

A Feasibility Study on the Treatment of HYBRID-D Decontamination Solution

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1. Introduction

The decontamination solution developed in KAERI is called HBRID-D (HYdrazine Base Reductive metal Ion Decontamination for Decommissioning). The solution is used for the decontamination of the internal loop of the NPP coolant system. 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 the large volume of the secondary waste. HYBRI-D solution consists of hydrazine, sulfuric acid and cuprous ion. Hydrazine and the sulfate ion 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 Sr²⁺ ion.

2. Methods and Results

2.1 Hydrazine Decomposition

100 ml of 0.044 M N₂H₄ solution was used for the decomposition tests at [Cu⁺] = 0 M and [Cu⁺] = 5 X 10⁻⁴ M, respectively. The reaction temperature was in the range from 50 °C to 80 °C and solution pH was controlled between 2 and 5. In the initial reaction stage 0.4 ml of 30 % H₂O₂ solution was added to the N₂H₄ solution. Then, 0.3 ml of 30 % H₂O₂ solution was added every 10 minutes.

Hydrazine forms a complex with p-dimethylamino benzaldehyde. Hydrazine concentration was analyzed by UV spectrometer at 455 nm.

Fig. 1 shows the variation of [N₂H₄] against the accumulated volume of H₂O₂ 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 N₂H₄ and H₂O₂ in the absence of Cu⁺ ion occurs as two steps as expressed in Eq. (1) and (2).

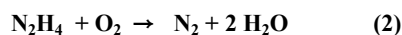
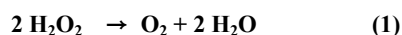
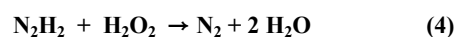
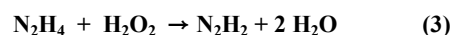


Fig. 2 shows the variation of [N₂H₄] against the accumulated volume of H₂O₂ at 60 °C. The efficiency of

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 [N₂H₄] against the accumulated volume of H₂O₂ at pH=3 and [Cu⁺] = 5 X 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 N₂H₄ and H₂O₂ in the presence of Cu⁺ ion occurs as two steps as expressed in Eq. (3) and (4).



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

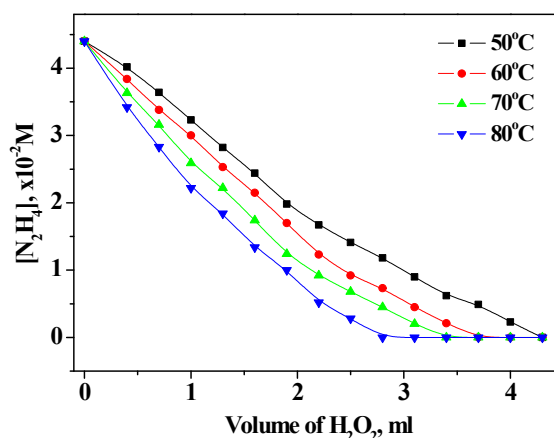


Fig. 1. Variation of [N₂H₄] against the accumulated volume of H₂O₂ under different temperature, [Cu⁺] = 0 M, pH= 3.0.

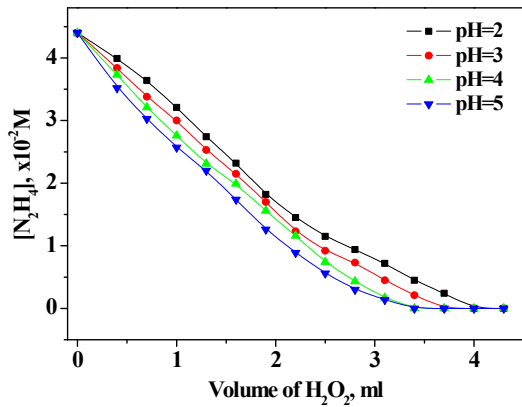


Fig. 2. Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different pH, $[Cu^+] = 0 \text{ M}$, $60 \text{ }^\circ\text{C}$.

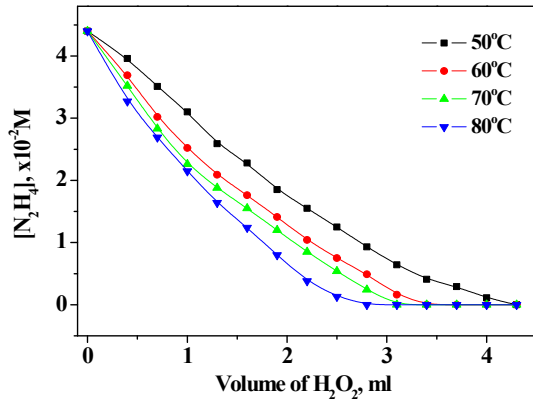


Fig. 3. Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different temperature, $[Cu^+] = 5 \times 10^{-4} \text{ M}$, $\text{pH}=3.0$.

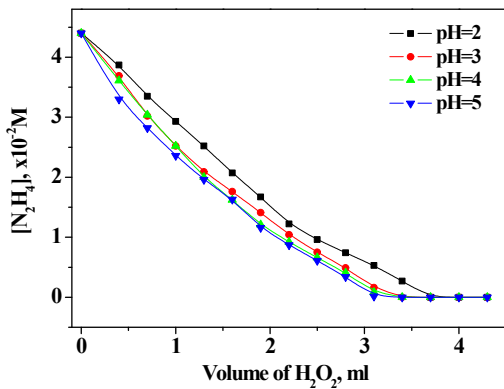


Fig. 4. Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different pH, $[Cu^+] = 5 \times 10^{-4} \text{ M}$, $60 \text{ }^\circ\text{C}$.

Fig. 4 shows the variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 at $60 \text{ }^\circ\text{C}$. 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.

2.2 Precipitation of Sulfate ion

Fig. 5 shows the change of size distribution of $SrSO_4$ particles against time. Same equivalent of SO_4^{2-} ion was mixed with Sr^{2+} ion. The reaction is expressed by following equation.



From the UV analysis of sulfate ion, it was found that greater than 98 % of sulfate ion was removed by Sr^{2+} ion. Particle size of $SrSO_4$ increased with time. This is attributed of agglomeration among particles. The precipitant was fully settled down within 30 minutes.

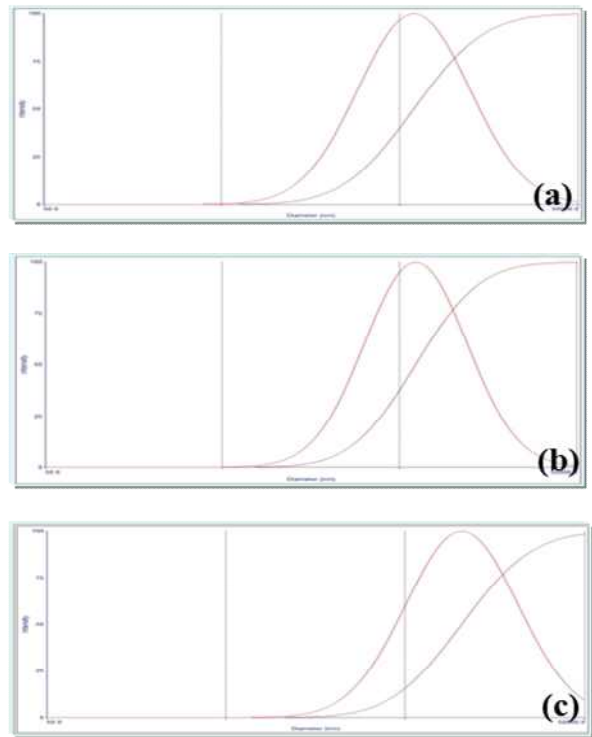


Fig. 5. Size distribution of $SrSO_4$, (a) 5 min, $5.0 \mu\text{m}$, (b) 35 min, $6.2 \mu\text{m}$, (c) 65 min, $10.3 \mu\text{m}$, $60 \text{ }^\circ\text{C}$.

3. Conclusions

A feasibility study on the treatment of $\text{N}_2\text{H}_4\text{-Cu}^+\text{-H}_2\text{SO}_4$ 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 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 nature. 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 reduce the generation of the secondary waste.

ACKNOWLEDGEMENTS

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