

Evaluation of dissolution behavior of magnetite in an inorganic acidic solution for the PHWR system decontamination

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1. Introduction

Chemical decontamination of a nuclear reactor should be performed to remove the deposited oxides from the reactor coolant surface. These oxides play host for radionuclides, be it activated corrosion products of fission products resulting in exposure to decommissioning workers. These deposited oxides are generally oxides of iron such as Fe₃O₄, Fe₂O₃, and mixed ferrites such as nickel ferrites, chromium ferrites and cobalt ferrites.

The heat transport system (HTS) in pressurized heavy water reactor (PHWR) circulates pressurized D₂O coolant through the fuel channels to remove the heat produced by fission in the nuclear fuel. The coolant transports the heat to steam generators, where it is transferred to light water to produce steam to drive the turbine. The HTS piping is fabricated from corrosion resistant carbon steel. In PHWRs, magnetite is the major corrosion product as the primary heat transport (PHT) system made up of carbon steel. Many previous studies also showed the presence of thick magnetite layer during the operation time. In the PHWR system, typical film thickness of oxide layer is 2-3 μm on stainless steel (SS) surface but on carbon steel surfaces is about 75 μm. The PHT system of 220 MWe PHWR, such as Douglas Point nuclear power plant, formed very thick magnetite oxide of 30~35 mg/cm²[1].

A new chemical decontamination technology for domestic CANDU type reactors is a challenging problem due to variations in oxide compositions from different structural materials of a pressurized water reactors (PWRs) system. KAERI already developed a chemical decontamination process for PWRs called 'HyBRID' (Hydrazine-Based Reductive metal Ion Decontamination) that does not use organic acids or organic chelating agents at all[2].

As the first step to develop a new chemical decontamination technology for PHWR system, we investigated magnetite dissolution behaviors in an inorganic acidic solution, a HyBRID solution to assess their applicability to the PHWR reactor system, which forms a thicker oxide film.

2. Materials and methods

Experiments on the magnetite dissolution were carried in a stirred batch glass reactor using HyBRID solution. Typical HyBRID solution contains 50 mM of hydrazine and 0.5 mM of Cu ion. Hydrazine is basic, so H₂SO₄ is used to meet pH 2.6(±0.5), the condition of an acidic HyBRID solution.

In order to understand the behavior of magnetite dissolution with time, the effects of initial input amount of magnetite and Cu ion concentration were varied in the experimental conditions as listed in Table 1.

Table 1: Experimental conditions

Parameters	Fe ₃ O ₄ conc. (g/l)	Cu conc. (mM)	N ₂ H ₄ conc. (mM)	pH
Fe ₃ O ₄ conc.	0.5~2.5	0.5	50	2.6 (adjusted by H ₂ SO ₄)
Copper conc.	1.25	0~1.5		

Periodic samples were taken during entire experiment period and analyzed the dissolved concentration of Fe ion in the solution by using atomic absorption spectrophotometer (AAnalyst 400, Perkin Elmer). The dissolution experiments have been done in a stirred batch glass reactor controlled with rotation speed of 500 rpm and the solution temperature of 95 °C. The changes of pH and the hydrazine concentration with time have been checked for the reaction mechanism study.

3. Results and Discussion

3.1 Dissolution characteristics according to initial concentration of magnetite

Magnetite dissolution test in the HyBRID solution was investigated to evaluate the dissolution behaviors according to initial input amount of magnetite into stirred batch reactor. The results are shown in Fig. 1.

As predicted, the initial dissolution rate of magnetite shows a tendency to increase as the initial input amount of magnetite into a stirred glass batch reactor increases due to an increase in the active surface area. Under the condition of typical HyBRID solution, it showed that magnetite can be dissolved up to about 1,000 ppm. According to the reported data[3], 2,000~3,500 ppm of Fe ions are known to be dissolved through the chemical decontamination of PHWRs. Therefore, it can be seen that the HyBRID solution is somewhat applicable to the chemical decontamination of PHWRs system.

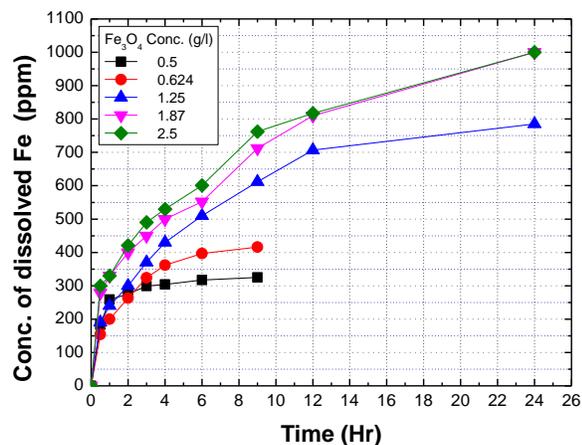


Fig 1. Dissolution behavior of magnetite according to initial input amount of magnetite.

3.2 Effect of Cu concentration on the dissolution behavior of magnetite

It is reported that Cu ion in the HyBRID solution plays a key role to enhance the magnetite dissolution rate as a catalyst[2]. In this study, in order to set the more effective Cu ion concentration in magnetite dissolution, the effect of the Cu ion concentration on the magnetite dissolution behavior was investigated. The results are shown in Fig. 2.

The dissolution rate of magnetite was increased with increase in Cu ion concentration in the HyBRID solution. Based on this experimental condition in which up to 900 ppm of Fe ions can be dissolved, it can be seen that almost complete dissolution of magnetite takes place after 9 hours under Cu ion concentration of 1.0 mM or more.

It has been shown that, the concentration of Cu ion in the HyBRID solution for application to chemical decontamination of the PHWR is judged to be much

more effective at 1.0 mM than 0.5 M set for existing HyBRID process for PWRs.

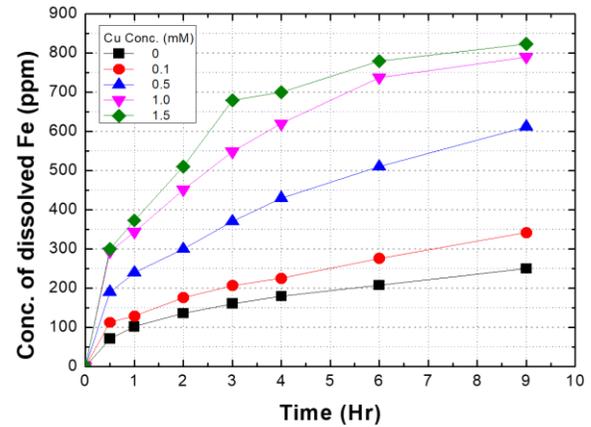


Fig 2. Dissolution behavior of magnetite according to the concentration of Cu ion.

4. Conclusion

The main function of chemical decontamination for the reactor system of PHWRs is high dissolution capability enough to remove radioactive corrosion products. From experimental results it was evaluated that magnetite can be dissolved up to about 1,000 ppm under the condition of typical HyBRID solution. In case of high Cu concentration up to 1.0mM, it was very effective magnetite dissolution. As a results, it is considered that the HyBRID solution is applicable to the chemical decontamination of PHWRs system, which is formed very thick oxides. Further study will be continued to investigate the reaction mechanism and the optimum condition for a new chemical decontamination technology for PHWRs.

5. References

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