Comparison of Radiolytic Decomposition of Oxidation Decontamination Solutions

N.O. Chang[1,2], H.J. Won[1*], S.Y. Park[1], S.B. Kim[1], and Y.S. Kim[2]
[1]Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Korea
[2]Department of Nuclear Engineering, Hanyang University, 222Wangsimri-ro, Seongdong-gu, Seoul, Korea
[*] nhjwon@kaeri.re.kr

1. Introduction

Before decommissioning, it is necessary to remove the radionuclides in the primary system of NPP. To remove it, HyBRID(Hydrazine-Base Reductive metal Ion Decontamination) chemical decontamination process developed by KAERI can be used. It consists of SP or SP(Cu) oxidizing and reducing process. In each process, the control of $KMnO_4$ or N_2H_4 concentration is important for removing oxide layer. However, permanganate ion and hydrazine decompose under the high radiation field during the decontamination. In this study, the radiolytic products of $KMnO_4$ are analyzed. Also, the results are compared with results of N_2H_4.

2. Methods and Results

2.1 Sample preparation and γ-ray irradiation

SP oxidizing decontamination agent was prepared with 6.33 mM $KMnO_4$ and 3.25 mM H_2SO_4. SP(Cu) agent was made of 6.33 mM $KMnO_4$, 3.25 mM H_2SO_4, and 0.5 mM $CuCl_2$. The absorbed doses of the samples were 0, 5, 10, 20, 40 and 80 kGy, respectively by using low-dose γ-ray irradiator of jeongeup.

2.2 Comparison of radiolytic decomposition Between SP and SP(Cu)

To analyze concentration of [$KMnO_4$], UV analysis method(UV spectrometer DR5000 of Hach Co.) was used. The amount of MnO_2 was calculated using relation of concentration of total manganese and [$KMnO_4$]. AA analysis(AAnalyst 400 of Perkin Elmer Co.) was used to analyze [Mn^{2+}]. The concentration change of each species against absorbed dose is shown in Fig. 1.

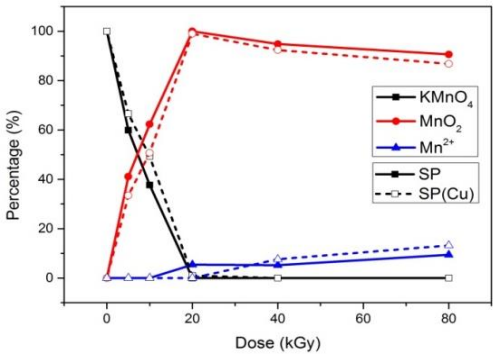

Fig. 1. Concentration change of $KMnO_4$, MnO_2, and Mn^{2+}.

As shown Fig. 1, it can be explained that [$KMnO_4$] decreases due to the reaction between MnO_4^- and radiolysis products of the water($\dot{O}H$, e_{aq}^-, etc.). After this reaction, MnO_4^{2-} is produced. MnO_4^{2-} reacts with H^+ rapidly and generates MnO_2 because it is unstable in acidic condition. After $KMnO_4$ is completely decomposed, MnO_2 reacts with e_{aq}^- and produce Mn^{2+} and OH^- [1]. However, as listed in Table 1, $KMnO_4$ in the SP agent decomposes but it remains in the SP(Cu) at 20 kGy. This can be explained by the eqs. (1) and (2) [2].

$$H^+ + Cu^{2+} + \dot{O}H \rightarrow Cu^{3+} + H_2O \quad (1)$$

$$e_{aq}^- + Cu^{2+} \rightarrow Cu^+ \quad (2)$$

As Cu^{2+} ion reacts with H^+ or e_{aq}^- in an acidic condition, the probabilities of reaction between MnO_4^{2-} and H^+, and MnO_2 and e_{aq}^- decrease. Thus,

SP(Cu) agent is expected to be more stable than SP agent in the radiation field.

Table 1. Percentage change of $KMnO_4$

Absorbed dose(kGy)	$KMnO_4$ in SP(%)	$KMnO_4$ in SP(Cu)(%)
0	100.0	100.0
5	59.0	66.6
10	37.7	49.3
20	0.0	1.0
40	0.0	0.0
80	0.0	0.0

2.3 Comparison of radiolysis between oxidizing and reducing decontamination agent

In the previous study, it is founded that radiolysis of N_2H_4 depends on existence of Cu^{2+} ions [3]. The result is shown in the Fig. 2.

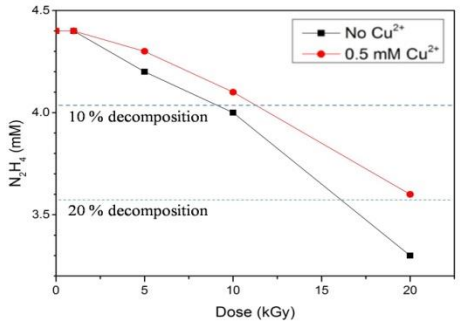

Fig. 2. Decomposition of [N_2H_4] under varied doses [3].

As shown in the Fig. 2, when Cu^{2+} ions are added, less N_2H_4 decomposes at the same absorbed dose. This phenomenon is similar to the [$KMnO_4$] change in the oxidizing decontamination agent.

3. Conclusions

$KMnO_4$ in the oxidizing decontamination agent decomposes during the γ-ray irradiation. SP(Cu) agent has higher stability than SP under the radiation field. The reason is explained by the reaction between Cu^{2+} ions and H^+ or e_{aq}^-. This phenomenon also occurs in the reducing decontamination agent N_2H_4. However, when high absorbed dose is irradiated, $KMnO_4$ decomposes completely regardless of presence of Cu^{2+} ions. Thus, it is necessary to estimate the absorbed dose of $KMnO_4$ during the decontamination and to decide the application times. It is also necessary to study the effect of other metal ions on the radiation stability of $KMnO_4$.

ACKNOWLEDGMENT

This work has been carried out under the Nuclear R&D Program (NRF-2017M2A8A5015144) funded by Ministry of Science and ICT.

REFERENCES

[1] R. Puspalata et al, "Gamma radiation induced formation and characterization of the nano-oxides of manganese", Radiation Physics and Chemistry, 85, 142-160 (2013).

[2] Paul Y. Feng et al, "High-Intensity Radiolysis of Aqueous Ferrous Sulfate-Cupric Sulfate-Sulfuric Acid Solutions", The Journal of Physical Chemistry, 74(6), 1221-1227 (1970).

[3] Wang-Kyu Choi et al., "Development of Advanced Decontamination Technology for Nuclear Facilities", KEARI/RR-3964/2014 (2015).