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Radiolytic decomposition of hydrazine in N_2H_4-Cu^+-HNO_3 system

Naon Chang[a,b], Huijun Won[a*], Sangyoon Park[a], Heechul Eun[a], Sunbyeong Kim[a], and Yongsoo Kim[b]
[a]*Decommissioning technology research division, Korea Atomic Energy Research Institute, 111 Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon*
[b]*Department of Nuclear Engineering, Hanyang University, 222 Wangsimri-ro, Seongdong-gu, Seoul*
[*]*Corresponding author: nhjwon@kaeri.re.kr*

1. Introduction

Before decommissioning the nuclear power plant, the chemical decontamination is applied to remove the radioactive materials from a primary system. Chemical decontamination process is carried out with an oxidation and a reductive step. Especially, N_2H_4-Cu^+-HNO_3 solution can be used as the reductive decontamination agent for removing Fe oxide layer by reducing the Fe^{3+} ions to Fe^{2+} ions [1]. However, it is possible that hydrazine in the decontamination agent decomposed due to the radiation from the primary system during the application. The typical radiation source in the primary system is Co-60, therefore, ɤ-ray causes the radiolytic decomposition of hydrazine into N_2, NH_3, and NH_4^+ as the final products [2]. Decrease of hydrazine concentration in the agent could affect the efficiency of the decontamination. In this reason, we studied the ɤ-irradiation effects on the hydrazine decomposition. In addition, we suggest the expected mechanism of the hydrazine radiolysis in N_2H_4-Cu^+-HNO_3 system. Furthermore, the radiolytic decomposition results of the hydrazine are compared according to pH of the each solution.

2. Methods

2.1 Sample preparation and ɤ-irradiation

The samples solutions were composed of hydrazine monohydrate (Junsei), copper(I) chloride (SIGMA-ALDRICH), and nitric acid (EMSure). Nitric acid was used for adjusting pH of the sample solutions. The experimental conditions of the solutions are listed in Table I. All sample solutions were irradiated with ɤ-ray by using Co-60 source high-dose ɤ-ray irradiator from Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute. The absorbed doses of ɤ-ray to the sample solutions were 0, 20, and 40 kGy, respectively.

Table I. Experimental conditions.

	Conditions		
$[N_2H_4]$	0.05 M	0.05 M	0.05 M
$[Cu^+]$	0.5 mM	0.5 mM	0.5 mM
pH	1	3	5

2.2 Analysis

An UV Spectrometer (DR5000, Hach Co.) was used to measure the concentration of hydrazine in the samples before and after ɤ-irradiation using the p-dimethylamino benzaldehyde method.

3. Results and discussions

2.1 Radiolysis reactions of hydrazine

The probable reactions of hydrazine decomposition in N_2H_4-HNO_3 and N_2H_4-Cu^+-HNO_3 systems are listed in Table II [2-6].

Hydrazine in an aqueous solution exists as N_2H_4, $N_2H_5^+$, and $N_2H_6^{2+}$ according to the variation of pH. Hydrazine generally hydrolyzed to $N_2H_5^+$ in an acidic solution. Additionally, $N_2H_6^{2+}$ coexists with $N_2H_5^+$ below pH 1.

When ɤ-ray irradiates to the aqueous solution, as represented in Eq. (1), water is preferentially decomposed into e_{aq}^-, $H^\bullet$, $^\bullet OH$, and so on. e_{aq}^- reacts with H^+ ion in the solution and also generates $H^\bullet$ as listed in Eq. (2). These $^\bullet OH$, e_{aq}^-, and $H^\bullet$ radicals cause the radiolysis of hydrolyzed species.

In N_2H_4-HNO_3 system, $N_2H_6^{2+}$ reacts with $^\bullet OH$ and produces N_2 at pH 1, the final product of hydrazine radiolysis. The reaction is expressed as following;

$$N_2H_6^{2+} + 4^\bullet OH \rightarrow N_2 + 4H_2O + 2H^+$$

At pHs 1, 3, and 5, $N_2H_5^+$ reacts with e_{aq}^-, $^\bullet OH$, and $H^\bullet$ during ɤ-irradiation as listed in Eqs. (4-6). When the reaction between $N_2H_5^+$ and e_{aq}^- occurs as represented in Eq. (4), N_2H_4 is generated. N_2H_4 can be hydrolyzed as mentioned or consecutively radiolyzed as listed in Eq. (7). The reactions are summarized as followings;

$$N_2H_5^+ + e_{aq}^- \rightarrow H^\bullet + N_2H_4$$

$$N_2H_4 + xH^+ \rightarrow N_2H_5^+ \text{ or } N_2H_6^{2+},\ x = 1, 2$$

$$N_2H_4 + {}^\bullet OH \rightarrow {}^\bullet N_2H_3 + H_2O$$

In the case of $N_2H_5^+$ reacts with $^\bullet OH$, $N_2H_4^{\bullet +}$ is produced as listed in Eq. (5). $N_2H_4^{\bullet +}$ reacts with each other and generates N_2H_2 and $N_2H_5^+$ as listed in Eq. (8). $N_2H_5^+$ in Eq. 8 causes the reactions as listed in Eqs. (4-6).

On the other hand, $^{\bullet}N_2H_3$ is produced through the reaction between N_2H_2 and $H^{\bullet}$ as listed in Eq. (9).

$$N_2H_5^+ + {}^{\bullet}OH \rightarrow N_2H_4^{\bullet+} + H_2O$$

$$N_2H_4^{\bullet+} + N_2H_4^{\bullet+} \rightarrow N_2H_2 + N_2H_5^+ + H^+$$

$$N_2H_2 + H^{\bullet} \rightarrow {}^{\bullet}N_2H_3$$

In the case of $N_2H_5^+$ reacts with $^{\bullet}H$ as listed in Eq. (6), $^{\bullet}NH_2$ and NH_4^+ are generated. $^{\bullet}NH_2$ reacts with N_2H_4, $^{\bullet}N_2H_3$ and NH_3 are formed as represented in Eq. (10).

$$N_2H_5^+ + H^{\bullet} \rightarrow {}^{\bullet}NH_2 + NH_4^+$$

$$^{\bullet}NH_2 + N_2H_4 \rightarrow {}^{\bullet}N_2H_3 + NH_3$$

$^{\bullet}N_2H_3$ generated by reaction Eq. (7), (9), and (10) causes the dimerization or reacts with $N_2H_4^{\bullet+}$. The final products of these two reactions are N_2 and NH_3 as listed in Eqs. (11) and (12).

$$^{\bullet}N_2H_3 + {}^{\bullet}N_2H_3 \rightarrow N_4H_6 (\rightarrow N_2 + 2NH_3)$$

$$^{\bullet}N_2H_3 + N_2H_4^{\bullet+} \rightarrow N_4H_7^+ (\rightarrow N_2 + 2NH_3)$$

Considering N_2H_4-Cu^+-HNO_3 system, a study on the radiolysis reaction has not yet been reported. Zhong and Lim reported the results of thermal decomposition [5]. They mentioned that Cu^+ ion forms complex with hydrazine and acts as a catalyst in a hydrazine decomposition reaction. In this study, small amount of Cu^+ ion exists as compared with the amount of hydrazine in an acidic solution. As listed in reaction Eq. (13), Cu^+ ion and N_2H_4 can form a complex and reacts with N_2H_2. $Cu(^{\bullet}N_2H_3)_2$, product of the complex and N_2H_2 reaction, decomposes into Cu^+ ion and $^{\bullet}N_2H_3$. Cu^+ ion forms the complex with N_2H_4, furthermore, $^{\bullet}N_2H_3$ decomposed into N_2 and NH_3 following as Eq. (11) and (12).

$$Cu^+N_2H_4 + N_2H_2 \leftrightarrow Cu({}^{\bullet}N_2H_3)_2 \rightarrow Cu^+ + 2{}^{\bullet}N_2H_3$$

In addition, nitric acid accelerates the hydrazine radiolysis. As listed in Eq. (14) and (15), $NO_3^{\bullet}$ produced by the reaction between nitric acid and $^{\bullet}OH$ reacts with $N_2H_5^+$ in this system. It causes the generation of $N_2H_4^{\bullet+}$, which is the intermediate products of hydrazine radiolysis. $N_2H_4^{\bullet+}$ consecutively participates in the decomposition reaction. Therefore, it is expected that hydrazine radiolysis in N_2H_4-Cu^+-HNO_3 system occurs more than N_2H_4 solution.

$$HNO_3 + {}^{\bullet}OH \rightarrow NO_3^{\bullet} + OH^-$$

$$N_2H_5^+ + NO_3^{\bullet} \rightarrow N_2H_4^{\bullet+} + NO_3^- + H^+$$

Table II. Probable radiolytic decomposition reactions of hydrazine in N_2H_4-Cu^+-HNO_3 system [2-6]

Eq.	**Reaction**	**Rate constant ($M^{-1}s^{-1}$)**
A. Hydrazine hydrolysis		
B. Water radiolysis		
1	$H_2O \rightarrow 0.27e_{aq}^-, 0.06H^{\bullet}, 0.26{}^{\bullet}OH, 0.045H_2\ 0.08H_2O_2, 0.27H_3O^+$	-
2	$e_{aq}^- + H^+ \rightarrow H^{\bullet}$	-
C-1. Hydrazine radiolysis		
3	$N_2H_6^{2+} + 4{}^{\bullet}OH \rightarrow N_2 + 4H_2O + 2H^+$	-
4	$N_2H_5^+ + e_{aq}^- \rightarrow H^{\bullet} + N_2H_4$ ($\rightarrow$ hydrolysis, radiolysis)	1.6×10^8
5	$N_2H_5^+ + {}^{\bullet}OH \rightarrow N_2H_4^{\bullet+} + H_2O$	8.2×10^7
6	$N_2H_5^+ + H^{\bullet} \rightarrow {}^{\bullet}NH_2 + NH_4^+$	1.0×10^4
7	$N_2H_4 + {}^{\bullet}OH \rightarrow {}^{\bullet}N_2H_3 + H_2O$	5.4×10^9
8	$N_2H_4^{\bullet+} + N_2H_4^{\bullet+} \rightarrow N_2H_2 + N_2H_5^+ + H^+$	1.0×10^8
9	$N_2H_2 + H^{\bullet} \rightarrow {}^{\bullet}N_2H_3$	3.0×10^9
10	$^{\bullet}NH_2 + N_2H_4 \rightarrow {}^{\bullet}N_2H_3 + NH_3$	1.0×10^7
11	$^{\bullet}N_2H_3 + {}^{\bullet}N_2H_3 \rightarrow N_4H_6 (\rightarrow N_2 + 2NH_3)$	4.0×10^8
12	$^{\bullet}N_2H_3 + N_2H_4^{\bullet+} \rightarrow N_4H_7^+ (\rightarrow N_2 + 2NH_3)$	3.0×10^8
C-2. Copper-catalyzed reaction		
13	$Cu^+N_2H_4 + N_2H_2 \leftrightarrow Cu({}^{\bullet}N_2H_3)_2 \rightarrow Cu^+ + 2{}^{\bullet}N_2H_3$	-
C-3. Nitric acid radiolysis with hydrazine		
14	$HNO_3 + {}^{\bullet}OH \rightarrow NO_3^{\bullet} + OH^-$	5.3×10^7
15	$N_2H_5^+ + NO_3^{\bullet} \rightarrow N_2H_4^{\bullet+} + NO_3^- + H^+$	1.0×10^9

2.2 ɤ-irradiation tests on N_2H_4-Cu^+-HNO_3 system

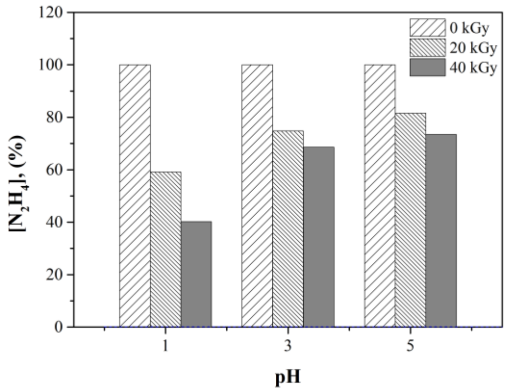

Fig. 1. Remaining portion of hydrazine according to pH during irradiation of each absorbed doses.

The results of hydrazine decomposition in solution during ɤ-irradiation are represented in Fig. 1. As shown in Fig. 1. The remaining concentration of hydrazine decreases when the absorbed dose of ɤ-ray increases. In addition, the amount of hydrazine remained is less when the pH was lower at the same absorbed dose of ɤ-ray.

When the absorbed dose increases, the amount of water radiolysis products listed in Eqs. (1) and (2) increases. This causes the increase of the hydrazine radiolysis reactions listed in Table II. Therefore, concentration of hydrazine decreases with increasing the absorbed dose regardless pH of the samples.

The pH effects on the hydrazine radiolysis can be explained by reaction between chemical species of hydrazine and $H^\bullet$ and $NO_3^\bullet$. When pH of the sample was lower, the amount of HNO_3 added was larger. The increase of HNO_3 concentration causes the increase the amount of $H^\bullet$ and $NO_3^\bullet$ in solution due to Eqs. (2) and (14). These $H^\bullet$ and $NO_3^\bullet$ promoted the radiolytic decomposition of hydrazine as mentioned. Therefore, hydrazine radiolysis more when the pH was lower.

3. Conclusions

Hydrazine in N_2H_4-Cu^+-HNO_3 decontamination solution could be decomposed during the application due to the ɤ-irradiation. The radiolytic decomposition mechanism of hydrazine suggested in this study was composed of water radiolysis, hydrazine radiolysis, copper-catalyzed reaction and nitric acid radiolysis. This mechanism could explain the absorbed dose and pH effects on the hydrazine decomposition. However, the radiolysis products of hydrazine was not investigated in this study. Therefore, it is necessary to analyze the ammonium ion to confirm above mechanism. Additionally, the effect of the copper ions on the hydrazine radiolysis needs to be studied by experiment.

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