Spontaneous Reductive Decomposition Behavior of Permanganic Acid Depending on Initial Concentration and Reaction Temperature for the Chemical Decontamination of NPP

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1. Introduction

Permanganic acid ($HMnO_4$) is used as an oxidizing agent to dissolve chromium oxide (Cr_2O_3) [1]. However, because $HMnO_4$ is unstable, MnO_4^- reacts with H^+ in a 1:1 molar ratio and spontaneously decomposes to form MnO_2, as shown in the following equation [2]:

$$4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 3O_2 + 2H_2O \quad (1)$$

The spontaneous reductive decomposition characteristics of MnO_4^- have not been studied under chemical decontamination conditions, such as the HP CORD process, using $HMnO_4$.

In this study, the spontaneous reductive decomposition behavior of $HMnO_4$ was investigated within the range of concentrations and temperatures used in the HP CORD process.

2. Experimental details

All experiments were performed in a 500 mL glass reaction vessel equipped with a reflux condenser, thermometer, and an electric heating stirring mantle (MS-DMSB, Misung Scientific Co. Ltd., Korea).

The effect of the initial $HMnO_4$ concentration on its spontaneous reductive decomposition was evaluated at 95 °C for 360 min with initial $HMnO_4$ concentrations varying from 1 to 6 mM. To evaluate the effect of the reaction temperature, 3 mM of $HMnO_4$ solution was heated to 40, 60, 80, and 95 °C for 360 min.

3. Results and discussion

It was experimentally determined that the two-step reaction of the spontaneous reductive decomposition of $HMnO_4$ was judged to follow the characteristics of the MnO_2 nucleation and crystal growth. Based on the experimental results and classical nucleation theory, the following mathematical model was applied to prediction of the spontaneous reductive decomposition behavior of $HMnO_4$.

$$X(\mathrm{t}) = \omega e^{-k_n t_n} + (100 - \omega) e^{-k_c t_c} \quad (2)$$

where X represents the residual fraction (%) of MnO_4^-, t is the reaction time (min), ω and $100 - \omega$ denote $X_n(t)$ and $X_c(t)$ respectively, and k_n and k_c are the rate constants of MnO_2 nucleation and crystal growth, respectively.

The experimental data for the spontaneous reductive decomposition of MnO_4^- as a function of initial $HMnO_4$ concentration and reaction temperature were fitted by Eq. (2), and the results are shown in Fig. 1 and 2, respectively. The coefficient of determination of the curve fitting by the model

was estimated to be ≥ 0.96 at all concentrations and temperatures. Therefore, it was confirmed that the proposed model accurately reproduces the experimental data.

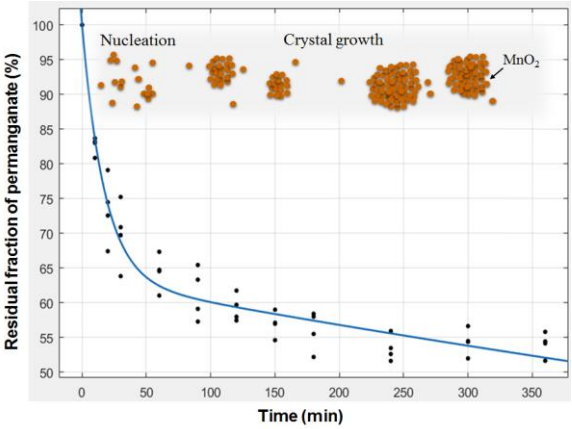

Fig. 1. Results of the mathematical model estimation of the $HMnO_4$ decomposition at 95 °C for initial $HMnO_4$ concentrations of 1, 2, 3, and 6 mM (dots are experimental data, solid line is a nonlinear least square fit).

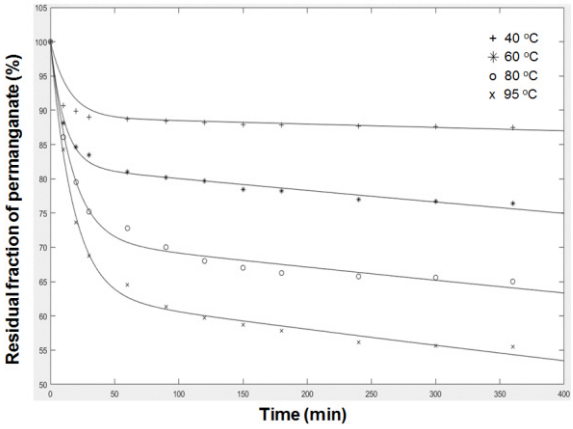

Fig. 2. Results of the mathematical model estimation of the $HMnO_4$ decomposition at 3 mM $HMnO_4$ at 40, 60, 80, and 95 °C (dots are experimental data, solid line is a nonlinear least square fit).

4. Conclusions

The proposed mathematical model consisting of two first-order reactions accurately predicted the spontaneous reductive decomposition behavior of $HMnO_4$. This behavior was dependent on the residual $HMnO_4$ concentration and reaction temperature within the experimental error range as follows:

$$X(\mathrm{t,T}) = \omega e^{-k_n t_n} + (100-\omega)e^{-k_c t_c} \qquad (3)$$

where $k_n = 5.3\times10^{-5}T^2 - 0.038T + 6.92$, $k_c = 7\times10^{-6}T - 0.002$, $\omega = 0.48T - 140$, X (%), ω (%), t (min), and T (K).

Based on the good fit of the experimental data with the proposed model, k_n and ω accurately simulate the nucleation step, and k_c and 100-ω accurately reproduce the crystal growth step.

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