Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 12-13, 2016

Destruction of Hydrazine and Corrosion Monitoring

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1. Introduction

KAERI developed a dilute chemical decontamination agent applicable to the internal loop of a nuclear power plant. This agent does not use a chelating organic acid. The agent uses Cu ion and hydrazine in an inorganic acid solution. This agent is used for the dissolution of Fe and Ni ions in a spinel type nickel chromium ferrite. After decontamination, 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 [1].

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

As the decrease of the hydrazine concentration, the solution pH also becomes to decrease. The decrease of solution pH can affect the integrity of structural metal.

The objective of the study is to investigate the decomposition characteristics of hydrazine by hydrogen peroxide. The corrosion compatibility of metal after the decomposition of hydrazine is also investigated.

2. Methods and Results

2.1 Experimental condition

80 % hydrazine monohydrate from Junsei Chemical Co. was used as received. pH was adjusted by H_2SO_4. Tests were performed at pH = 4 and 5. 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 variation of corrosion rate after the decomposition of hydrazine was measured by Corrator from Rohrback Cosasco System (RCS 9000). The ORP of solution was also measured using a pH meter.

2.2 Test results

Contrary to the decomposition of hydrazine to ammonia under high radiation field [2], hydrazine was decomposed to water and nitrogen gas.

Fig. 1 shows the variation of hydrazine concentration with respect to the accumulated volume of hydrogen peroxide at pH= 5. The efficiency of hydrogen peroxide on the decomposition of hydrazine increases with the increase of temperature. Fig. 2 shows the variation of hydrazine concentration with respect to the accumulated volume of hydrogen peroxide at pH= 4. As shown in Fig. 2, the efficiency of hydrogen peroxide on the decomposition also increases with the increase of temperature.

The efficiency of hydrogen peroxide on the decomposition of hydrazine increases with the increase of temperature and solution pH.

Lin et al. reported that hydrazine decomposition by $[H_2O_2]$ increased three folds by the addition of copper ions [3]. But, the catalytic effect was negligible in this study because the hydrazine concentration was low. Hydrazine was decomposed satisfactorily after a given time. The solution pH, however, decreased to 1.9 when the decomposition reaction was terminated.

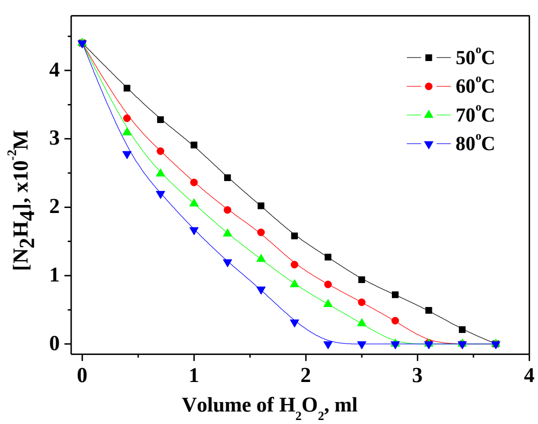

Fig. 1. Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different temperature, $[Cu^{2+}]$ = 5 X10^{-4} M, pH=5.

Fig. 3 shows the variation of corrosion rate of Inconel 600 specimen and of ORP of sulfuric acid solution against time at 40 ℃. Just after the bubbling of nitrogen gas, corrosion rate of Inconel 600 increases to 130 MPY drastically. Then, it becomes to decrease to 10 MPY slowly. The variation of ORP is negligible. Fig. 4 shows the variation of corrosion rate of Inconel 600 specimen and of ORP of sulfuric acid solution against time at 60 ℃

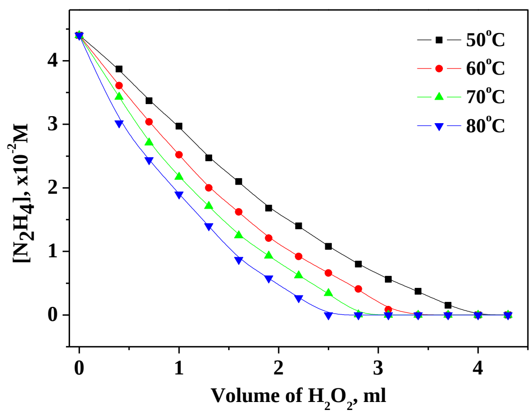

Fig. 2. Variation of $[N_2H_4]$ against the accumulated volume of H_2O_2 under different temperature, $[Cu^{2+}]$ = 5 X10^{-4} M, pH=4.

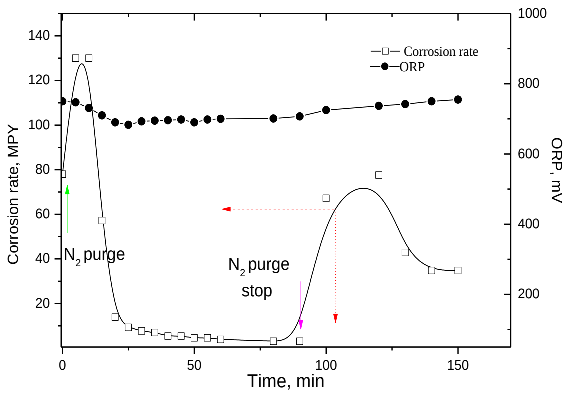

Fig. 3. Variation of corrosion rate and ORP against time [Inconel 600, 40℃, $[H_2SO_4]$ = 0.028M].

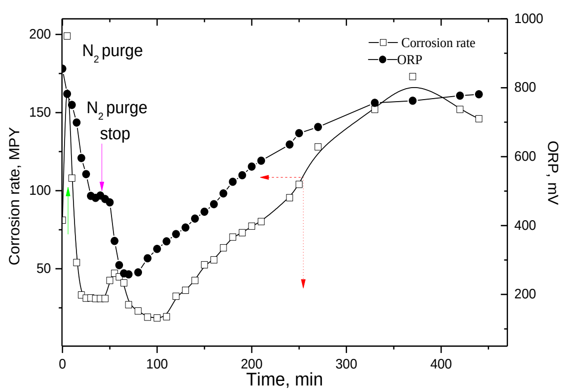

Fig. 4. Variation of corrosion rate and ORP against time [Inconel 600, 60℃, $[H_2SO_4]$ = 0.028M].

The corrosion rate of Inconel 600 increases with the increase of temperature. As shown in Fig. 4, the variation of corrosion rate of Inconel 600 specimen is similar to the variation of ORP of sulfuric acid solution.

3. Conclusion

Our results indicate that hydrazine was decomposed satisfactorily by the continual addition of hydrogen peroxide. The decomposition efficiency of hydrazine increased with the decrease of the solution acidity. During the decomposition of hydrazine, the solution pH becomes to decrease. From the test results, we found that the corrosion of Inconel 600 during the treatment of a newly developed dilute chemical decontamination agent is negligible.

In a previous study, we demonstrated the high decontamination performance of the newly developed dilute chemical decontamination agent. The application of a decontamination solution to the primary coolant system before decommissioning is necessary to minimize the personnel dose rates. In foreign countries, system decontaminations have been performed several times by applying the dilute organic chemical decontamination process. To prepare against the decommissioning of the nuclear power plant, it is necessary to develop the unique domestic chemical decontamination process.

Acknowledgement

This work was carried out under the Nuclear R & D Program funded by the Ministry of Science, ICT & Future Planning of Korea (Contract number: NRF-2012M2A8A 5025655).

REFERENCES

[1] C. R. Wellman, Kinetics of the Oxidation of Hydrazine by Hydrogen, Catalyzed by Hydrated Copper (II), Journal of the American Chemical Society, Vol. 98, No. 7, pp. 1683-1984, 1976.

[2] O. P. Arkhipov, V. L. Bugaenko, S. A. Kabakchi and V. I. Pashevich, Thermal and Radiation Characteristics of Hydrazine in the Primary loop of Nuclear Power plants with Water-cooled, Water-moderated reactors, Atomic Energy, Vol. 82, No. 2, pp. 92-98, 1997.

[3] X. Lin, O. P. Garry, L. Rempel, Cupric Ion Catalyzed Diimide Production from the Reaction between Hydrazine and Hydrogen Peroxide, Applied Catalysis A: General, Vol. 263, No. 1, PP. 27-32, 2004.