Volume Reduction of the Secondary Waste Generated from N_2H_4-Cu^+-H_2SO_4 Decontamination Solution

Huijun Won[1*], Joonyoung Jung, Seonbyung Kim, Sangyoon Park, Wangkyu Choi, Jeikwon Moon

NPP D & D Technology Development Division, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea

Abstract: Decomposition characteristic of N_2H_4 in a N_2H_4-H_2SO_4-Cu^+ solution by H_2O_2 was investigated in the temperature range from 50°C to 80°C. The decomposed portion of N_2H_4 at a given quantity of H_2O_2 was increased with temperature and solution pH. Catalytic effect of cuprous ion on the decomposition of N_2H_4 was negligible in the experimental range. N_2H_4 was decomposed perfectly to N_2 and H_2O by the continual addition of H_2O_2. Removal performance of SO_4^{2-} ion in the remaining solution by a precipitation method was also investigated. SO_4^{2-} ion was precipitated to $BaSO_4$ by the same equivalent of Ba^{2+} ion and removed from the solution satisfactorily.

Key words: decontamination; waste; treatment; decomposition; precipitation

Introduction

KAERI developed the decontamination solution called HYBRID-D (Hydrazine Base Reductive metal Ion Decontamination for Decommissioning). The solution is used to decontaminate an internal loop of the coolant system of the nuclear power plant. After the application of the decontamination solution, the solution will be purified and the generation of the secondary waste should be reduced as much as possible. To remove decontamination chemicals, radio-nuclides and metal ions in a decontamination solution, ion exchange resin is widely used. It, however, generates a large volume of the secondary waste. HYBRI-D solution consists of N_2H_4, H_2SO_4 and Cu^+ ion. N_2H_4 and H_2SO_4 can be removed by the decomposition of hydrazine and the precipitation of sulfate ion. The objective of the study is to evaluate the decomposition performance of hydrazine by hydrogen peroxide and the precipitation characteristics of sulfate ion by Ba^{2+} and Sr^{2+} ion.

*Corresponding author: *nhjwon@kaeri.re.kr, Fax: +82-42-868-4797*

Experimental

100 ml of 0.044 M N_2H_4 solution was used for the decomposition tests at $[Cu^+]$ = 0 M and $[Cu^+] = 5 \times 10^{-4}$ M, respectively. The reaction temperature was in the range from 50°C to 80 ^{0}C and solution pH was controlled between 2 and 5. In the initial reaction stage 0.4 ml of 30 % H_2O_2 solution was added to the N_2H_4 solution. Then, 0.3 ml of 30 % H_2O_2 solution was added every 10 minutes. N_2H_4 forms a complex with p-dimethyl aminobenzaldehyde. Hydrazine concentration was analyzed by UV spectrometer (Hach DR 5000) at 455 nm.

100 ml of 0.046 M H_2SO_4 solution was used to the precipitation test. Equal equivalent of $Ba(OH)_2$ and $Sr(OH)_2$ reacted with H_2SO_4 solution. The concentration of sulfate ion was also analyzed by UV spectrometer at 450 nm. Particle size distribution of precipitants was measured by zeta potential analyzer (Zetaplus).

Results and Discussion

Hydrazine decomposition

Figure 1 shows the variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 at pH=3. The efficiency of hydrogen peroxide on the decomposition of hydrazine increases with the increase of temperature. Graham [1] reported that the reaction between N_2H_4 and H_2O_2 in the absence of Cu^{+1} ion occurs as two steps as expressed in Eqs. (1) and (2).

$$\mathbf{2\ H_2O_2 \rightarrow O_2 + 2\ H_2O} \quad \textbf{(1)}$$

$$\mathbf{N_2H_4 + O_2 \rightarrow N_2 + 2\ H_2O} \quad \textbf{(2)}$$

Figure 2 shows the variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 at 60°C. The efficiency of hydrogen peroxide on the decomposition of hydrazine increases with the increase of solution pH. The standard oxidation potential of hydrazine is 1.17 V and the oxidation potential increases with the solution pH [2].

Fig. 3 shows the variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 at pH=3 and $[Cu^+] = 5 \times 10^{-4}$ M. Similar to Fig.1, the efficiency of hydrogen peroxide on the decomposition of hydrazine also increases with the increase of temperature. Lin et al. reported [3] that the reaction between N_2H_4 and H_2O_2 in the presence of Cu^{+1} ion occurs as two steps as expressed in Eq. (3) and (4).

$$\mathbf{N_2H_4 + H_2O_2 \rightarrow N_2H_2 + 2\ H_2O} \quad \textbf{(3)}$$

$$\mathbf{N_2H_2 + H_2O_2 \rightarrow N_2 + 2\ H_2O} \quad \textbf{(4)}$$

They suggested that the coordination compound between Cu ion and hydrazine initiated the decomposition reaction as expressed in Eq. (5).

$$\mathbf{Cu^+N_2H_4 + H_2O_2 \rightarrow Cu^+ + N_2H_2 + 2\ H_2O} \quad \textbf{(5)}$$

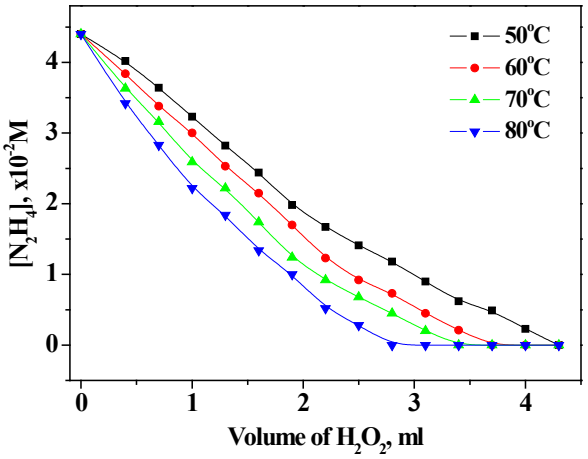

Figure 1: Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different temperature, $[Cu^+]$ = 0 M, pH= 3.0

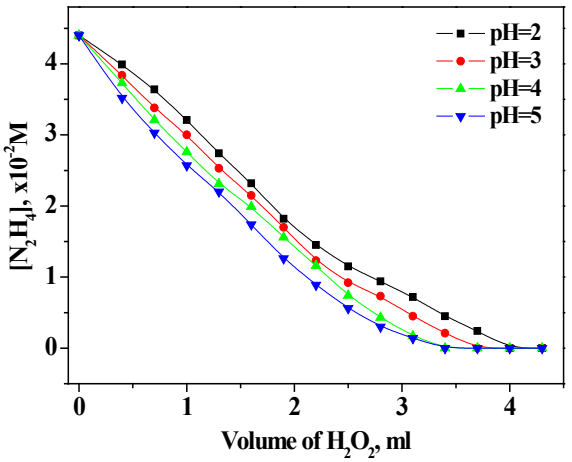

Figure 2: Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 accumulated volume of H_2O_2 under different pH, $[Cu^+]$ = 0 M, 60°C

Fig. 4 shows the variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 at 60°C. The efficiency of hydrogen peroxide on the decomposition of hydrazine also increases with the increase of solution pH.

For all the test results, it was found that hydrazine is perfectly decomposed by the continual addition of hydrogen peroxide. The amount of hydrogen peroxide necessary to decompose hydrazine, however, was 3 times higher than that of the theoretical value. The catalytic effect of Cu^+ ion on the decomposition of hydrazine was negligible.

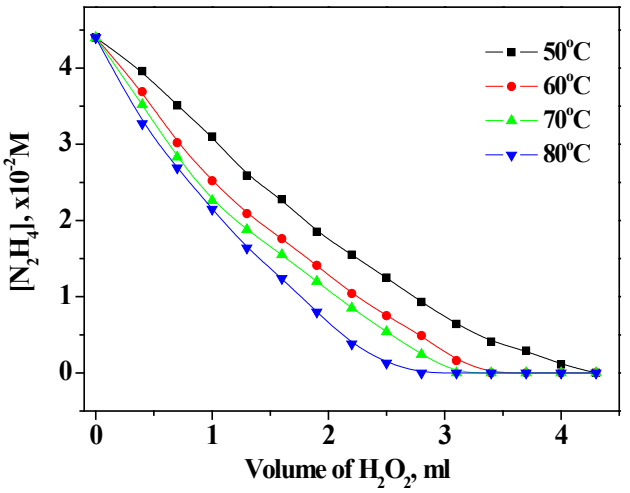

Figure 3: Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different temperature, $[Cu^+]$ = 5 X10^{-4} M, pH= 3.0

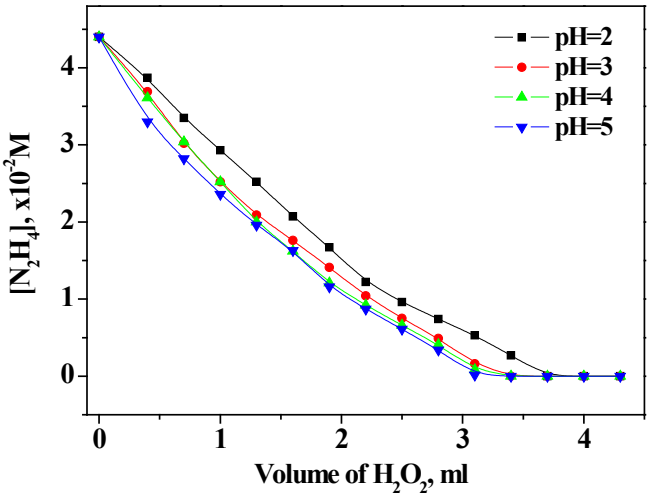

Figure 4: Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different pH, $[Cu^+]$ = 5 X10^{-4} M, 60°C

Precipitation of sulfate ion

Table 1 lists the size distribution of $BaSO_4$ and $SrSO_4$ particles. Same equivalent of SO_4^{2-} ion was mixed with Ba^{2+} ion Sr^{2+} ion. The reaction between and H_2SO_4 $Ba(OH)_2$ is expressed by following equation.

$$H_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 \downarrow + 2\ H_2O \quad (6)$$

From the UV analysis of sulfate ion, it was found that greater than 98 % of sulfate ion was removed by Sr^{2+} ion and the entire sulfate ion was removed by Ba^{2+} ion. Particle size of precipitants increased with time. This is attributed of agglomeration among particles.

Table 1
Size distribution of precipitants

Time (min)	*Size (μm)*	
	$BaSO_4$	*$SrSO_4$*
5	2.55	5.99
35	2.71	6.17
65	2.90	10.30

Conclusions

A feasibility study on the treatment of N_2H_4-Cu^+- H_2SO_4 system was performed. Hydrazine was perfectly decomposed to nitrogen gas and water by hydrogen peroxide. Greater than 98 % of sulfate ion was precipitated by strontium and barium ion and the precipitant could be easily removed from the decontamination solution. As nitrogen gas and water are not toxic materials, hydrazine does not exert a bad influence on the environment. The inorganic precipitant is safe state for disposal. Nuclear grade ion exchange resin is widely used to purify the chemical decontamination solution. Chemical decontamination technology using ion exchange resin, however, will generate a large quantity of the secondary waste. The HYBRID-D process will greatly reduce the generation of the secondary waste.

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