Transactions of the Korean Nuclear Society Autumn Meeting
Gyoungju, Korea, October 24-25, 2013

A Comparative Study on the Destruction of Hydrazine

Woo-Seong Lee, Hui-Jun Won*, Sang-Yoon Park, Wang -Kyu Choi and Jei-Kwon Moon,
Korea Atomic Energy Research Institute, 989 Daedeokdaero, YuseongGu, Daejeon, 305-353, Korea
**Corresponding author: nhjwon@kaeri.re.kr*

1. Introduction

Korea Atomic Energy Research Institute (KAERI) developed a new chelate free chemical decontamination agent. The agent uses Cu ion and hydrazine in an acid solution. The generation of the secondary waste can be reduced by the destruction of hydrazine. Wellman et al. reported that hydrazine is decomposed to water and nitrogen by hydrogen peroxide in the presence of Cu^{2+} ion in the pH range of 9 to 10 [1].

$$N_2H_4 + 2H_2O_2 \xrightarrow{Cu^{2+}} N_2 + 4\,H_2O$$

Decomposition of hydrazine by the radiation field is important during the application of chemical decontamination agent. Arkhipov et al. reported that the radiolysis products of hydrazine are ammonia, nitrogen and hydrogen [2].

$$N_2H_4 \xrightarrow{radiation} x\,N_2 + yNH_3 + z\,H_2$$

The objective of the study is to compare the decomposition products of hydrazine by hydrogen peroxide and the decomposition products of hydrazine by the radiation field. Especially, the remaining portion of hydrazine by hydrogen peroxide and by radiation field was investigated.

2. Methods and Results

2.1 Experimental condition

80 % hydrazine monohydrate from Junsei Chemical Co. was used as received. pH was adjusted by HNO_3. All tests were performed at pH = 3. The concentration of hydrazine was analyzed at 455 nm by the UV spectrophotometer from Hach Company (DR 5000).

p-dimethylaminobenzaldehyde was used as an indicator. The concentration of ammonium ion was analyzed by ion chromatograph from Metrohm Company. Eluent composition was 1.7 mM HNO_3 + 0.7 mM PDCA. The experimental condition for radiolysis is listed in Table 1.

Table 1. Experimental condition

$[N_2H_4]$	$[Cu^{2+}]$	pH	Absorbed dose, kGy
0.04M	0.0005M	3	0, 0.1, 0.2, 0.5, 1, 5, 10, 20
	0M		

2.2 Test results

Hydrazine was decomposed to ammonia in the high radiation field. Ammonia was dissolved and turn into the ammonium ion. Fig. 1 shows the variation of ammonium ion concentration in respect to the absorbed dose. Radiolysis of hydrazine occurs when the absorbed dose exceeds 1 kGy. The concentration of ammonium ion is proportional to the amount of absorbed dose. Arkhipov et al. reported that the radiolysis of hydrazine is catalyzed by the metal in solution [2]. As shown in Fig. 1, the presence of copper ion increased the radiolysis of hydrazine.

Fig. 2 shows the variation of hydrazine concentration in terms of time at constant $[H_2O_2]$. At the initial stage, the decomposition of hydrazine increased by presence of copper ion. Lin et al. reported that hydrazine decomposition by $[H_2O_2]$ increased three folds by the addition of copper ions [3]. But, the decomposed portion of hydrazine is nearly same when the reaction time exceeds 90 minutes. These two results are contrary. From the ion chromatograph analysis, it was found that ammonium ion was not produced during the chemical decomposition of hydrazine by $[H_2O_2]$.

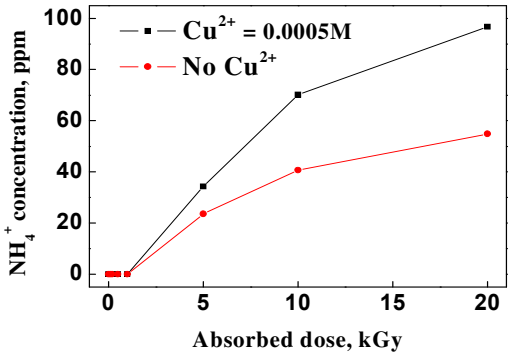

Fig. 1. NH_4^+ ion concentration according to absorbed dose.

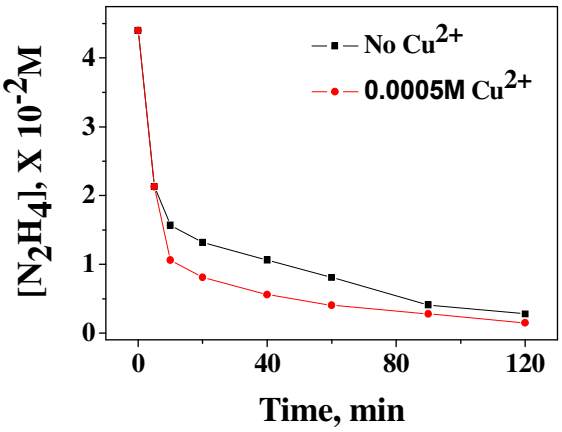

Fig. 2. N_2H_4 concentration according to time(pH=3, $[N_2H_4]$=0.04M, 80°C 2hr).

Table 2 lists the decomposed portion of hydrazine for the two cases. When the absorbed dose is 20 kGy, the decomposed portion of hydrazine exceeds 20 %. To reduce the decomposed portion, it is necessary to add the decomposition inhibitor or more hydrazine.

The decomposition of hydrazine by hydrogen peroxide is very effective. This is related to high reducing power of hydrazine and high oxidizing power of hydrogen peroxide.

Table 2. Decomposed portion. When the absorbed dose is 20 kGy, the decomposed portion of hydrazine exceeds 20 %

	Radiolysis, 20kGy		Chemical decomposition, 80°C	
	$[Cu^{2+}]$ 0.0005M	No Cu^{2+}	$[Cu^{2+}]$ 0.0005M	No Cu^{2+}
Decomposed portion, %	26.30	20.13	96.59	93.64

3. Conclusion

During the application of a dilute chemical decontamination method to the internal of the primary coolant system, the concentration of chemical agent becomes to reduce by radiation exposure. The control of the concentration of the main decontamination agent is necessary when the radiation field is very high. The variation of hydrazine concentration by radiolysis is suggested. To effectively reduce the secondary waste generation, on the contrary, the decomposition of hydrazine after decontamination is also necessary. Our experiments resulted in the decomposition of hydrazine more than 96% by the addition of hydrogen peroxide. By the variation of the decomposition process condition, hydrazine would be decomposed completely.

Acknowledgement

This work was carried out under the Nuclear R & D Program funded by the Ministry of Science, ICT & Future Planning.

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