Copper Catalyzed Oxidative Dissolution of Chromium(III) Oxide in Alkaline PDS Solution

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1. Introduction

Decontamination is one of the radiation protections to minimize the worker's exposure during the work of maintenance and/or decommissioning of nuclear facilities. In order to achieve the target decontamination factor during decontamination of the primary coolant system of a pressurized water reactors (PWRs), it is essential to repeatedly apply the pre-oxidative decontamination and reductive decontamination processes in consideration of the characteristics of the corrosion oxide film formed inside surface of the primary coolant system. In the pre-oxidative decontamination process, it is common to use permanganate (MnO_4^-) as a chemical decontamination agent. Typical examples include NP (nitric acid permanganate) or SP (sulfuric acid permanganate) and HP (acid permanganate) processes applied in acidic conditions and AP (alkaline permanganate) process applied in basic conditions.

In the case of repeatedly applying the pre-oxidative decontamination process using permanganate as an oxidizing agent, that is, when the second pre-oxidative decontamination step is applied after the reductive decontamination step applied following the first pre-oxidative decontaminationt spep is applied, if a considerable amount of manganese ions are present in the decontamination solution, most of the oxidizing agent injected into the second pre-oxidative decontaminationt step reacts with manganese ions to be converted into manganese oxide (MnO_2) and consumed, hence significantly decreasing the efficiency of the pre-oxidative decontamination process.

In this study, peroxydisulfate (PDS, $S_2O_8^{2-}$) was selected as an oxidizing agent capable of replacing permanganate as one of the solutions to the above problem, and the possibility of an alternative pre-oxidative decontamination process was investigated through evaluation of the dissolution characteristics of chromium(III) oxide (Cr_2O_3) with the process variables such as PDS concentration, NaOH concentration, and temperature.

2. Methods and Results

All the chemicals used in the study were of AR/GR grade and all solutions were made in demineralized water. Experiments on the dissolution of Cr_2O_3 were carried out in a stirred batch glass reactor. For most of the experiments, an amount of Cr_2O_3 equivalent to 1.316×10^{-2} M (1,368 ppm of Cr upon complete dissolution) was employed. All experiments were carried out at a constant stirring speed with 500 rpm to avoid a change in mass transfer. The concentration of dissolved Cr ions into the solutions were determined by an inductively coupled plasma.

Cr_2O_3, one of the main components of the primary system corrosion oxide film of nuclear power plants, can be dissolved by PDS as shown in the following reaction equation (1).

$$Cr_2O_3 + 3S_2O_8^{2-} + 10\,OH^- \rightarrow 2\,CrO_4^{2-} + 6\,SO_4^{2-} + 5H_2O \qquad (1)$$

It is known that PDS can be activated by heat, light, base, transition metal, zero valent iron, and so on. Through the experimental results, it was found that heat and basic conditions were not effective in enhancing the dissolution performance of Cr_2O_3 by PDS. Therefore, as another method for improving the dissolution efficiency of Cr_2O_3 by PDS, the effect of addition of transition metal ions was investigated and the results are given in Fig. 1. When metal ions (Co, Ag, Cu) are added, the oxidative dissolution performance of Cr_2O_3 is enhanced, and the addition of Cu is shown to be the most effective.

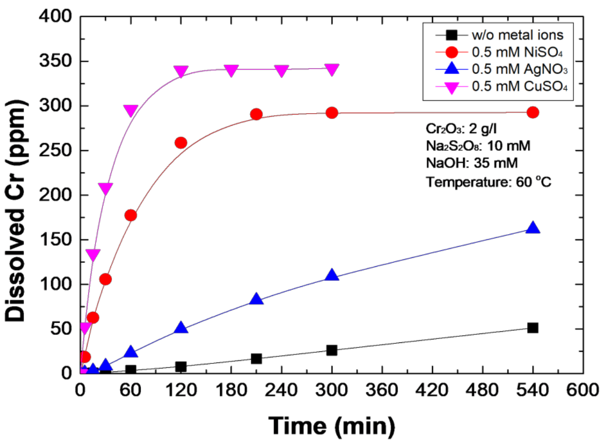

Fig. 1. The effect of addition of transition metal ions on the dissolution behavior of Cr_2O_3.

Based on these results, the effect of Cu concentration on the oxidative dissolution performance of Cr_2O_3 by PDS was are shown in Fig. 2. The dissolution rate of Cr_2O_3 increased as the Cu concentration increased, but it is expected that the rate increase will not be very large above a certain concentration. From the experimental results and the dissolved fraction caculated based on the reaction formula(1), it was found that the reaction effincy of PDS for dissolving Cr_2O_3 was almost 100%. Therefore, it was confirmed that Cu, which plays a key role in enhancing dissolution efficiency, is a reaction catalyst, not an activator that produces radicals.

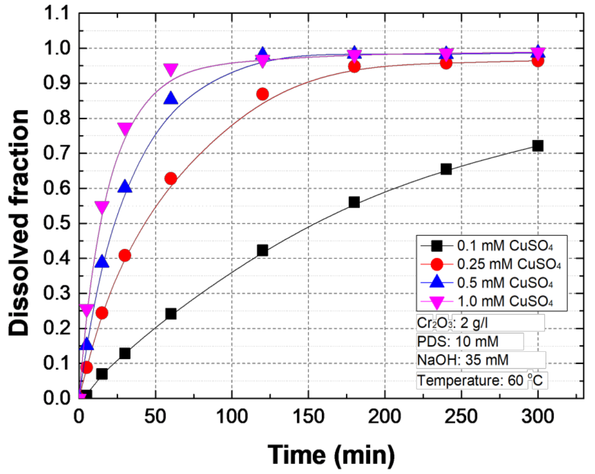

Fig. 2. The effect of Cu concentration on the dissolution behavior of Cr_2O_3.

The effect of NaOH concentration on the dissolution performance of Cr_2O_3 was investigated. The dissolution behavior of Cr_2O_3 using PDS solutions having various NaOH compositions is shown in Fig. 3. The dissolution efficiency of Cr_2O_3 was found to be optimal when the [NaOH]/[PDS] concentration ratio was 3.5 or higher. This proves that the dissolution of Cr_2O_3 proceeds according to the reaction formula(1).

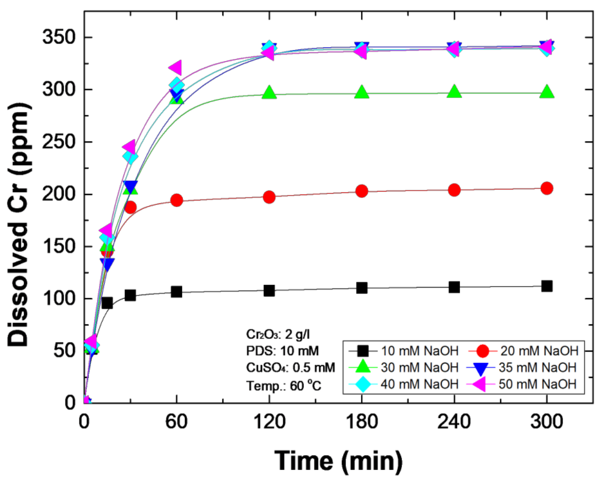

Fig. 3. The effect of alkalinity on the dissolution behavior of Cr_2O_3.

The effect of the dissolution behavior of Cr_2O_3 using PDS solutions on temperature is investigated. The dissolution rate can be obtained by fitting the dissolution behavior to the 1st order random nucleation model. The dissolution rate of Cr_2O_3 increased in proportion to the increase in temperature. From the kinetic data according to the temperature, the activation energy for oxidative dissolution of Cr_2O_3 in alkaline PDS solution containing Cu catalyst was 44.8 kJ/mol.

The results of comparing the dissolution behavior of Cr_2O_3 in the alkaline PDS solution containing 0.5 mM Cu catalyst with the conventional SP process are shown in Fig. 4. In an oxidative decontamination process with alkaline PDS solution containing Cu catalyst, the dissolution performance of Cr_2O_3 is equal or superior to that of the conventional SP process.

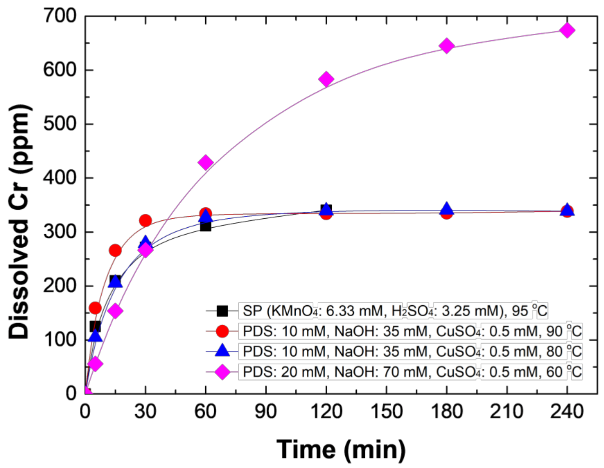

Fig. 4. Comparison of dissolution behavior of Cr_2O_3 in alkaline PDS solutions with that in conventional SP process.

3. Conclusions

The dissolution performance of Cr_2O_3 in alkaline PDS solution containing Cu catalyst is equal or superior to that in conventional SP process. Therefore, it is considered that the oxidative decontamination process using alkaline PDS solution containing Cu catalyst has potential to replace the conventional NP or SP process using acidic permanganate as an oxidizing agent.

ACKNOWLEDGEMENT

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