive decomposition reactions. For this reason, the fraction of N$_2$ and NH$_3$ in the solution after $\gamma$-ray irradiation was calculated by subtracting the amount of remaining chemical species of N$_2$H$_4$ and NH$_4^+$ ions produced after irradiation from the initial amount of N$_2$H$_4$. 
As shown in Figure 6, N₂H₄ decomposed into N₂, NH₃, and NH₄⁺ ion. It is well known that most of NH₃ reacts with H⁺ ions in the acidic solution and exists in the form of NH₄⁺ [40]. Therefore, it was considered that most of the remaining gas phase end product was composed of N₂ after irradiation in this study. It was judged that the NH₃ was converted into NH₄⁺ ion after the irradiation. When the Cu⁺ ion is present in the N₂H₄–HNO₃ solution, N₂H₃⁺ is generated, as indicated in Figure 5 and Equation (41). N₂H₃⁺ participated in the reaction, generating N₂ or NH₃, as shown in Equations (19) and (20). Therefore, it was confirmed that the fraction of N₂ and NH₄⁺, the form of NH₃ in the acidic condition, increased when the Cu⁺ ions were present in the N₂H₄–HNO₃ solution, as represented in Figure 6.

To confirm the effect of HNO₃ on the decomposition mechanism of N₂H₄ in the N₂H₄–Cu⁺ solution, the fraction of remaining N₂H₄ and end products in each sample after 40 kGy of absorbed dose irradiation at pH 1, 3, and 5 was analyzed. The initial concentrations of N₂H₄ in the solutions were 50 × 10⁻³ mol dm⁻³. The result is represented in Figure 7. As mentioned above, NH₃ is converted into NH₄⁺ ion in the solution because of the acidic condition. As shown in Figure 7, NH₄⁺ ions were not generated after 40 kGy of absorbed dose irradiation at pH 1. Therefore, it was considered that most of N₂H₄ was decomposed into N₂. The obtained result at pH 1 can be explained as follows. At pH 1, N₂H₄ exists in the form of N₂H₆²⁺ as a result of hydrolysis, as shown in Equation (3). The N₂H₆²⁺ ion generated N₂ through the decomposition reaction, as indicated in Equation (5).

In addition, the amount of end products of N₂H₄ decomposition were decreased with increasing pH. This was the case because the large amount of H⁺ produced by the reaction between H⁺ ions and eaq⁻ affected the N₂H₄ decomposition, as shown in Figure 5. For this reason, the decrease in the concentration of end products of N₂H₄ decomposition following an increase in the pH was caused by a decrease in the N₂H₄ decomposition reaction.
However, the concentration of NH$_4^+$ ions generated after irradiation increased with increasing pH. This was the case because the N$_2$H$_4$ exists as a form of the N$_2$H$_5^+$ ion rather than the N$_2$H$_6^{2+}$ ion as the pH increases. As indicated in Equations (6)–(23), the end products of the reactions with a high reaction rate, among the consecutive reactions of N$_2$H$_5^+$ ion decomposition in which H$^*$ participated, were mainly N$_2$ and NH$_3$. The NH$_3$ reacted with the H$^+$ ion in an acidic condition and existed in the form of NH$_4^+$ ions, as mentioned above. NO$_3^-$ ions were also related to the generation of N$_2$ and NH$_3$. The reaction between the N$_2$H$_5^+$ ion and NO$_3^-$ shown in Equation (43) might affect the generation of N$_2$H$_4^{••}$, NO$_3^-$ ion and H$^+$ ion. As shown in Equations (15) and (16), the end products generated by the reactions of N$_2$H$_4^{••}$ were mostly N$_2$ and NH$_3$. Otherwise, the N$_2$H$_2$ is produced when the N$_2$H$_4^{••}$ reacts with NO$_3^-$ ions, as shown in Equation (42). N$_2$H$_2$ is the intermediate of N$_2$H$_4$ decomposition and it generates *N$_2$H$_3$ after the reaction with H$,^*$ as represented in Equation (23). The end reaction products involving *N$_2$H$_3$ are also N$_2$ and NH$_3$, as represented in Equations (17)–(22). The NH$_3$ generated by the reaction between N$_2$H$_5^+$ and NO$_3^*$ also existed in the form of NH$_4^+$ ion in the acidic condition. Therefore, it is concluded that HNO$_3$ can affect the decomposition of N$_2$H$_4$ through the mechanisms listed in Equations (5)–(23) and Equations (42) and (43) by investigating the end product of the expected decomposition paths.

4. Materials and Methods

4.1. Chemicals and Sample Preparation

Hydrazine monohydrate (Junsei, Tokyo, Japan, 98.0%), nitric acid (EMSure, Darmstadt, Germany, 65.0%) and copper (I) chloride (SIGMA-ALDRICH, St. Louis, MO, USA, 97.0%) were used to prepare N$_2$H$_4$–Cu$^{+}$–HNO$_3$ solution in this study. The conditions of each sample is listed in Table 4. All the solutions contain 50.0 mM of N$_2$H$_4$. In order to investigate the effects of Cu$^+$ ions on N$_2$H$_4$ decomposition, the solutions were prepared according to the presence of 0.5 mM of copper ions. Each sample was adjusted to pH 3 by adding nitric acid. To analyze the effects of HNO$_3$ on N$_2$H$_4$ decomposition, each solution was adjusted to pH 1, 3, and 5 by adding 144.7 mM, 50.8 mM, and 49.9 mM of nitric acid, respectively.
All the sample solutions included 0.5 mM of copper ions. The 30 mL of sample solutions were stored in the 50 mL vials. After storing the solution in the vial, the nitrogen purging was conducted for 10 min. during the γ-ray irradiation.

Table 4. Sample preparation.

| Sample Solution         | Concentration (mM) | Concentration (mM) |
|-------------------------|--------------------|--------------------|
|                         | N₂H₄ | Cu⁺ Ions | HNO₃ |
| pH 1                    | 50   | 0.5      | 144.7 |
| pH 3 (without Cu⁺ ion)  | 50   | -        | 50.8  |
| pH 3 (with Cu⁺ ion)     | 50   | 0.5      | 50.8  |
| pH 5                    | 50   | 0.5      | 49.9  |

4.2. γ-rradiation

A high-dose γ-ray irradiator (Co-60 source) at the Korea Atomic Energy Research Institute was used for irradiation on the solutions. Quantities of 0, 5, 10, 20, and 40 kGy of absorbed doses were given to each sample to compare the dose effects on the decomposition of N₂H₄. All irradiation experiments were carried out with a dose rate of 10 kGy/hr at room temperature.

4.3. Analysis

The concentration of chemical species of N₂H₄ in the solutions was measured using a UV Spectrometer (DR 5000, Hach Co., Ames, IA, USA). The p-dimethylaminobenzaldehyde method was applied to detect the chemical species of N₂H₄.

5. Conclusions

The radiolysis of N₂H₄ in the N₂H₄–Cu⁺–HNO₃ solution during γ-ray irradiation was verified through the irradiation experiment and the analysis of a chemical species of N₂H₄ concentration. When copper ions were present in the N₂H₄–HNO₃ solution, the N₂H₄ decomposition, via the decomposition of the Cu⁺N₂H₄ complex, was promoted by the catalytic reaction of Cu⁺ ions. HNO₃ also accelerated the N₂H₄ decomposition in the N₂H₄–Cu⁺–HNO₃ system through the influence of the H⁺ ion and NO₃⁻ ion. This is because H⁺ produced by the reaction between H⁺ ion and eaq⁻ participated in the N₂H₄ decomposition reaction. Owing to the H⁺ ion effect, the N₂H₄ decomposition during irradiation was raised when the pH was decreased. NO₃⁻ ion and NO₃⁻ led to an increase in the N₂H₄ decomposition through the reaction with N₂H₄⁺ or the reaction with N₂H₅⁺. These additional paths, due to the existence of the Cu⁺ and NO₃⁻ ions, improved the N₂H₄ decomposition under irradiation condition. These findings can be applied, in accordance with the characteristics of radiolysis, to define the conditions of N₂H₄ concentration during chemical decontamination processes.

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References

1. Nakula, H.; Okitsub, K.; Maedab, Y.; Nishimu, R. Hydrazine degradation by ultrasonic irradiation. J. Hazard. Mater. 2007, 146, 636–639. [CrossRef]

2. Choudhary, G.; Hansen, H.; Donkin, S.G.; Kirman, C. Toxicological Profile for Hydrazine; U.S. Department of Health and Human Services: Washington, DC, USA, 1997; pp. 1–3.

3. Ionuranov, V.; Pasheevich, V.; Bogancs, J.; Tilky, P.; Schunk, J.; Pinter, T. Influence of hydrazine primary water chemistry on corrosion of fuel cladding and primary circuit components. In Water Chemistry and Corrosion Control of Cladding and Primary Circuit Components, Hluboka nad Vltavou, Czech Republic, 28 Sep–2 Oct 1998; International Atomic Energy Agency: Vienna, Austria, 1999.

4. Severa, J.; Bár, J. Handbook of Radioactive Contamination and Decontamination, 1st ed.; Elsevier Science Publishers: Amsterdam, The Netherlands, 1991; pp. 1–387.

5. Won, H.J.; Chang, N.O.; Park, S.Y.; Kim, S.B. Reductive Dissolution of Spinel-Type Iron Oxide by N2H4–Cu(I)–HNO3. J. Korean Ceram. Soc. 2019, 56, 387–393. [CrossRef]

6. Jung, J.Y.; Park, S.Y.; Won, H.J.; Choi, W.K.; Moon, J.K.; Park, S.J. Crevice Corrosion Properties of PWR Structure Materials under Reductive Decontamination Conditions. J. Nucl. Fuel Cycle Waste Technol. 2014, 12, 199–209. [CrossRef]

7. Eun, H.C.; Park, S.Y.; Choi, W.K.; Kim, S.B.; Won, H.J.; Chang, N.O.; Lee, S.B.; Park, J.S.; Seo, B.K.; Kim, K.C. A waste-minimized chemical decontamination process for the decontamination of a nuclear reactor coolant system. J. Radioanal. Nucl. Chem. 2020, 326, 665–674. [CrossRef]

8. Choi, W.; Won, H.; Jung, C.; Park, S.; Kim, S.; Yoon, I.; Moon, J.; Choi, J.; An, B.; Choi, M.; et al. Development of Decommissioning, Decontamination, and Remediation Technology for Nuclear Facilities: Development of Advanced Decontamination Technology for Nuclear Facilities; Korea Atomic Energy Research Institute: Daejeon, Korea, 2017; pp. 1–479.

9. Chen, L.; Chambelain, D.B.; Conner, C.; Vandegrift, G.F. A Survey of Decontamination Processes Applicable to DOE Nuclear Facilities; Argonne National Laboratory: Lemont, IL, USA, 1997; pp. 1–91.

10. Sophie, L.C. Water Radiolysis: Influence of Oxide Surfaces on H2 Production under Ionizing Radiation. Water 2011, 3, 235–253.

11. Pedzinski, T.; Gryzb, K.; Skotnicki, K.; Filipiak, P.; Bobrowski, K.; Chatgilialoglu, C.; Marcinia, B. Radiation- and Photo-Induced Oxidation Pathways of Methionine in Model Peptide Backbone under Anoxic Conditions. Int. J. Mol. Sci. 2021, 22, 4773. [CrossRef] [PubMed]

12. Buxton, G.V.; Sims, H.E. On the mechanism of the γ-radiolysis of deoxygenated aqueous solutions of hydrazine. Phys. Chem. Chem. Phys. 2000, 2, 4941–4946. [CrossRef]

13. Garana, G.; Hrme, G.P.; Venault, L.; Moisy, P.; Pimblott, S.M.; Marignier, J.L.; Mostafavi, M. Decay Mechanism of NO2 in Highly Concentrated Nitrate and Nitric Acidic Solutions in the Absence and Presence of Hydrazine. J. Phys. Chem. B 2016, 120, 5008–5014. [CrossRef] [PubMed]

14. Mootoka, T.; Sato, T.; Yamamoto, M. Effect of gamma-ray irradiation on the deoxygenation of salt-containing water using hydrazine. J. Nucl. Sci. Technol. 2013, 50, 363–368. [CrossRef]

15. Schmidt, E.W. Hydrazine and Its Derivatives: Preparation, Properties, Applications, 2nd ed.; Wiley-Interscience: Chichester, UK, 1984; pp. 1–212.

16. Ware, G.C.; Spulnik, J.B.; Gilbert, E.C. The Ionization Constant of Hydrazine Hydroxide. J. Am. Chem. Soc. 1936, 58, 1605–1606. [CrossRef]

17. Schwarzenbach, G. Die Dissosziationskonstante von Hydrazin. Helv. Chim. Acta 2004, 19, 178–182. [CrossRef]

18. Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. Deamination of α-amino acids induced by hydroxyl radicals and monovalent copper ions. A pulse radiolysis study. Inorg. Chim. Acta 1992, 192, 87–93. [CrossRef]

19. Nakui, H.; Okitsu, K.; Maeda, Y.; Nishimura, R. The effect of pH on sonocochemical degradation of hydrazine. Ultrason. Sonochem. 2007, 14, 627–632. [CrossRef] [PubMed]

20. Buxton, G.V.; Stuart, C.R. Radiation Chemistry of aqueous solutions of hydrazine at elevated temperatures. Part 1. Oxidation-free solutions. J. Chem. Soc. Faraday Trans. 1996, 92, 1519–1525. [CrossRef]

21. Sunaryo, G.R. The effect of hydrazine addition on the formation of oxygen molecule by fast neutron radiolysis. KNE Energy 2016, 1, 155–162. [CrossRef]

22. Dey, G.R. Reduction of the copper ion to its metal and clusters in alcoholic media: A radiation chemical study. Radiat. Phys. Chem. 2005, 74, 174–184. [CrossRef]

23. Filimonov, E.V.; Scherbakov, A.I. Catalytic Effect of Copper Ions on Nitrate Reduction. Prot. Met. 2004, 40, 280–285. [CrossRef]

24. Abedini, A.; Daud, A.R.; Hamid, M.A.A.; Othman, N.K.; Saion, E. A review on radiation-induced nucleation and growth of colloidal metallic nanoparticles. Nanoscale Res. Lett. 2013, 8, 474. [CrossRef] [PubMed]

25. Goldstein, S.; Czapski, G.; Cohen, H.; Meyerstein, D. Hydroxyl Radical Induced Decarboxylation and Deamination of 2-Methylalanine Catalyzed by Copper Ions. Inorg. Chem. 1992, 31, 2439–2444. [CrossRef]

26. Friedlich, L.C.; Machulek, A., Jr.; Silva, V.O.; Quina, F.H. Interference of inorganic ions on phenol degradation by the Fenton reaction. Sci. Agric. 2012, 69, 347–351. [CrossRef]

27. Liu, R.; Goodell, B.; Jellison, J.; Amirbahman, A. Electrochemical Study of 2,3-Dihydroxybenzoic Acid and Its Interaction with Cu(II) and H2O2 in Aqueous Solutions: Implications for Wood Decay. Environ. Sci. Technol. 2005, 39, 175–180. [CrossRef]

28. Katsumura, Y.; Jiang, P.Y.; Nagai, R.; Oishi, T.; Ishiqure, K.; Yoshida, Y. Pulse Radiolysis Study of Aqueous Nitric Acid Solutions: Formation Mechanism, Yield, and Reactivity of NO3 Radical. J. Phys. Chem. 1991, 95, 4435–4439. [CrossRef]
29. Forni, L.G.; Mora-Arellano, V.O.; Packer, J.E.; Willson, R.L. Nitrogen Dioxide and Related Free Radicals: Electron-transfer Reactions with Organic Compounds in Solutions containing Nitrite of Nitrate. *J. Chem. Soc. Perkin Trans. II* 1986, 1, 1–6. [CrossRef]

30. Dey, G.R. Nitrogen compounds’ formation in aqueous solutions under high ionizing radiation: An overview. *Radiat. Phys. Chem.* 2011, 80, 394–402. [CrossRef]

31. Horne, G.P.; Donochift, T.A.; Sims, H.E.; Orr, R.M.; Pimblott, S.M. Multi-Scale Modeling of the Gamma Radiolysis of Nitrate Solutions. *J. Phys. Chem. B* 2016, 120, 11781–11789. [CrossRef] [PubMed]

32. Ponomarev, A.V.; Bludenko, A.V.; Makarov, I.E. Effect of formate on the radiolytic degradation of nitrate in deaerated aqueous solutions. *Mendeleev Commun.* 2002, 12, 92–94. [CrossRef]

33. Faraggi, M.; Zehavi, D.; Anbar, M. Radiolysis of Aqueous Nitrate Solutions. *Trans. Faraday Soc.* 1971, 67, 701–710. [CrossRef]

34. Wellman, C.R.; Ward, J.R.; Kuhn, L.P. Kinetics of the oxidation of hydrazine by hydrogen peroxide, catalyzed by copper(II). *J. Am. Chem. Soc.* 1976, 98, 1683–1684. [CrossRef]

35. Cheng, Y.; Wu, X.; Xu, H. Catalytic decomposition of hydrous hydrazine for hydrogen production. *Sustain. Energy Fuels* 2019, 3, 343–365. [CrossRef]

36. Lim, P.K.; Zhong, Y. The Copper-Catalyzed Redox Reaction between Aqueous Hydrogen Peroxide and Hydrazine. 1. New Experimental Results and Observations. *J. Am. Chem. Soc.* 1989, 111, 8398–8404. [CrossRef]

37. Lim, P.K.; Zhong, Y. The Copper-Catalyzed Redox Reaction between Aqueous Hydrogen Peroxide and Hydrazine. 2. Reaction Mechanism, Model Analysis, and a Comparison of Model and Experimental Results. *J. Am. Chem. Soc.* 1989, 111, 8404–8410. [CrossRef]

38. Haesik, Y.; Seheon, K.; Jeongwook, S.; Gamwoo, K.; Jongchang, K.; Juyoun, G. Electrochemical Study of Chrome Nickel Ferrites under a HyBRID Decontamination Condition; Korea Atomic Energy Research Institute: Daejeon, Korea, 2017; pp. 1–47.

39. Belova, E.V.; Egorov, G.F. Radiochemical behavior of hydrazine nitrate in aqueous nitric acid solutions. *At. Energy* 1997, 83, 622–626. [CrossRef]

40. Weiner, I.D.; Verlander, J.W. Role of NH₃ and NH₄⁺ transporters in renal acid-base transport. *Am. J. Physiol.-Ren. Physiol.* 2011, 300, F11–F23. [CrossRef] [PubMed]