

# Studies on the Behavior of Spontaneous Reductive Decomposition of Hydrogen Permanganate in Water for HP/CORD Process

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## 1. Introduction

The permanganic acid (HMnO<sub>4</sub>) as oxidizing agent is usually used to dissolve the NPP oxide layers containing Cr (III) in HP/CORD process [1]. However, little attention has been made for the spontaneous reductive decomposition of HMnO<sub>4</sub>, which is a competing reaction with the oxidation of the chromium oxide by permanganate. The objective of this study is to investigate the spontaneous reductive decomposition behavior of HMnO<sub>4</sub> for HP/CORD process, depending on the variation of initial concentration of HMnO<sub>4</sub>.

## 2. Materials and methods

### 2.1 Reagents

All reagents were analytical grade and were used without further purification. Deionized water (18.3 MΩ·cm), which was prepared using a water purification system (Nex Power 1000, Human corporation, Korea) was used to prepare all aqueous solutions. Potassium permanganate (KMnO<sub>4</sub>, above 99.3%) was purchased from DAEJUNG, Korea. Ambelite IRN-77 (cation exchange resin) was obtained from Rohm and Haas, USA.

### 2.2 Preparation of HMnO<sub>4</sub>

HMnO<sub>4</sub> was prepared in the following manner: A known amount of potassium permanganate (KMnO<sub>4</sub>) was dissolved in a known volume of deionized water. Then, the KMnO<sub>4</sub> solution was passed through the packed glass column containing cation exchange resin at a flow rate of 5 BV/h. After passing through the glass column, the pH value and K<sup>+</sup> concentration of the source solution were measured by pH meter (STARA211, Thermo Orion, USA) and ICP-OES

(Optima 2100DV, PerkinElmer Co., USA), respectively, for determining whether the cation exchange (K<sup>+</sup>→H<sup>+</sup>) was completely conducted.

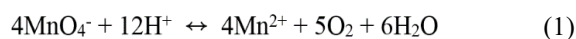
### 2.3 Apparatus and procedure

All experiments were carried out in 500 mL glass reaction vessels equipped with reflux condenser, thermometer, mechanical stirrer, and electric heating mantle. Reaction volumes were normally 200 mL and were stirred at 250 rpm. The temperature was maintained at 90°C. Aliquots obtained from each experiment were quickly cooled, diluted, and placed in a dark bottle to avoid further reaction. The concentration of residual permanganate was determined by UV-visible spectrophotometer (Agilent 8453, Agilent technologies, USA) after filtration (0.2 μm, Whatman, nylon membrane filters).

## 3. Results and discussion

### 3.1 Effect of the initial concentration of HMnO<sub>4</sub>

The change of concentration of residual permanganate against time at different initial concentration (1, 2, 3, 6 mM) of HMnO<sub>4</sub> is shown in fig. 1. Although, during the first 10 min of the reaction, the spontaneous reductive decomposition behavior of HMnO<sub>4</sub> appeared to be a first-order reaction, the overall reaction has almost approached equilibrium after 60 min reaction. These phenomenons are because the rapid, reversible equilibrium between permanganate and manganous ions, according to the following chemical equations [2]:



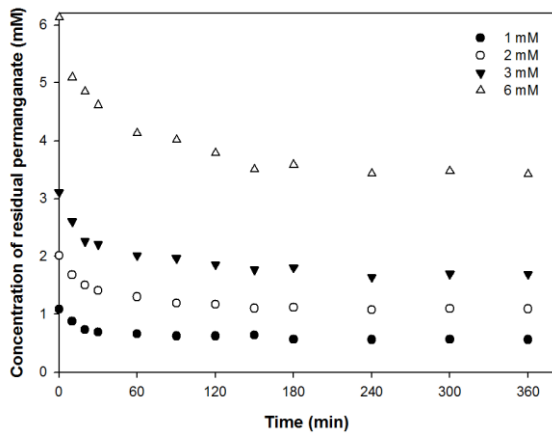


Fig. 1. Concentration of residual permanganate according to time with different initial concentration of  $\text{HMnO}_4$ .

The difference of the initial concentration of  $\text{HMnO}_4$  did not affect the rate of spontaneous reductive decomposition of  $\text{HMnO}_4$  (Fig. 2). The fractions of residual permanganate were similar in all conditions after 360 min reaction.

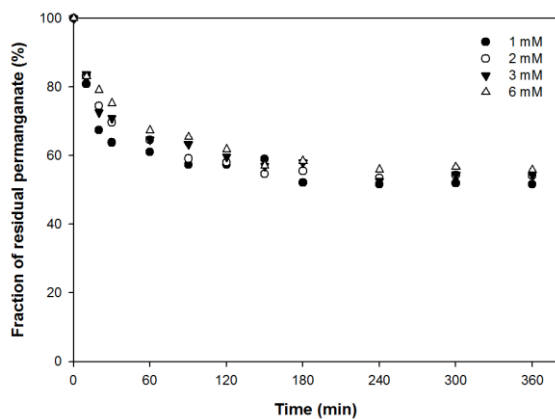


Fig. 2. The fraction of residual permanganate according to time with different initial concentration of  $\text{HMnO}_4$ .

### 3.2 Effect of manganese dioxide

The effect of decomposition product  $\text{MnO}_2$  on the reaction of spontaneous reduction of  $\text{HMnO}_4$  was studied. In Fig. 3, the spontaneous reduction of  $\text{HMnO}_4$  was rapidly processed within 30 min and nearly reached to equilibrium after 60 min, which was maintained for 630 min. However, after filtering the produced  $\text{MnO}_2$  particles from  $\text{HMnO}_4$  in the reaction at 210 and 420 min, the spontaneous reduction of  $\text{HMnO}_4$  was again processed, even if the reaction of spontaneous reduction of  $\text{HMnO}_4$  was in equilibrium before filtering  $\text{MnO}_2$ . The removal of  $\text{MnO}_2$  from a solution approached equilibrium reaction of spontaneous reductive decomposition of

$\text{HMnO}_4$  could lead to spontaneous reduction of permanganate again.

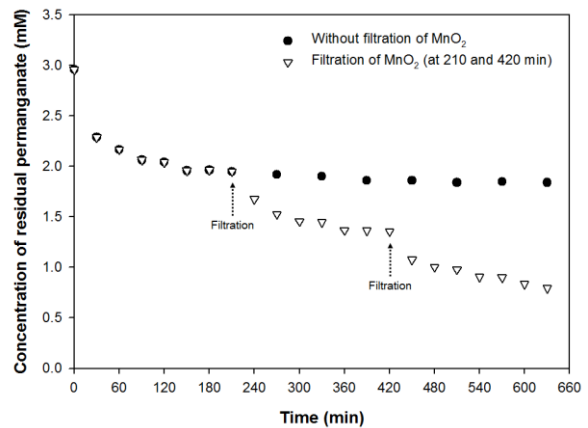


Fig. 3. Effect of removal of  $\text{MnO}_2$  on spontaneous reductive decomposition of  $\text{HMnO}_4$  during the decomposition reaction.

## 4. Conclusions

The spontaneous reductive decomposition of permanganate in  $\text{HMnO}_4$  showed the slow decomposition behavior followed by the rapid decomposition in the early times. The decomposition product ( $\text{MnO}_2$ ) is considered to take the main roles on the decomposition kinetics in the early stage of the crystal growth.

## ACKNOWLEDGMENTS

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- [2] A. W. Adamson, The kinetics of the manganous-permanganate reaction. *Journal of physical chemistry*, 55(2), 293-303 (1951).