Dissolution study of oxide layer on carbon steel using oxalic acid solution

Sion Kim [a,b], Miguta Faustine Ngulimi [a,b], Mohammad Shabpiray [a,b], Kamal Asghar [a,b], Bum Kyoung Seo [a], and Changhyun Roh [a, b*]
[a] *Decommissioning Technology Division, Korea Atomic Energy Research Institute, Daejeon 34057, Korea*
[b] *Nuclear Science and Technology, University of science and Technology, Daejeon 34113, Korea*
**Corresponding author: chroh@kaeri.re.kr*

Keywords : Carbon steel, Dissolution, Oxalic acid, Oxide layer, Chemical decontamination

1. Introduction

The structural materials of the nuclear reactor's primary cooling system are generally made of carbon steel (CS) [1]. On the surface of CS, a radioactive corrosive oxide layer forms due to the harsh operating environment of the nuclear power plants. Effective and chemical decontamination is essential because these oxide layers reduce the performance of nuclear power plants and pose a risk of radiation exposure to workers and the environment during maintenance, repair, or decommissioning [2]. Research and development on decontamination methods for radioactive corrosion oxide layers are being conducted in many countries, and the developed technologies are being commercialized. Wolseong Unit 1, Korea's first PHWR, was permanently shut down in December 2019 and dismantlement will begin this year [3]. In this study, oxalic acid from the CORD process, one of the chemical decontamination agents to be used when dismantling Wolseong Unit 1, was used to dissolve the corrosive oxide layer on the structural material. To simulate the corrosion of CS106 Gr-B, a structural material of PHWR's cooling system, a corrosion oxide layer was fabricated on the surface of carbon steel using an autoclave in a high temperature/high pressure atmosphere. The CS coupons before and after oxidation were then characterized.

2. Methods and Results

2.1 Fabrication of corrosion oxide layer on CS

The corrosion oxide layer on the surface of the CS coupon was fabricated under steam conditions and high temperature/high pressure using an autoclave. The solution for corrosion is 50mM EDTA, 400mM Hydrazine in 1L of aqueous solution. The corrosion solution was added to a 3L autoclave reactor. CS coupons were hung on two levels towards the bottom of the vessel. After the corrosion solution and coupons were added to the reactor, the reactor and lid were completely combined. Afterwards, nitrogen gas was purged inside the reactor for 30 minutes. The gas line of the reactor after purging was closed, and the temperature inside the reactor was set to 340°C. After the temperature inside the reactor reached 340°C, the reaction was continued for 3 days and then the reaction was terminated. At this time, the internal pressure of the reactor is 13 MPa. The carbon steel coupon before and after oxidation is shown in Fig. 1.

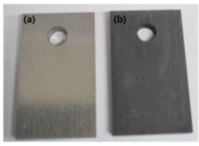

Fig. 1. Carbon steel coupon (a) before oxidation (b) after oxidation

2.2 Characterization of CS coupons

Scanning electron microscope (SEM) and electron probe micro-analysis (EPMA) analysis were performed to analyze the surface shape and elements of the CS coupon before and after oxidation. (Fig. 2) Crystal particles were formed on the surface of oxidized CS. Looking at the results of EPMA, the base metal is mostly composed of Fe atoms, and the oxidized CS surface is mostly composed of Fe and O. From the results of EPMA, the presence of iron oxide on the CS surface can be confirmed.

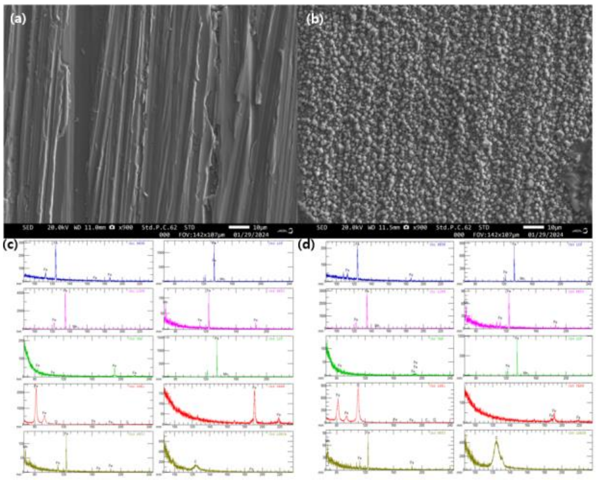

Fig.2. SEM images of CS coupon surface (a) base metal (b) oxidized CS, EPMA results of (c) base metal (d) oxidized

The base metal and oxidized CS were analyzed by Glow Discharge Optical Emission Spectrometry (GD-OES) to confirm the thickness of the oxide layer on the surface of the oxidized CS (Fig. 3.) As a result of GD-OES analysis, 4 ㎛ oxide layers were formed on the surface of the oxidized CS coupon.

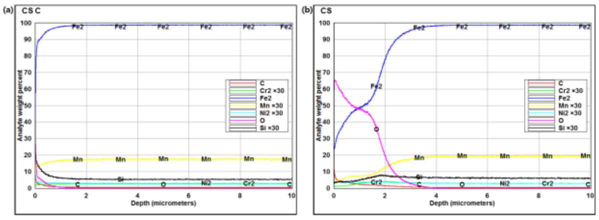

Fig. 3. GD-OES analysis of CS coupon (a) base metal (b) oxidized

2.3 Dissolution of oxide layer using oxalic acid

The oxide layer of oxidized CS was dissolved by 10mM and 20mM oxalic acid. The dissolution test equipment is shown in fig. 4. All dissolution conditions except for the concentration of oxalic acid were set to be the same, and the pH of the solution and the concentration of dissolved Fe were compared according to the oxalic acid concentration. To conduct a dissolution test, 300ml round flasks were inserted into the heating mantle and 150ml of 10mM and 20mM oxalic acid were respectively added. The reactor lid with three inlets was combined with the reactor and fixed with a clamp. A thermostat was connected at the left entrance of the lid to control the temperature of the solution, a stopper was connected in the middle, and a condenser was connected on the right. The coupon was hung with stainless steel wire and fixed in the solution without contacting the magnetic bar. The solution was stirred at 95 degrees with a magnetic bar at 500 rpm for 18 hours.

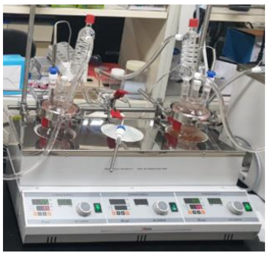

Fig. 4. Oxide layer dissolution test equipment on oxidized CS

The pH of the solution before and after the dissolution test was measured. The concentration of Fe ions dissolved in the solution was analyzed using an atomic absorption spectrophotometer (AAnalyst 400).

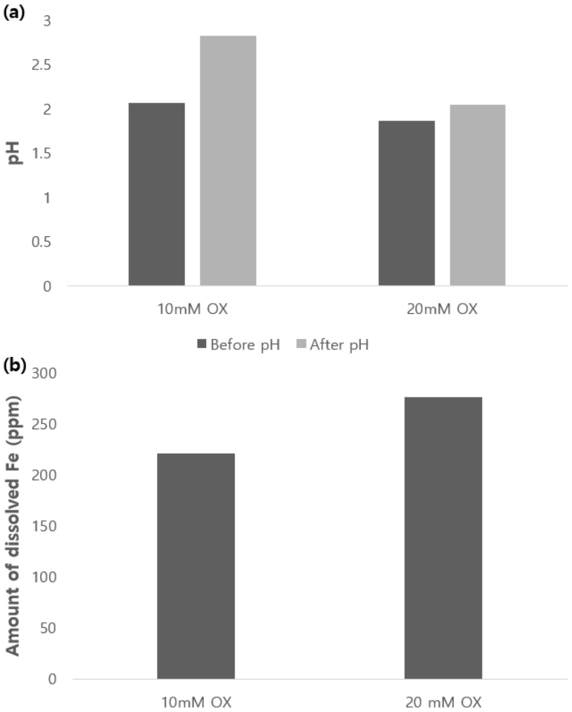

Fig. 5. (a) Change of pH in solution before/after dissolution (b) Amount of dissolved Fe, according to concentration of oxalic acid

Figure 5 shows the pH change of the solution before and after dissolution and the concentration of Fe ions dissolved in the solution. It was confirmed that the pH of both 10mM and 20mM oxalic acid solutions after dissolution increased. Iron oxides produced by corrosion of Cs are magnetite (Fe_3O_4), hematite (Fe_2O_3), and wuestite (FeO) [4]. Magnetite, hematite, and wuestite dissolve into Fe^{3+} ions and/or Fe^{2+} ions under acidic conditions. Since H^+ in the solution is consumed during dissolution, the pH of the solution increases after dissolution [5, 6]. Additionally, as the concentration of oxalic acid increased (lower pH), the amount of Fe dissolved in the solution increased. In acidic conditions, an increase in H^+ concentration further reduced Fe, resulting in an increase in the amount of dissolved Fe.

3. Conclusions

In this study, a corrosion oxide layer was manufactured and characterized by oxidized CS by EDTA and hydrazine corrosive solution, and a simulated CS coupon with oxide layer was dissolved according to the concentration of oxalic acid, a commercial chemical decontamination agent. It was confirmed that iron oxide was formed on the CS surface under high temperature/high pressure. Oxalic acid showed excellent performance in dissolving iron oxide, and its solubility changes depending on concentration. This study will serve as the basis for research on dissolving the simulated oxide layer by manufacturing a higher thickness corrosion oxide layer.

REFERENCES

[1] T. F. J. Marchl, “Occupational radiation exposures in Simens designed PWRs” SFEN, Chemistry In Water Reactors : Operating experience and new developments, pp. 24-27, 1994.
[2] Kim, W. S., Nam, S., Chang, S., Kim, H., and Um, W., Removal of Chalk River unidentified deposit (CRUD) radioactive waste by enhanced electrokinetic process. Journal of industrial and engineering chemistry, Vol.57, p. 89, 2018.
[3] Chang, N., Eun, H., Won, H., Choi, W., Kim, S., & Kim, Y., Study on the Removal of Corrosion Oxide Layers in the Heat Transport System of PHWR.
[4] Dubey, V., & Kain, V., Oxidation behavior of carbon steel: effect of formation temperature and pH of the environment. Journal of Materials Engineering and Performance, Vol. 26, p. 5312, 2017.
[5] Vehmaanperä, P., Sihvonen, T., Salmimies, R., and Häkkinen, A., Dissolution of Magnetite and Hematite in Mixtures of Oxalic and Nitric Acid: Mechanisms and Kinetics. Minerals, Vol. 12, p. 560, 2022.
[6] Lee, B. C., and Oh, W., Temperature and concentration dependencies of chemical equilibrium for reductive dissolution of magnetite using oxalic acid. Journal of Nuclear Fuel Cycle and Waste Technology (JNFCWT), Vol. 19, p. 187, 2021.