

Radiolytic Decomposition of KMnO_4

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1. Introduction

It is necessary to carry out the chemical decontamination process in primary system of nuclear power plant before decommissioning. The process of chemical decontamination is dissolving oxide film and removing radio-nuclide (Co^{58} , Co^{60} , etc.) by the repetitive applications of oxidation-reduction processes using chemical agent. The SP and SP(Cu) processes are the oxidizing decontamination process. SP process uses ' $\text{KMnO}_4 + \text{H}_2\text{SO}_4$ ' mixed solution as decontamination agent and SP(Cu) process uses ' $\text{KMnO}_4 + \text{H}_2\text{SO}_4 + \text{CuCl}_2$ ' mixed solution. KMnO_4 in the decontamination solution is important because it oxidizes the Cr^{3+} of the oxide film to Cr^{6+} . However, the permanganate ion decomposes under the high radiation field during the application. In this study, the radiolytic products of KMnO_4 in SP and in SP(Cu) processes were investigated before and after γ -ray irradiation. In addition, the results in the acidic condition were compared with those in the basic condition.

2. Methods and Results

2.1. Sample preparation and γ -ray irradiation

A mixed solution of '6.33 mM KMnO_4 and 3.25 mM H_2SO_4 ' was used as a SP process. A mixed solution of '6.33 mM KMnO_4 , 3.25 mM H_2SO_4 , and 0.5 mM CuCl_2 ' was used as a SP(Cu) process.

γ -ray irradiation tests were performed using a low-dose gamma ray irradiator of irradiation facility in Jeongeup city. The test conditions are listed in Table I.

Table I. Absorbed dose

Absorbed dose (kGy)	Dose rate (kGy/hr)	Distance (cm)	Time (hr)
0	0.0	0.0	0.0
5	4.6	71.3	17.5
10	2.3	119.7	17.5
20	10.0	32.8	2.0
40	5.0	66.1	2.0
80	2.5	112.5	2.0

Color change of the test solution is shown in Fig. 1.

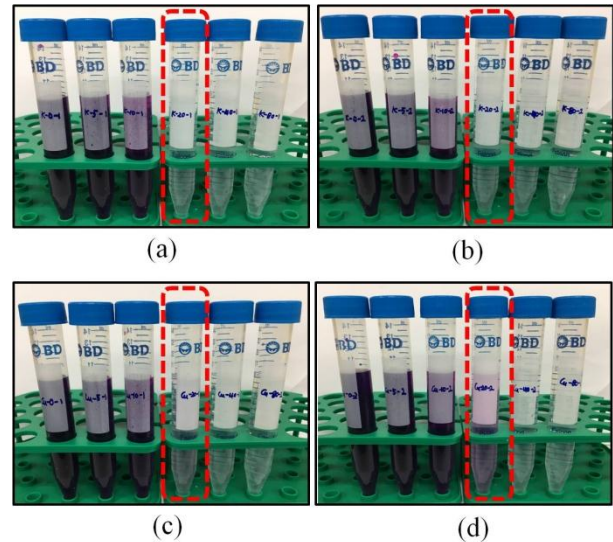


Fig. 1. (a,b) SP decontamination agent and (c,d) SP(Cu) decontamination agent.

2.2. Analysis

UV spectrometer of Hach Co. (Model: DR 5000) was used. UV analysis was performed to determine the concentration of KMnO_4 . Before UV analysis, MnO_2 created was filtered. The relationship between the absorbance and the concentration of KMnO_4 is given in Eq. (1).

$$y = 5712.7x + 0.0052 \quad (1)$$

Where x is concentration of KMnO_4 present in the sample solution and y is the absorbance of the sample solution obtained through UV analysis.

Atomic absorption spectrometer of Perkin Elmer Co. (AAAnalyst 400) was used to analyze the concentration of Mn^{2+} . Before performing AA analysis, MnO_2 also was removed through filtering. H_2SO_4 and H_2O_2 were used to reduce KMnO_4 in solution to Mn^{2+} .

pH measurement was carried out to predict the role of hydronium ion during the γ -ray irradiation.

2.3. Variation of $[\text{KMnO}_4]$ and the absorbed dose

The change of $[\text{KMnO}_4]$ according to the absorbed dose is shown in Fig.2. As shown in Fig.2., $[\text{KMnO}_4]$ decreases as the absorbed dose increases in the dose range from 0 to 20 kGy. Above 20 kGy, KMnO_4 completely decomposes.

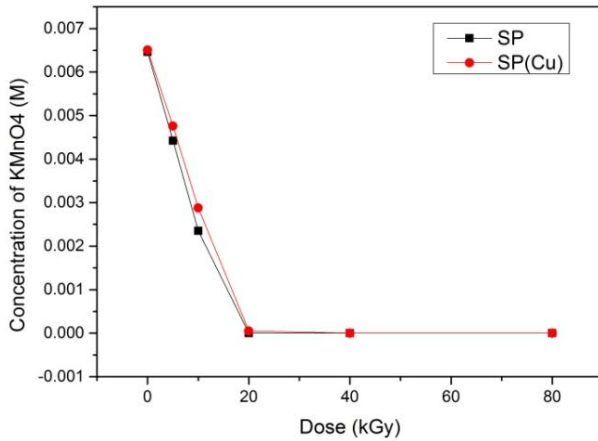
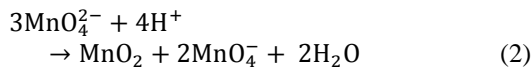


Fig. 2. Change of [KMnO₄] following dose

During the γ -ray irradiation, permanganate ion reacts with H radicals, $\dot{O}H$ radical, e_{aq}^- , O_2^- , HO_2 , etc. generated from radiolysis of water and produce manganate ion or MnO_4^- radical. However, since manganate ion is unstable in an acidic environment, it reacts with H^+ and precipitates as MnO_2 . {Eq. (2)} [1]



2.4. Amount of MnO_2 and the absorbed dose

The percentage of MnO_2 precipitated was obtained from the total concentration of manganese ion by subtracting [KMnO₄]. The results are listed in Table II. The amount of MnO_2 precipitated increases with the increase of absorbed dose in the range between 0 and 20 kGy. Then it decreases with the increase of absorbed dose.

Table II. MnO_2 formed by γ -ray irradiation.

Absorbed Dose (kGy)	MnO_2 in SP (%)	MnO_2 in SP(Cu) (%)
0	0.0	0.0
5	41.0	33.4
10	62.3	50.7
20	100.0	99.0
40	94.8	92.4
80	90.6	86.8

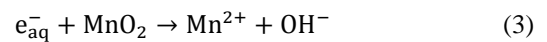
2.5. Variation of $[Mn^{2+}]$ and the absorbed dose

The concentration of Mn^{2+} in the sample solution is listed in Table III.

Table III. Concentration of Mn^{2+}

Absorbed Dose (kGy)	Mn^{2+} in SP (mM)	Mn^{2+} in SP(Cu) (mM)
0	0.00	0.00
5	0.00	0.00
10	0.00	0.00
20	0.00	0.00
40	0.33	0.48
80	0.59	0.84

After all the permanganate ion in the solution is exhausted, MnO_2 reacts with e_{aq}^- to form Mn^{2+} and OH^- . (Eq. (3)) [2]



Based on reaction (2), $KMnO_4$ in the decontamination agents can decompose into MnO_2 through MnO_4^{2-} . When $KMnO_4$ completely decomposes, it can be predicted that MnO_2 is reduced to Mn^{2+} ion {Eq. (3)}.

2.6. Variation of pH

pH of solution against the absorbed dose is shown in Fig. 3. For both of SP and the SP (Cu) processes, pH increases as the absorbed dose increases. Consulting Eqs. (2) and (3), this means that $[H^+]$ is consumed and $[OH^-]$ is generated during the decomposition of permanganate ion and MnO_2 .

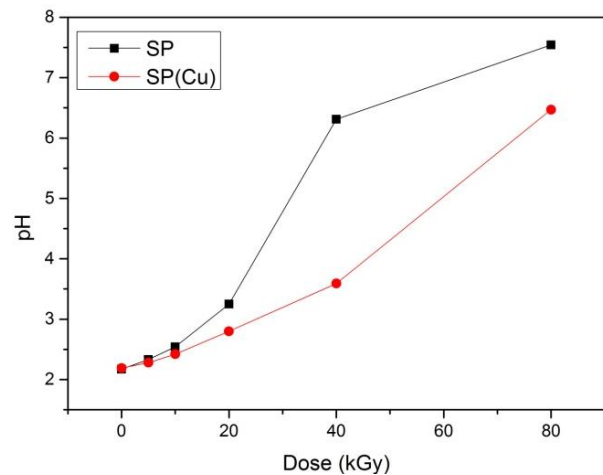


Fig. 3. pH change of SP and SP(Cu) sample solution.

2.7. Comparison between SP and SP(Cu)

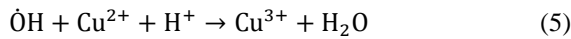
The percentage of $KMnO_4$, MnO_2 and Mn^{2+} was calculated and is listed in Table IV.

$KMnO_4$ of SP process completely decomposes at 20 kGy. In case of SP(Cu) process, $KMnO_4$ remains at 20 kGy. It is inferred that $KMnO_4$ completely decomposes between 20 and 40 kGy. It is expected that decontamination agent absorbs 10 kGy of γ -ray during

Table IV. Percentage of KMnO_4 , MnO_2 , and Mn^{2+}

Absorbed Dose (kGy)	SP process			SP(Cu) process		
	KMnO_4 (%)	MnO_2 (%)	Mn^{2+} (%)	KMnO_4 (%)	MnO_2 (%)	Mn^{2+} (%)
0	100.0	0.0	0.0	100	0.0	0.0
5	59.0	41.0	0.0	66.6	33.4	0.0
10	37.7	62.3	0.0	49.3	50.7	0.0
20	0.0	100	0.0	1.0	99.0	0.0
40	0.0	94.8	5.2	0.0	92.4	7.6
80	0.0	90.6	9.4	0.0	86.8	13.2

the decontamination of the primary coolant system. As shown in Table IV, 37.7% of KMnO_4 remains in the SP process at 10 kGy. 49.3% of KMnO_4 , however, remains in the SP(Cu) process. Therefore, it was confirmed that SP(Cu) process is more stable than SP process under the radiation field. It is predicted that this phenomenon is caused by the mechanism of radiolytic decomposition of Cu^{2+} . When Cu^{2+} ion in an aqueous solution is irradiated, reactions (4) and (5) occur. [3]



These reactions cause decreasing the number of e_{aq}^- , $\dot{\text{O}}\text{H}$ radical to react with permanganate ion, and consequently the number of KMnO_4 that will decompose decreases. Therefore, using SP(Cu) process for the primary system decontamination can increase the stability of radiation emitted in the system, rather than applying the SP process.

2.8. Comparison between acidic and basic conditions

In KAERI, the radiolytic decomposition of KMnO_4 was studied in the absorbed dose range from 0 to 1 Mrad (~10 kGy). The result is shown in Fig. 4. [4]

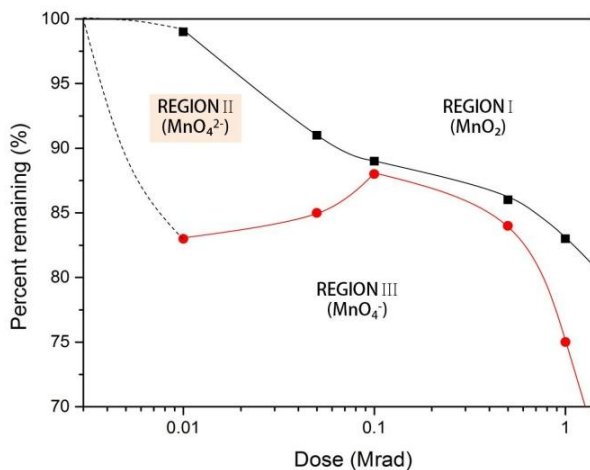


Fig. 4 Radiolytic decomposition of 0.02M potassium ion in a basic solution [4]

Contrary to the acidic condition, MnO_4^{2-} is present. This is because MnO_4^{2-} ion is stable in a basic condition but unstable in acidic condition. MnO_4^{2-} ion in an acidic condition disappears rapidly due to Eq. (2). Also Mn^{2+} ion is not observed in the basic condition. This is caused by the thermodynamic property of manganese ion. [5]

3. Conclusions

In an acidic condition, MnO_4^- ion decomposes into MnO_2 . In a basic condition, MnO_4^- ion decomposes into MnO_4^{2-} ion. Mn^{2+} ion becomes to form after complete decomposition of MnO_4^- ion in an acidic condition. KMnO_4 in the SP process completely decomposes at 20 kGy. KMnO_4 in the SP(Cu) process completely decomposes above 20 kGy. This is caused by the role of Cu^{2+} ion. Cu^{2+} ion reacts with e_{aq}^- and $\dot{\text{O}}\text{H}$ radical during the γ -ray irradiation and generates unstable Cu^+ or Cu^{3+} . In order to confirm this phenomenon, a further investigation on the identification of Cu^+ and Cu^{3+} ions is necessary. Also, It is confirmed that the SP(Cu) process is more stable against the radiation field. It is considered that the decontamination agent absorbs less than 10 kGy during the decontamination of the primary system. Therefore, more precise experiment is needed in the interval between 0 and 10 kGy.

ACKNOWLEDGMENT

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