

## Analysis of Electrochemical Behavior of Cu in Anaerobic Solution Considering Deep Geological Repositories Conditions

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### 1. Introduction

The ultimate strategy for managing Spent Nuclear Fuels (SNFs) involves the implementation of Deep Geological Repositories (DGRs), a solution adopted by numerous countries utilizing nuclear energy, including Republic of Korea. Copper (Cu) canisters are widely employed for SNF containment due to their superior corrosion resistance, which is critical for ensuring the integrity of the DGRs' multi-barrier[1].

After the repository is sealed, residual oxygen will quickly be depleted, leading to anoxic conditions where sulfides in the groundwater may significantly accelerate the corrosion of Cu[2]. Moreover, the decay heat generated by the SNFs will raise the temperature of the Cu canisters, potentially enhancing both chemical and electrochemical corrosion processes. Therefore, it is crucial to investigate the effects of anoxic conditions and elevated temperatures on the corrosion of Cu to predict the long-term stability of these canisters within DGRs.

In this study, the corrosion behavior of Cu was evaluated using electrochemical methods under anaerobic and elevated temperature conditions[3]. The corrosion solution, simulating the Korean groundwater environment, contained sulfide and chloride ions, and experiments were conducted under varying pH levels and elevated temperatures. This approach aims to predict long-term corrosion behavior, analyze the influence of each environmental factor on corrosion, and assess the overall performance of the Cu canister in such conditions.

### 2. Experimental Setup and Method

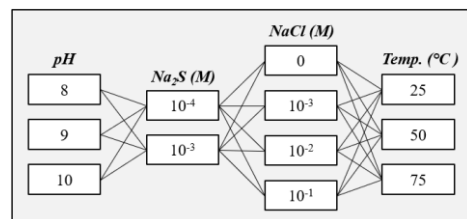
#### 2.1. Specimens

Oxygen-free rolled Cu specimens, with a purity of 99.99%, were provided by the Korea Atomic Energy Research Institute (KAERI) for this study. They were coin-shaped, measuring 15 mm in diameter and 2 mm in thickness. The specimens were ground with SiC papers of increasing grit sizes (800, 2400, 4000) and polished with 3  $\mu\text{m}$  and 1  $\mu\text{m}$  diamond suspensions for a smooth

finish. The specimens were then thoroughly cleaned with deionized water (18.2 M $\Omega$ ·cm) to eliminate any residues.

#### 2.2. Corrosion Solutions

All solutions were prepared using ultrapure deionized water (18.2 M $\Omega$ ·cm) and ACS-grade reagents. The pH was maintained within the range of 8 to 10 ( $\pm 0.2$ ) using a 0.02M sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) buffer, with fine adjustments made by adding boric acid ( $\text{H}_3\text{BO}_3$ ) and sodium hydroxide (NaOH). Sodium sulfide ( $\text{Na}_2\text{S}$ ) was added at concentrations of  $10^{-4}$  M and  $10^{-3}$  M, while sodium chloride (NaCl) was introduced at 0 M,  $10^{-3}$  M,  $10^{-2}$  M, and  $10^{-1}$  M. Temperature control of the corrosion solution was achieved using a heating block fabricated from 6061 aluminum alloy (AL6061), with solution temperatures maintained at 25°C, 50°C, and 75°C ( $\pm 2^\circ\text{C}$ ). These variables, illustrated in **Fig. 1**, were chosen to replicate anoxic conditions expected in Korea's granite geology within DGRs. Experimental repeatability was rigorously ensured for reliability.



**Fig. 1.** Overview of the corrosion test conditions: varying pH levels, sulfide and chloride concentrations, and temperature.

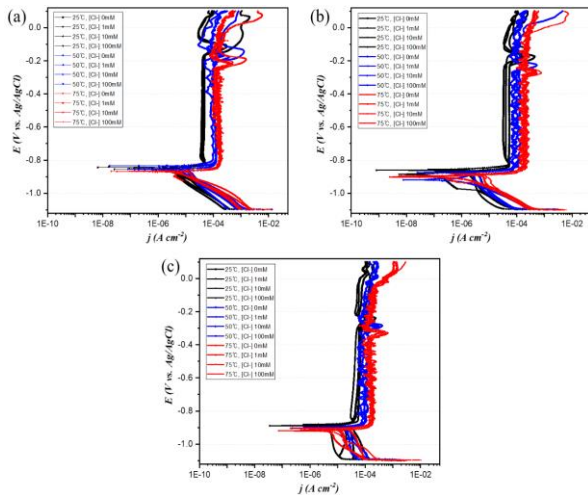
#### 2.3. Electrochemical Cell and Equipment

The electrochemical experiments were performed in a single-compartment cell with a tightly sealed PTFE lid. The working electrode, a prepared Cu disc, was secured in a Teflon holder with an exposed area of 1 cm<sup>2</sup>. A platinum mesh (9 cm<sup>2</sup>) served as the counter electrode, and an Ag/AgCl reference electrode (-197 mV vs. SHE) monitored the potential. Potentials were controlled using an PARSTAT potentiostat, with data acquisition and analysis via VersaStudio software.

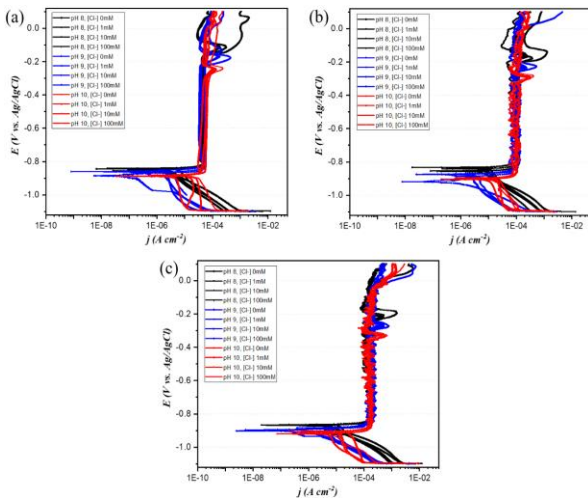
### 3. Results and Discussion

#### 3.1. Anodic polarization tests

An anodic polarization test was conducted using the previously described combination of variables (**Fig. 1**). A scan rate of 0.1667 mV/s was applied, with a scan range from -1.1 to 0.1 V. The results revealed several insights that extend beyond the established effects of sulfide concentration reported in earlier studies [4]. **Fig. 2** presents the anodic polarization curves as a function of temperature at different pH levels. It was observed that with increasing temperature, the corrosion potential ( $E_{\text{corr}}$ ) decreased while the limiting current density increased across all pH levels. Notably, the region where the limiting current density plateaued indicated the absence of an active state, which is characteristic of corrosion in sulfide-containing conditions. Additionally, the increase in limiting current density with rising temperature suggests a thermodynamic change in the sulfide film on Cu [5].



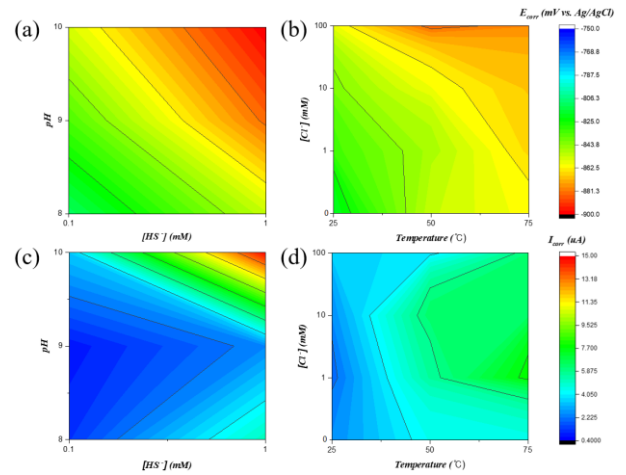
**Fig. 2.** Anodic polarization curves as a function of temperature at (a) pH 8, (b) pH 9, and (c) pH 10.



**Fig. 3.** Anodic polarization curves as a function of pH at (a) 25 °C, (b) 50 °C, and (c) 75 °C.

**Fig. 3** shows anodic polarization curves as a function of pH at different temperatures. With increasing pH, both  $E_{\text{corr}}$  and the film breakdown potential ( $E_b$ ) decreased, although the limiting current density remained constant. The presence of sulfide likely alters corrosion resistance, suggesting that higher pH accelerates corrosion, highlighting sulfide's impact in anaerobic environments.

**Fig. 4** shows the correlations between various experimental variables and their respective impacts on  $E_{\text{corr}}$  and the corrosion rate. All four variables exhibit a clear trend of decreasing  $E_{\text{corr}}$  as their values increase, as seen in **Figs. 4a** and **4b**. The corrosion rate, depicted in **Figs. 4c** and **4d**, is highest under conditions of elevated pH and increased sulfide concentrations. In contrast, no consistent trend in corrosion rate is observed under other conditions.



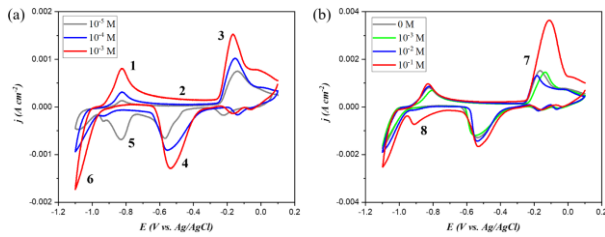
**Fig. 4.** Correlations between various variables and their impact on  $E_{\text{corr}}$  (a, b) and corrosion rate (c, d)

#### 3.2. Cyclic voltammetry

Cyclic voltammograms (CVs) were plotted to examine the effects of varying sulfide and chloride concentrations. The scan rate was 0.025 V/s, with a scan range from -1.1 to 0.1 V. **Fig. 5a** shows how peak characteristics change with increasing sulfide concentration. Region 1 corresponds to copper sulfide ( $\text{Cu}_2\text{S}$ ) formation on the Cu surface. The increased peak height and sharpness with higher sulfide levels indicate greater susceptibility to corrosion. In Region 2, current density increases with sulfide concentration, suggesting more extensive electrochemical reactions at the Cu interface. Region 3 involves the thermodynamically driven dissolution of  $\text{Cu}_2\text{S}$ , with higher sulfide levels possibly leading to localized corrosion. The reduction reactions in Regions 4 to 6 correspond to the oxidation reactions in Regions 1 to 3, with Region 5 showing a decrease as sulfide concentration rises.

**Fig. 5b** shows how peak characteristics change with varying chloride concentrations. Significant changes

were noted only in Regions 7 and 8, where higher chloride levels promote Cu dissolution, suggesting sulfide film compromise and localized corrosion.



**Fig. 5.** CVs at (a) varying sulfide concentrations in pH 10 at 25°C without chloride, and (b) varying chloride concentrations in pH 10 at 25°C with  $10^{-3}$  M sulfide.

#### 4. Conclusion

This study demonstrates that pH, sulfide, chloride concentrations, and temperature significantly influence the corrosion behavior of Cu under conditions relevant to DGRs. Anodic polarization tests indicated that all these variables affect the  $E_{\text{corr}}$ , with sulfide playing a particularly critical role in diminishing Cu corrosion resistance. The cyclic voltammetry measurements revealed that elevated sulfide levels promote the formation and subsequent dissolution of  $\text{Cu}_2\text{S}$ , which could lead to localized corrosion, especially with high chloride concentrations. The ongoing SEM analyses are expected to provide further insights into the growth mechanisms of sulfide films, delivering essential data for developing reliable models of Cu canisters designed for the long-term storage of SNF.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- [1] F. King, C. Lilja, K. Pedersen, P. Pitkänen, and M. Vähänen, "An update of the state-of-the-art report on the corrosion of copper under expected conditions in a deep geologic repository," Swedish Nuclear Fuel and Waste Management Co., 2010.
- [2] H. R. Müller *et al.*, "Implementation of the full-scale emplacement (FE) experiment at the Mont Terri rock laboratory," *Mont Terri Rock Laboratory, 20 Years: Two Decades of Research and Experimentation on Claystones for Geological Disposal of Radioactive Waste*, pp. 289-308, 2018.
- [3] M. Guo, "The electrochemical and corrosion study of copper for nuclear waste containers under deep geological

disposal conditions," The University of Western Ontario (Canada), 2020.

[4] J. Chen, Z. Qin, and D. Shoesmith, "Long-term corrosion of copper in a dilute anaerobic sulfide solution," *Electrochimica acta*, vol. 56, no. 23, pp. 7854-7861, 2011.

[5] D. Kong *et al.*, "Long-term polarisation and immersion for copper corrosion in high-level nuclear waste environment," *Materials and Corrosion*, vol. 68, no. 10, pp. 1070-1079, 2017.