Effect of copper concentration on initial dissolution rate of magnetite in an inorganic acidic solution for the PHWR system decontamination

Byung-Seon Choi [1], Ayantika Banerjee [1], Wangkyu Choi[1], Sanyoon Park[1], Seon-Byeong Kim[1]
[1]*Decommissioning Technology Research Division, KAERI, Daejeon, 34057, Korea*

1. Introduction

Chemical decontamination of nuclear power is one of necessary process to remove the deposited oxide film from the out of core surfaces. Before dismantling of reactor coolant system nuclear power plants (NPPs), the major related components like reactor coolant pumps (RCP), steam generators (SGs), pressurizer (PZR) and reactor coolant pipe should perform to remove the deposited oxides from the reactor coolant surface by chemical decontamination. The major parameter influencing the behavior of radioactivity, such as ^{60}Co in the coolant, is the corrosion product oxides. These oxide layer also plays as host of radioactive isotopes and be it activated corrosion products of fission products resulting in exposure to decommissioning workers. The oxide originates from the circuit materials in contact with the coolant of the primary circuit. These deposited oxides are generally oxides of iron such as Fe_3O_4, Fe_2O_3, and mixed ferrites such as nickel ferrites, chromium ferrites and cobalt ferrites [1].

The heat transport system (HTS) in pressurized heavy water reactor (PHWR) circulates pressurized D_2O 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 2-3μm on stainless steel (SS) surface but on carbon steel surfaces is about 75μm. The PHT system of 220 MWe PHWR, such as Douglas Point nuclear power plant, formed very thick magnetite oxide of 30~35 mg/cm^2[1,4]. Current technologies like CAN-DECON, CAN-DEREM were generated secondary waste due to use of chelating agents such as EDTA, citric acid, and oxalic acid [2,5]. The high concentration of Fe ions dissolved in the decontamination process solution can be redeposited as a form Fe_3O_4 and can interrupt the Fe_3O_4 dissolution reactions [5].

In order to develop a new chemical decontamination process for PHWRs we have evaluated many experimental combinations to improve the magnetite dissolution capacity and dissolution rate for the establishing the best condition based on the HyBRID which was already developed for the decontamination of PWRs by KAERI. In this paper the effect of copper on the initial dissolution rate of magnetite was investigated by the changes of copper concentration to understand the behavior of copper in hydrazine-based solution.

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 H_2SO_4 is used to meet pH 2.5(±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_3O_4 conc. (g/l)	Cu conc. (mM)	N_2H_4 conc. (mM)
Ranges	1.0~2.5	0.5	50
	1.87	0~10	

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.

3. Results and Discussion

The initial dissolution rates (IDR) of magnetite at 30 minute of reaction time were evaluated according to copper concentration into stirred batch reactor. Fig. 1 showed that higher the concentration of Cu ions, faster the rate of dissolution of magnetite. In particular, 10mM concentration of Cu^{2+} ion in the solution was able to dissolve up to 89% of magnetite within 30min. It is estimated the nearly 2 times greater than that of 5mM Cu concentration. Drastic increase of initial dissolution rate of magnetite is considered that copper in the solution assisted to accelerate the dissolution rate of magnetite. The bond in between the Cu^{+} ion and hydrazine can facilitate the transfer of an electron from the Cu^{+} ion to the Fe^{3+} of magnetite. The initial dissolution rate (IDR) of magnetite at the early stage reaction time was plotted as a function of coper concentration in Fig. 2

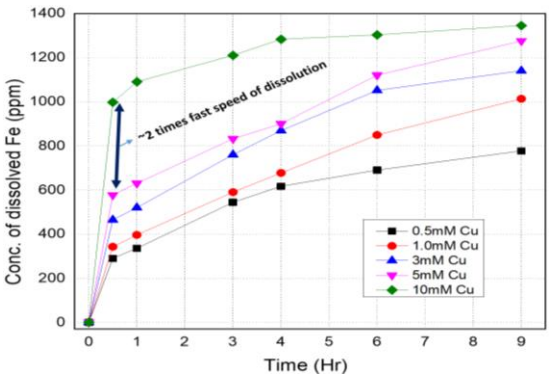

Fig 1. Dissolution behavior of magnetite according to the concentration of Cu ion.

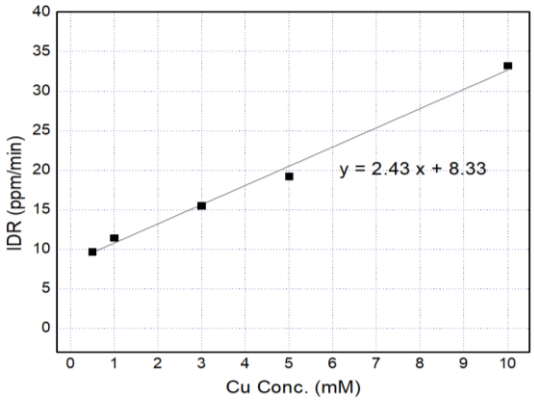

Fig 2. Initial dissolution rate (IDR) to copper concentration in solution.

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 by increasing copper concentration in solution. In case of high Cu concentration up to 10mM, it was able to dissolve up to 89% of magnetite within 30min. From this result it is very effective that the presence of higher copper in solution does influence the dissolution of magnetite. 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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