1D Pencil Electrode Experiment to Describe Pitting Corrosion of Copper Canister under Sulfide-rich Deep Geological Repository Environment

Pilhyeon Ju[a], Kwanil Chae[a], Nakkyu Chae[b], Samuel Park[c], Richard I. Foster[d], Sungyeol Choi[a,d,e*]
[a] *Department of Nuclear Engineering, Seoul National University, 1 Gwanak-ro, Gwanak-gu,Seoul 08826, Republic of Korea*
[b] *Disposal Performance Demonstration Research Division, Korea Atomic Energy Research Institute, 111 Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea*
[c] *Economic Analysis Division, Korea Atomic Energy Research Institute, 111 Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea*
[d] *Nuclear Research Institute for Future Technology and Policy, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea*
[e] *Institute of Engineering Research, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea*

Corresponding author: choisys7@snu.ac.kr

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1. Introduction

As the Spent Nuclear Fuels (SNFs) in the Republic of Korea are accumulated, safe isolation and disposal of them has become important. The Republic of Korea considers a Deep Geological Repository (DGR) concept for the final disposal of the SNFs, establishing Improved KAERI Reference Disposal System (KRS+) which involves cast iron inserts inserted within copper canisters. Each copper canister is supposed to improve the corrosion resistance of the engineered barrier system of the KRS+. Therefore, it is crucial to evaluate the integrity of the copper from the viewpoint of corrosion.

The objective of this study is to conduct an experiment which can understand the pitting corrosion of copper under the sulfide-rich DGR environment. As pitting corrosion is referred to as the accelerated corrosion at a pit, occurring due to the damage on the corrosion product film at the metal surface, it may affect to the DGR's chemical integrity. This study describes the pitting corrosion condition of copper to see the pit growth under the sulfide-rich environment.

2. Methodologies

2.1. Experimental condition

This study utilizes the experimental methodology of previous pitting corrosion experiments for Stainless Steel (SS) 304, examining the pit growth over time with an electrochemical method [1-2]. The solution for the experiment is set to be 0.001 M of Sodium Sulfide (Na_2S) under pH 9, with ACS-grade Na_2S and Sodium Tetraborate ($Na_2B_4O_7$) in ultrapure deionized water (18.2 MΩ·cm). All experiments are conducted inside a glovebox at room temperature (25 °C), controlling the oxygen concentration to be minimum. A potential of +0.6 V vs. Saturated Calomel Electrode (SCE) is applied.

2.2. Specimen preparation

A coin-shaped specimen is prepared with a copper wire at the middle, the diameter of which is 25 μm. It can be fabricated by pouring epoxy into the cylindrical mold. The small area of the wire's cross section can function as a pit, due to its non-conductive characteristic of the epoxy.

2.3. Electrochemical cell

A three-electrode system was selected to conduct the electrochemical experiment. The working electrode was mounted with a Teflon holder of PTFE, the revealed area of which is 1 cm^2. The coin-shaped specimen was connected with the holder using conductive silver paste. A platinum mesh of 9 cm^2 was selected as the counter electrode, and the SCE is selected as the reference electrode.

2.4. Experiment procedure

The specimen was left under the open circuit condition for the first 60 seconds, and cathodic cleaning was conducted during 60 seconds (Experiment 1) and 30 seconds (Experiment 2) with an applied potential of -1.2 V vs. SCE. Then the potential of +0.6 V vs. SCE was applied for the pitting corrosion, measuring the current signal during 200 seconds. The current signal (i) can be converted into the pit depth (h) by Faraday's 2nd Law (Equation 1) [1].

$$h = \frac{a}{nF\rho}\int i\,dt \qquad (1)$$

Here, a means the atomic weight, n means the stoichiometric dissolution, and ρ means the density of copper, while F is Faraday constant [1].

3. Results and Discussion

Fig. 1 shows the current density signals during the first 200 seconds after cathodic cleaning. The initial peaks indicate the activation of pitting corrosion, while the gradual decrease of the current density occurs over time. This can be interpreted as the decrease of the corrosion due to the accumulation of corrosion product – copper sulfide (Cu_2S) – on the surface of the pit. The Cu_2S is generated with the following reaction of Equation 2.

$$2Cu + HS^- \leftrightarrow Cu_2S + H^+ + 2e^- \quad (2)$$

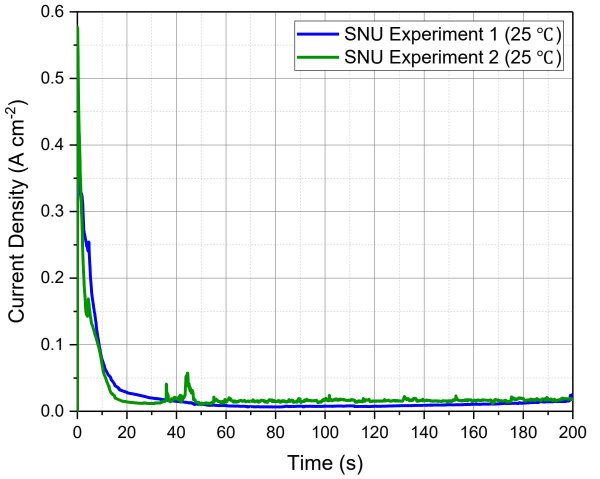

Fig. 1. Current density signals of copper pitting corrosion over time under 25 °C, pH 9, 0.001 M Na_2S solution with the applied potential of +0.6 V vs. SCE.

Fig. 2 shows the pit depths derived with the current density signals and Faraday's 2nd Law. The rapid increase at the initial phase happens due to the pitting corrosion activation at the bare pit, and the saturated corrosion rates are shown in both experiments.

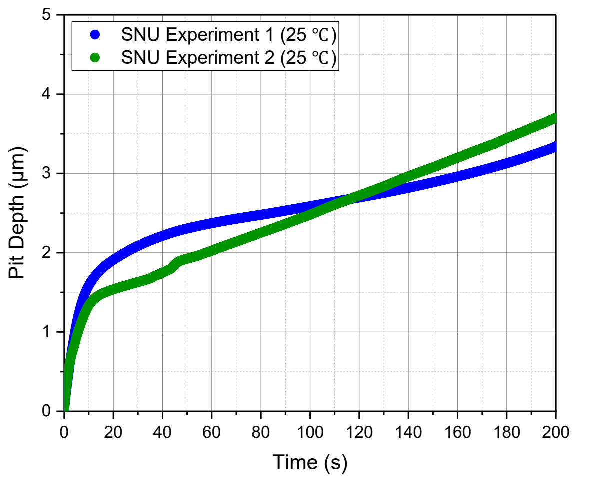

Fig. 2. Pit depth of copper pitting corrosion over time under 25 °C, pH 9, 0.001 M Na_2S solution with the applied potential of +0.6 V vs. SCE, calculated with Faraday's 2nd Law.

4. Conclusion

This study investigated the behavior of copper pitting corrosion under the sulfide-rich DGR environment by the electrochemical experiment. The pitting corrosion was activated with the positive potential applied into the copper pit surrounded by non-conductive epoxy, showing the gradual decrease of corrosion due to the effect of the corrosion product.

This study is a preliminary experiment with one of the conditions for the solution concentration and with the short timeframe of 200 seconds. The future works will aim more integrated understanding of copper pitting corrosion with diverse conditions and time scale.

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