Hydrogen Peroxide Catalytic Oxidation of Hydrazine in Decontamination Solution†

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Decomposition tests of hydrazine were conducted in an acidic solution using a hydrogen peroxide solution in a temperature range of 50 to 80 °C. The decomposed fraction of hydrazine was calculated from an analysis of the hydrazine ion concentration in solution by a UV-visible spectrometer. The increase of $[Cu^{2+}]$ increased the decomposition reaction rate of hydrazine. The decomposition reaction rate of hydrazine also increased with the increase of temperature and the solution pH. It was explained that the formation of $N_2H_5^+$ ion retards the reaction in the lower pH region. One step excess injection of hydrogen peroxide could not decompose the hydrazine efficiently. The decomposed portion of hydrazine could be increased by the repetitive injection of hydrogen peroxide.

Keywords: Decomposition, N_2H_4, Copper ion, H_2O_2, Injection, Decontamination.
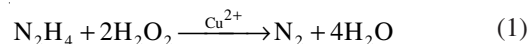
INTRODUCTION

Chemical decontamination technology applicable to the internal loop of a nuclear power plant should have a good decontamination performance and should generate a small amount of secondary waste. To get a good decontamination performance, concentrated chemical solution is sometimes used. But it generates a large volume of secondary waste. The dilute solution of organic ligands such as EDTA, NTA, HEDTA and picolinic acid has a good decontamination performance. The decontamination solution, however, is not easily decomposed by the conventional oxidation method.

A new dilute chemical decontamination reagent that does not contain an organic ligand was developed. It consists of hydrazine, inorganic acid and metal ion. From the test result, it was found that a new dilute chemical decontamination reagent satisfactorily dissolves the spinel type iron oxide[1].

The decomposition of the hydrogen peroxide and the concomitant oxidation of the hydrazine were studied by Graham[2]. He reported that the oxidation of hydrazine in the presence of copper ion as a catalyst is closely related to that of the decomposition of hydrogen peroxide since the variations in catalyst concentration affect the same trends in both reactions. He suggested that hydrazine is oxidized both by the oxygen liberated in the reaction of the catalyst intermediate

with the hydrogen peroxide and by that catalyst intermediate itself. The stoichiometry of the reaction was reported as:

$$N_2H_4 + 2H_2O_2 \xrightarrow{Cu^{2+}} N_2 + 4H_2O \qquad (1)$$

The stoichiometry was confirmed by measuring the total amount of nitrogen produced. Lin *et al.*[3] studied the diimide production kinetics for the reaction between hydrazine and hydrogen peroxide under alkali conditions and the effects of cupric ion, boric acid and gelatin on the reaction kinetics. They reported that the reaction was shown to be first order with respect to each of hydrazine and hydrogen peroxide. They concluded that the reaction was difficult to control as the cupric ion is not stable in hydrazine. Wellman *et al.*[4] studied the kinetics of the oxidation of hydrazine by hydrogen peroxide. They reported that hydrazine is oxidized by hydrogen peroxide in the presence of cupric ion to form nitrogen and water. They also reported that the rate law was first order with respect to concentration of hydrogen peroxide and cupric ion, but was independent of the concentration of hydrazine. Pham *et al.*[5] investigated the kinetics of reaction of nanomolar concentrations of cuprous and cupric ions with hydrogen peroxide. They concluded that the reaction between cupric ion and hydrogen peroxide occurred *via* a "free radical" mechanism in which cupric ion was utilized through a one-electron redox process that converted hydrogen peroxide into the intermediate reactive oxygen radical species.

The objective of the study is to optimize the decomposition condition of hydrazine by hydrogen peroxide in an acidic solution. The catalytic activity of copper ion and the effect of separate addition of hydrogen peroxide on the decomposition of hydrazine were also investigated.

EXPERIMENTAL

80 % $N_2H_4 \cdot H_2O$ (Junsei Chemical Co.), 30 % H_2O_2 (Junsei Chemical Co.), 65 % HNO_3 (Duksan Chemical Co.), $Cu(NO_3)_2 \cdot 3H_2O$ (Showa Chemical Co.) and 99% *p*-dimethyl-amino benzaldehyde (Sigma-Aldrich, Co.) were used as received. Hydrazine combines with *p*-dimethylaminobenzaldehyde to form a yellow coloured complex. Colour development follows a Beer's law. After decomposition test, the concentration of a residual hydrazine was analyzed at 455 nm by UV spectro-photometer (Model DR 5000, Hach Co.). The decomposition tests were conducted in an Erlenmeyer flask. To maintain a constant temperature, Erlenmeyer flask was placed in a shaking water bath.

Experimental condition: Two kinds of H_2O_2 injection method were used. Firstly, excess H_2O_2 was injected once only into the N_2H_4 solution at a given temperature. In the other experiment, a given quantity of H_2O_2 was injected several times. Experimental condition is listed in Table-1.

RESULTS AND DISCUSSION

Effect of Cu^{2+} ion: Fig. 1 shows the plot of the $[N_2H_4]$ against time under various $[Cu^{2+}]$. When Cu^{2+} ion is not in a solution, N_2H_4 is hardly decomposed within 10 min. As the increase of $[Cu^{2+}]$, the decomposition reaction becomes fast. Wellman *et al.*[4] suggested that the rate law for hydrazine decomposition is represented as

$$-\frac{d[N_2H_4]}{dt} = k_{obsd}[H_2O_2]_T[Cu^{2+}]_T \qquad (2)$$

where $[H_2O_2]_T$, $[Cu^{2+}]_T$ and k_{obsd} stand for the total concentration of hydrogen peroxide and Cu^{2+} and the apparent rate constant, respectively. Fig. 2 shows the plot of k_{obsd} against $[Cu^{2+}]_T$. As shown in Fig. 2, k_{obsd} is not constant and is in the range of 2.7 to 3.0. One or more rapid reactions between the intermediate products and hydrogen peroxide follow to give the final products. The probable explanation is the formation of Cu^{2+}- hydrazine complex[6]. The complex formation facilitates the formation of diimide as an active intermediate[3]. When $[Cu^{2+}]$ is 10.0×10^{-4} M, the formation of hydrolysis product may retard the formation of diimide. The results, shown in Fig. 2, are in accord with the rate law reported by the Wellman *et al.*[4].

Effects of pH and temperature: Fig. 3 shows the plot of $[N_2H_4]$ against time under various pHs. Within the pH range 2-5, the reaction is dependent on the pH. A pH less than 3 (where hydrazine exists as $N_2H_5^+$), the decomposition reaction proceeds slowly. This means that $N_2H_5^+$ is unreactive. As the
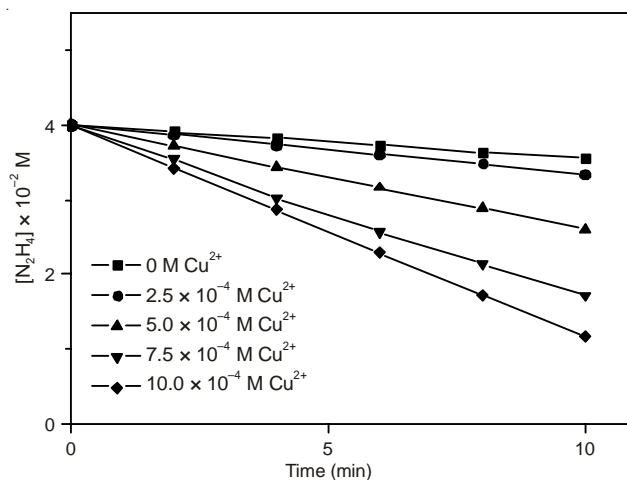

Fig. 1. Variation of $[N_2H_4]$ against time under various $[Cu^{2+}]$, (pH = 3, 50 °C)
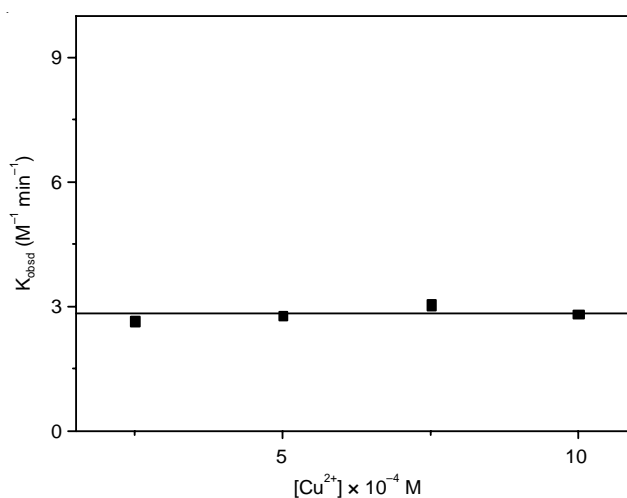

Fig. 2. Variation of k_{obsd} under various $[Cu^{2+}]$, (pH = 3, 50 °C)

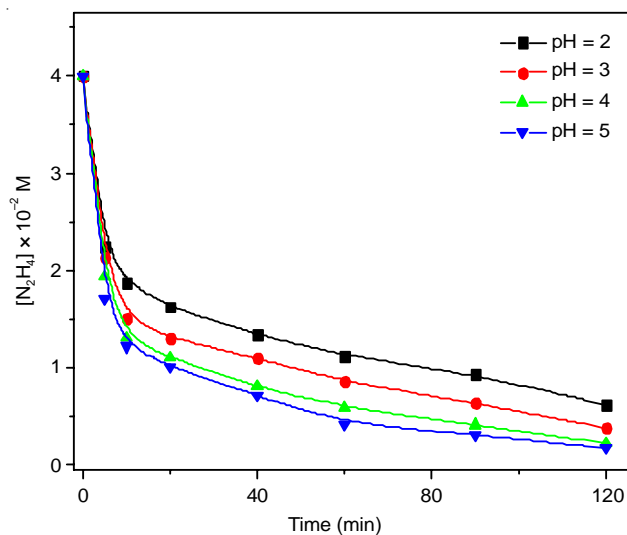Fig. 3. Variation of $[N_2H_4]$ against time under various pHs ($[Cu^{2+}]$ = 5 × 10^{-4} M and 70 °C)

| TABLE-1 |
| EXPERIMENTAL CONDITION FOR DECOMPOSITION OF HYDRAZINE |

$[N_2H_4]$	$[Cu^{2+}]$	$[H_2O_2]$	Temp. (°C)	pH	Remark
0.04 M	0~0.001 M	1.0 M	50, 60, 70, 80	2, 3, 4, 5	• One time injection: 90 mL mixed solution + 10 mL H_2O_2 • Repetitive injections: 90 mL mixed solution + 0.4 mL (1st time), then 0.3 mL H_2O_2 (every 10 min)

increase of the solution pH, decomposition reaction of hydrazine proceeds becomes fast. Hydrazine is decomposed completely at pH 5.

Fig. 4 shows a plot of $[N_2H_4]$ against time at various temperatures. The decomposition reaction proceeds rapidly during the initial 20 min. Then, the reaction rate decreases. The decomposition reaction rate is increased with the increase of temperature. As shown in Fig. 4, 84 % hydrazine is decomposed during 120 min at 50 °C and 95 % is decomposed during 120 min at 80 °C. From the test results, it was found that hydrazine is not completely decomposed by one time injection of the excess H_2O_2 at pH = 3 in a given time. Two explanations are possible. Firstly, $N_2H_5^+$ retards the decomposition reaction. Secondly, the auto-decomposition of H_2O_2 also retards the decomposition reaction at 80 °C.
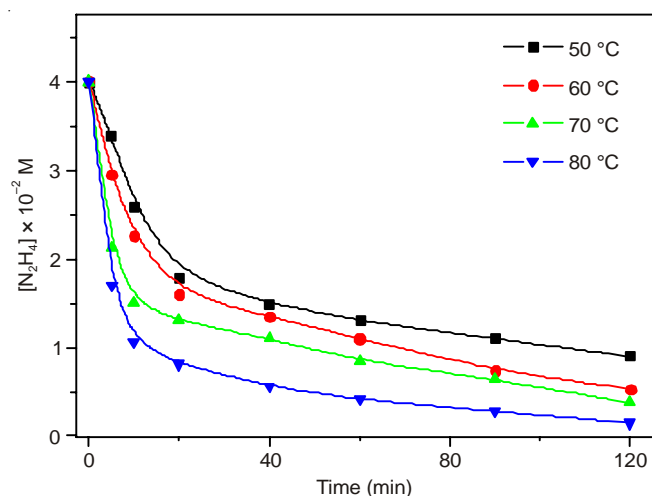

Fig. 4.   Variation of $[N_2H_4]$ against time under various temperatures ($[Cu^{2+}]$ = 5 × 10⁻⁴ M and pH = 3)

Effect of repetitive injections: The possibility that hydrogen peroxide may decompose the hydrazine efficiently in a given condition was investigated. Fig. 5 shows the plot of hydrazine concentration against the accumulated volume of hydrogen peroxide under two injection conditions. 96 % of hydrazine is decomposed when the 10 mL of hydrogen peroxide was injected into the solution once only. Hydrazine, however, is completely decomposed by the repetitive injections of 4.3 mL of hydrogen peroxide. The volume of hydrogen peroxide for the removal of hydrazine can be reduced significantly.

Although the copper–catalyzed peroxide hydrazine reaction occurs in a decontamination solution, the autocatalytic decomposition of hydrogen peroxide reduces the decomposition efficiency.

Conclusion

Chemical decontamination of internal loop of a nuclear power plant generates a secondary waste. The treatment of
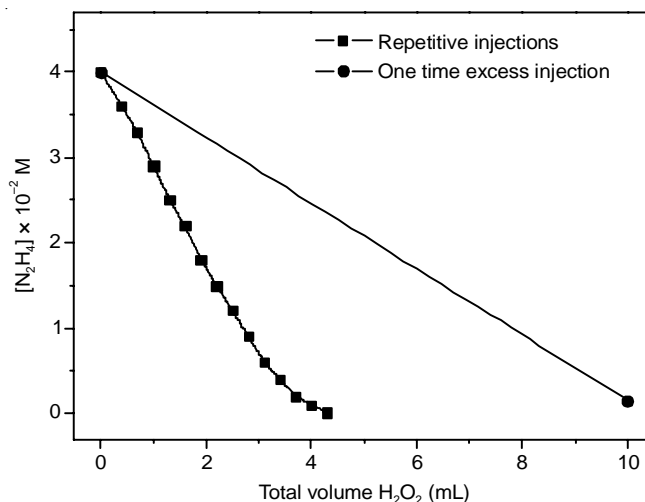

Fig. 5.   Comparison of decomposition efficiency ($[Cu^{2+}]$ = 5 × 10⁻⁴ M, pH = 3, 50 °C)

the radioactive waste and disposal of it in a repository site spend a time and pay expenditure. Many solution formulations have been developed to decontaminate the internal loop of a nuclear power plant. It was found that an organic acid free reductive decontamination solution reasonably decontaminated the internal loop of a nuclear power plant. If the main decontamination agent is decomposed into water and nitrogen, the generation of secondary waste can be greatly reduced. Since cupric ion is not stable in hydrazine, the reaction was difficult to control. Without cupric ion, the reaction is believed to proceed slowly. In this study, we found that hydrazine in a decontamination solution was completely decomposed to water and nitrogen by hydrogen peroxide solution.

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