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Decomposition Reaction of Hydrazine in a High Radiation Field

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1. Introduction

KAERI developed the organic chelate free chemical decontamination agent. The agent is used in an acidic solution and the main chemicals are hydrazine and cuprous ion. From the dissolution tests on magnetite particles and oxide layer formed on Type 304 SS contaminated with radionuclides, it was found that the decontamination agent successfully dissolved the oxides [1]. Furthermore, the decontamination agent shows good corrosion compatibility. As the decontamination is operated in a high radiation field, it is essential to evaluate the radiation stability of the developed chemical decontamination agent. The objectives of the study are to evaluate the radiation stability of hydrazine and to elucidate the decomposition reaction of hydrazine. Especially, the reaction mechanism for producing the ammonium ion from the decomposition of hydrazine is suggested. Radiation stability of the decontamination agents developed in foreign countries is also compared with that of the developed chemical decontamination agent.

2. Methods and Results

2.1 Experimental condition

Two different solutions of the 0.04M hydrazine and 0.04 M hydrazine with 0.0005 M copper ion were used for the tests of hydrazine decomposition. pH was adjusted to 3.0 by HNO_3. Decontamination solution (30 ml) was inserted into the 50 ml vial. Dose rates for irradiation were 20, 40, 100, 200 and 1000 Gy/hr, respectively. Samples were irradiated for five hours. In the separate tests performed for 4 hours in the high radiation field, dose rates for irradiation were 2.5 and 4 kGy/hr, respectively.

Hydrazine forms a complex with p-dimethylamino-benzaldehyde and color of the complex is yellow. After irradiation, the remaining concentration of hydrazine was analyzed by UV spectrometer at the wavelength of 455 nm. Identification and quantitative analysis of existing ions in hydrazine solution were performed by ion chromatograph..

2.2Test results

Fig. 1 shows the plot of the remaining portion of hydrazine against the absorbed dose. As shown in the figure, decomposition of hydrazine is accelerated by copper ion. No decomposition reaction of hydrazine occurs under 1 kGy. When the copper ion exists in the solution, it has increased decomposition ratio of hydrazine (i.e. 20% higher than the solution without copper ion under 20 kGy). Arkhipov et al. reported that hydrazine is decomposed in the high radiation field producing nitrogen gas, ammonia and hydrogen [2]. They also explained that metal ion acts as a catalyst in the decomposition of hydrazine.

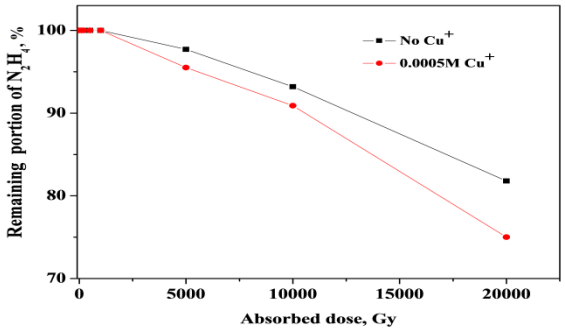

Fig. 1. Remaining portion of N_2H_4 according to absorbed dose.

Concentrations of ammonium ion at given absorbed doses are listed in Table 1. Ammonium ion is produced when the absorbed dose is above 1 kGy. At a given absorbed dose, more ammonium ion is produced when the copper ion exists in the solution. Lee et al. also reported that more ammonium ion is produced when the copper ion is in the solution [3].

Table 1. NH_4^+ concentration according to absorbed dose[3].

Absorbed Dose, kGy	$[NH_4^+]$, ppm	
	0.0005M Cu^+	No Cu^+
0	0	0
0.1	0	0
0.2	0	0
0.5	0	0
1	0	0
5	34.241	23.559
10	70.114	40.696
20	96.718	54.897

Protasova et al. performed a radiolysis test of hydrazine in 2 M HNO_3 solution at 1.2 Gy/s and at 313 K by changing the irradiation time [4]. In that study hydrazine concentration decreased with time. They proposed the reaction mechanism on the production of ammonium ion. The proposed radiolysis reactions and their rate constants are listed in Table 2. As listed in Table 2, there can be two pathways to produce ammonium ion by the radiolysis of hydrazine. e^-, OH^-, H^+, $OH\cdot$ and $H\cdot$ are the radiolysis products of water molecules [5]. The first pathway is simpler than the second pathway. However, the rate constant for the production of ammonium ion of the first pathway is much smaller than that of second pethway (3.0 X 10^{-6} /M.s). We can infer that ammonium ion is produced through the second pathway.

Table 2. Mechanism of radiolysis [4].

	Reaction	k, $M^{-1}s^{-1}$
	$N_2N_5^+ \leftrightarrow N_2H_4 + H^+$	pK_a =8.1
1st	$N_2H_5^+ + NO_3 \rightarrow N_2H_4^+ + H^+ + NO_3^-$	6.6×10^6
	$OH + HNO_3 \rightarrow H_2O + NO_3$	1.7×10^8
	$N_2H_4^+ + N_2H_4^+ \rightarrow N_4H_8^{2+}$	1.5×10^9
	$N_4H_8^{2+} \rightarrow 2NH_4^+ + N_2$	3.0×10^{-6}
2nd	$NO_3^- + e_{aq}^- \rightarrow NO_3^{2-}$	4.7×10^{10}
	$NO_3^- + H \rightarrow OH^- + NO_2$	2.4×10^6
	$NO_3^{2-} + H^+ \rightarrow OH^- + NO_2$	1.7×10^9
	$NO_2 + NO_2 \rightarrow N_2O_4$	6.4×10^8
	$N_2O_4 + H_2O \rightarrow HNO_2 + H^+ + NO_3^-$	1.0×10^6
	$HNO_2 + H^+ \rightarrow NO^+ + H_2O$	1.0×10^{10}
	$N_2H_5^+ + NO^+ \rightarrow N_2H_3^+ + HNO + H^+$	3.0×10^4
	$N_2H_3^+ + N_2H_3^+ \rightarrow N_4H_6^{2+}$	1.0×10^7
	$N_4H_6^{2+} \rightarrow HN_3 + NH_4^+ + H^+$	1.0×10^3

Fig. 2 shows the remaining ratio of the main chemicals against the absorbed dose for the three kinds of the chemical decontamination agents. There is no big difference between the three kinds of chemical decontamination agents in a low absorbed dose region. The remaining ratio is above 90 % for HYBRID, 60 % for CORD, and 70 % for CANDEREM at an absorbed dose of 10 kGy. This means that the main chemical of HYBRID is far more stable than the other chemical decontamination agents in a high absorbed dose region.

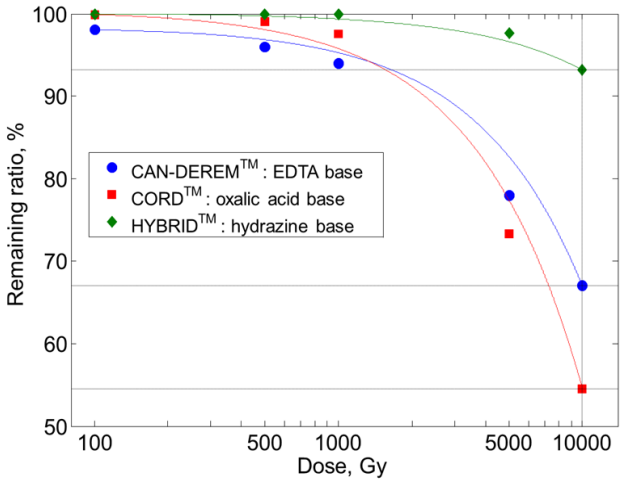

Fig. 2. Remaining ratio of the main chemicals according to absorbed dose.

3. Conclusion

In this study, we obtained that there is no decomposition of hydrazine by radiolysis below 1 kGy. In addition, we confirmed that the radiolysis of hydrazine and production of ammonium ion are affected by the copper ion in the chemical decontamination agents. These findings are supportive to the decomposition stability of hydrazine in a high radiation field and inferred to attribute the higher stability of HYBRID decontamination solution.

ACKNOWLEDGEMENT

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