

Research Article

Investigation of Early Corrosion Behavior of Canister Candidate Materials in Oxidic Groundwater by the EQCM Method

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This study investigated the corrosion mass changes of canister candidate materials (Cu, Ni, Ti, SS304) in an oxidic groundwater solution using the electrochemical quartz crystal microbalance method in order to estimate corrosion thickness. The materials were immersed in naturally aerated groundwater with and without the addition of chloride ions to observe the mass changes as well as the open-circuit potential (corrosion potential). In the oxidic groundwater solution, Ni, Ti, and SS304 exhibited negligible mass changes, indicating their insusceptibility to general corrosion. In contrast, the Cu electrode exhibited a relatively significant mass change (63.8 ng/cm^2 for 60 h), and the maximum corrosion thickness was estimated to be approximately $0.1 \text{ }\mu\text{m/yr}$. In the presence of chloride ions, the Ni and Ti electrodes did not reveal demonstrate any significant changes, whereas the SS304 electrode was slightly increased compared to an absence of chloride ions. A lower mass change occurred when the Cu electrode was immersed in the chloride-containing groundwater solution compared with the absence of chlorides because the dissolution of Cu as CuCl_2 was involved in Cu_2O formation.

1. Introduction

Deep geological disposal with an engineered-barrier system (EBS) is one of the options to treat spent nuclear fuel. It aims to isolate the spent fuel from human society by sealing it in a corrosion-resistant canister and embedding permanently in the deep underground bedrock [1–3]. Determining the corrosion rates of canister materials exposed to a geological repository environment is an important step toward evaluating the service life of canisters in an EBS. Given that corrosion causes mass change, the mass of canister materials before and after corrosion is measured to calculate corrosion thickness and to estimate the corrosion rate and lifetime of the canisters. Although the mass measurement test provides

more precise information on the actual canister behavior, it is time-consuming and expensive [4]. Electrochemical techniques offer alternative methods for calculating the canister corrosion rate. Tafel plot measurements are applied to obtain the corrosion rate as a form of corrosion current (i_{corr}). This is quick and easily observed; however, the i_{corr} value is unrealistic because it is the exchange current obtained by fitting the anodic and cathodic branches of the current-overpotential curve [5].

The electrochemical quartz crystal microbalance (EQCM) technique enables the simultaneous monitoring of mass changes and various electrochemical responses. The piezoelectric properties of a quartz crystal slice allow signal transduction of the QCM. The vibration (frequency) of

quartz crystals due to deformation in the electric field is converted to a subtle mass change in the nanogram order [6]. In this study, the EQCM method was applied to observe the early corrosion behavior of canister candidate materials and to measure the mass change accompanying the corrosion reaction in real time for the estimation of corrosion thickness. Four types of base metal electrodes (Cu, Ni, Ti, and SS304) were immersed in oxic groundwater sampled at the Korea Atomic Energy Research Institute (KAERI) underground research tunnel site. During the immersion of the metal electrodes, the frequency change as well as the open-circuit potential (OCP) of the electrodes were monitored, and the mass change amount was obtained by converting the frequency change. The corrosion thickness was then calculated based on the mass change amount of the metal canister material in the early oxic corrosion stage. Finally, the surface morphologies of the Cu corroded in the test solution with and without the presence of chloride ions were observed.

2. Materials and Methods

EQCM measurements were conducted using a QCM resonator with the deposited metal. Four types of resonators (Cu, Ni, Ti, SS304) were used as the working electrodes (diameter: 5 mm, thickness: 300 nm, surface area: 0.196 cm^2) with a 9 MHz oscillator (QCA922A, 9 MHz, SEIKO EG&G CO., LTD) connected to a potentiostat (Bio-Logic, Claix, France SP-300). The electrodes were immersed into the test solution, and monitoring of frequency changes and OCP measurements were performed. A saturated calomel reference electrode (SCE) and a Pt wire counter electrode were used for all electrochemical experiments. Figure 1 shows the experimental apparatus used for the EQCM measurements. The solution was prepared by filtration ($1 \mu\text{m}$ filter paper) of naturally aerated KAERI underground research tunnel (KURT) groundwater. The chemical composition of KURT groundwater (pH 7.9) has previously been reported [7, 8]. Sodium chloride (99.5%, Junsei Chemical CO., LTD.) was added to observe the effect of chloride ions. All experiments were performed at room temperature (25°C). The surface morphologies of the Cu resonator electrodes after the test were investigated by scanning electron microscopy (SEM, Hitachi SU-8020) and energy dispersive X-ray spectroscopy (EDS) measurements (Horiba EMAX).

3. Results and Discussion

Figure 2 shows the OCP (solid line) and mass change (dashed line) of base metal for canister candidates (Cu, Ni, Ti, SS304) immersed in oxic groundwater. For the Cu electrode, the OCP value was initially maintained near -0.05 V vs. SCE , then it decreased to -0.18 V vs. SCE as the immersion time increased (Figure 2(a)). A step-wise mass change of the Cu electrode was performed every 20 h, and the final mass change was approximately 63.8 ng/cm^2 . This increase in mass was induced by the formation of Cu_2O as a corrosion product on the Cu surface [9]. Each step can be divided into two stages; a rapid increase and a relatively

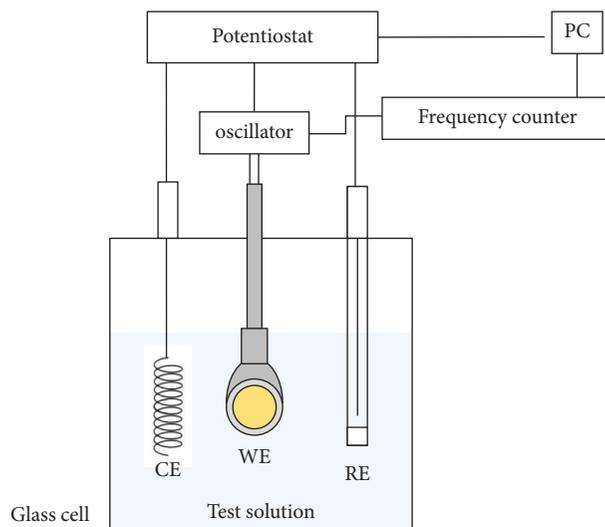


FIGURE 1: Experimental apparatus for the EQCM measurements used in this study.

stable stage. Although the stages in the mass change curve have not been elucidated, they can be attributed to the combined reactions of the ions in groundwater on the electrode surface [10]. The adsorption of ions on the Cu surface caused a mass increase. Once Cu was corroded, Cu^{2+} was transferred to the solution, resulting in mass loss, whereas when Cu_2O was formed, the mass increased. The total mass change was mainly determined by these reactions. For the Ni electrode, the OCP value gradually increased and reached -0.01 V vs. SCE during the measurement, whereas the total mass change was negligible when compared to the Cu electrode (Figure 2(b)). The increase and decrease in mass were repeated over very short cycles in the Ni electrode. Figure 2(c) shows the OCP and mass change of the Ti electrode in oxic groundwater. The OCP value of the Ti electrode stabilized at -0.03 V vs. SCE during measurement. Initially, the mass increase and decrease cycles were short; however, in the latter part of the measurement, the increased mass was maintained for approximately 30 h, induced by the formation of the TiO_2 film [11]. Figure 2(d) shows that the OCP value of the SS304 electrode decreased to 0.05 V vs. SCE during measurement, and its increased mass was less significant than that of the Cu electrode, similar to the Ni and Ti electrodes. This indicates that Cu is relatively more susceptible to general corrosion than the other materials in the test groundwater solution. Based on the measured mass change in the early period of corrosion, Cu corrosion thickness was estimated by considering the electrode surface area, the density of the corrosion product, and test time. It was assumed that mass change was only involved with the corrosion product (here, Cu_2O) on the electrode surface [12]. The maximum corrosion thickness of Cu in the test solution was estimated to be approximately $0.1 \mu\text{m/yr}$. When the disposal period was assumed as 1 million years, the maximum corrosion thickness of Cu is approximately 1 cm, even if it is calculated arithmetically. Moreover, because the aerobic period during disposal is only several hundred years, the corrosion caused by the inflow of oxic groundwater in

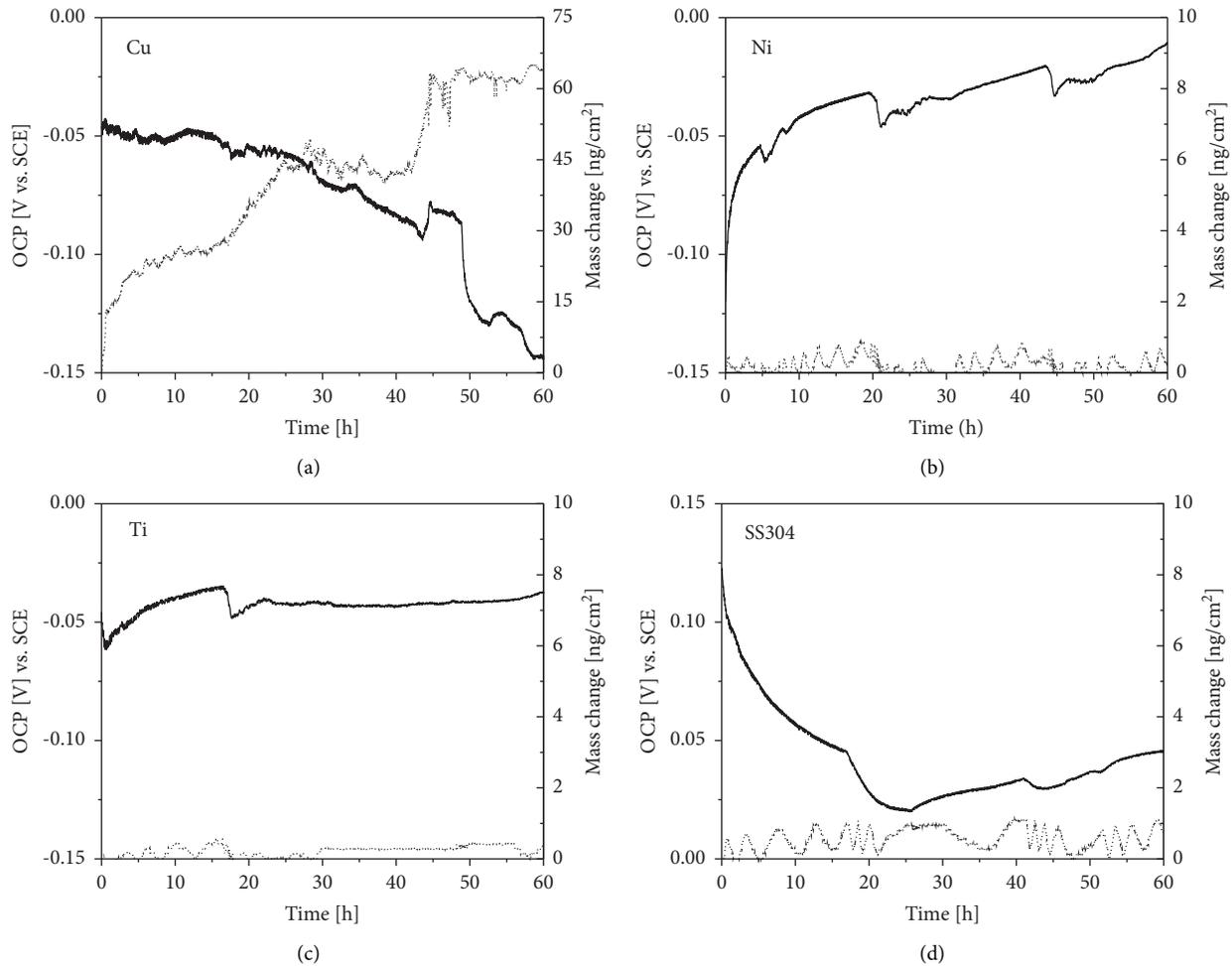


FIGURE 2: OCP (solid line) and mass change (dash line) of (a) Cu, (b) Ni, (c) Ti, and (d) SS304 in oxic KURT groundwater solution.

the actual disposal environment is expected to be much smaller than the estimated value. For comparison, the corrosion thickness of Cu, contacted with Na-type bentonite (MX-80) blocks and immersed in oxic KURT groundwater at 30°C for 10 years was 0.05 $\mu\text{m}/\text{yr}$, based on a typical weight loss method [13]. The difference in corrosion thickness according to the test methods is thought to be due to the presence or absence of a bentonite block. The bentonite has low hydraulic conductivity and it prevents the transfer of dissolved oxygen to the metal surface. Thus, the obtained value in this study can be used for relative comparison depending on the test materials or the experimental conditions.

Given that chloride ions are one of the main factors affecting the corrosion thickness of metal canisters [14], the mass changes of test metals were also investigated in oxic groundwater solutions with the addition of 0.1 M NaCl. Figure 3 shows the OCP (solid line) and mass change (dashed line) of the test metals immersed in 0.1 M NaCl-added oxic groundwater. In the presence of chloride ions, the Cu electrode OCP was maintained near -0.17 V vs. SCE, and the mass declined during the initial 2.5 h and then gradually increased (Figure 3(a)). Unlike in the groundwater

solution (Figure 2(a)), the Cu mass in the chloride-added groundwater solution initially decreased and then increased. We hypothesized that the initial mass decrease was related to the dissolution of Cu by chloride ions. The final mass change of Cu was approximately 12 ng/cm^2 , smaller than in the absence of chloride ions although a darker color change was observed even after 25 h of immersion (data not shown). The lower mass change obtained in the chloride-containing solution can be explained by the corrosion mechanism. In the presence of Cl^- , Cu_2O formation was accompanied by the dissolution of Cu as CuCl_2^- at a pH value < 9.2 (Figure 4) [15]. The initial mass loss was caused by the dissolution of Cu in the solution in the form of CuCl_2^- , which was greater than the mass increase caused by Cu_2O formation. Subsequently, mass change increased as the Cu_2O formation continued. Thus, a smaller mass change was detected than the amount of Cu that corroded. Consistently, there was a limit to predicting the corrosion thickness by the EQCM method based only on the mass increase of Cu in a chloride-containing environment during the initial corrosion stage. A more systematic calculation of corrosion kinetics is required to predict the corrosion rate of Cu in a chloride-containing environment, especially when it is accompanied by a mass

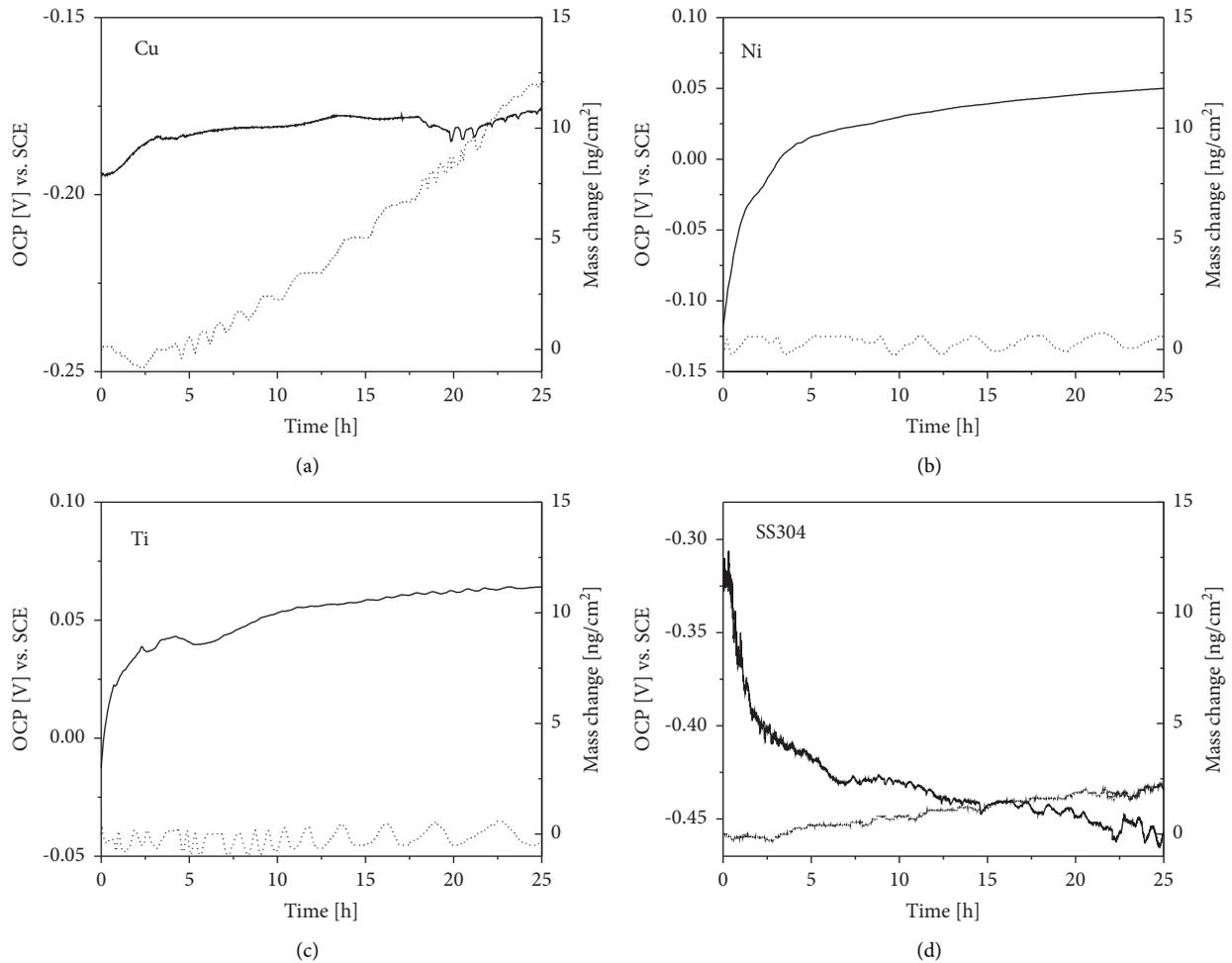


FIGURE 3: OCP (solid line) and mass change (dash line) of (a) Cu, (b) Ni, (c) Ti, and (d) SS304 in 0.1 M NaCl⁻ added oxidic KURT groundwater solution.

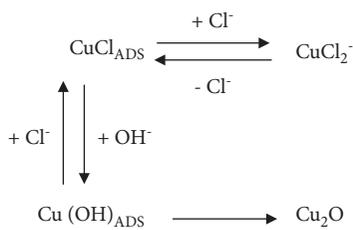


FIGURE 4: Formation of Cu₂O in chloride solution [12].

decrease rather than a simple mass increase. For the Ni electrode, the OCP value gradually increased and stabilized at approximately 0.05 V vs. SCE. The mass change was almost constant during the measurement (Figure 3(b)), unlike the increase and decrease trend observed over time in the groundwater without Cl⁻ (Figure 2(b)). As shown in Figure 3(c), the OCP of the Ti electrode in Cl⁻-added groundwater was 0.07 V vs. SCE, and the mass change gradually increased over time; however, it did not persist. This result indicates that Ni and Ti are not significantly affected by chloride ions. Figure 3(d) shows that the OCP value of the SS304 electrode decreased to -0.47 V vs. SCE,

and a distinguishable mass change in the Cl⁻-containing groundwater solution was observed as the measurement time increased. Compared with the absence of Cl⁻, the mass continued to accumulate, the mass change increased, and ultimately, the mass change was approximately 2.13 ng/cm².

Figure 5 shows the surface morphologies and EDS analysis of Cu before and after corrosion in the oxidic KURT groundwater solution with and without the addition of chloride ions. Cu surface corroded in the oxidic KURT groundwater solution was almost completely covered by copper oxide particles (Figure 5(b)). In contrast, in the Cl⁻-added groundwater solution, the Cu surface was nonuniformly covered with corrosion products, and some of the bases were observed as they were. The mass increase of Cu in the Cl⁻-added oxidic groundwater (Figure 3(a)) was confirmed to be smaller than in the condition without Cl⁻ because the presence of Cu₂O on the Cu surface caused a mass increase in this EQCM experiment (Figure 2(a)). The formation of corrosion products with dissolution reaction in the chloride solution was verified by surface observations. From the EDS analysis, only Cu and O were analyzed at the surface of Cu immersed in oxidic groundwater regardless of the addition of NaCl. It was thought that the

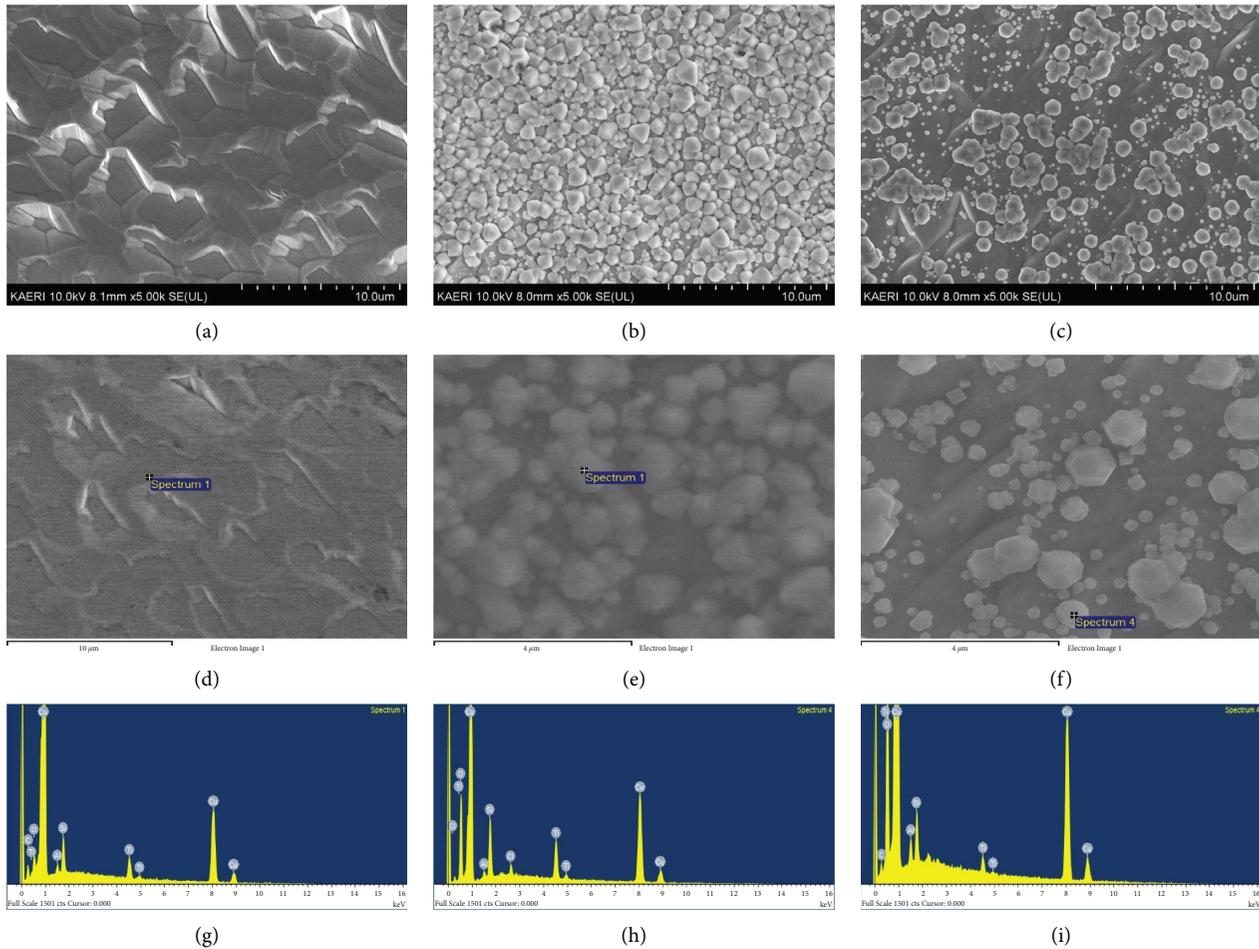


FIGURE 5: SEM/EDS analysis of (a), (d), (g) bare Cu, (b), (e), (h) Cu immersed in oxidizing KURT groundwater, and (c), (f), (i) Cu immersed in 0.1 M NaCl^- added oxidizing KURT groundwater.

CuCl_2^- hardly remains on the surface because it is a dissolved species.

4. Conclusions

In this study, the initial corrosion mass changes of the base canister materials were investigated using the EQCM method to estimate corrosion thickness. In the oxidizing KURT groundwater solution, Cu exhibited a relatively large mass change compared to the other materials (Ni, Ti, and SS304), and the maximum corrosion thickness of Cu was estimated to be approximately $0.1 \mu\text{m}/\text{yr}$ based on the initial measurement of mass change. In the groundwater solution with chlorides, the SS304 exhibited a slight increase in mass change, unlike the Ni and Ti. When Cu was immersed in the Cl^- -added groundwater solution, a lower mass change was observed compared in the absence of Cl^- , which was due to the dissolution reaction ($\text{Cu} \rightarrow \text{CuCl}_2^-$) involved in the corrosion mechanism ($\text{Cu} \rightarrow \text{Cu}_2\text{O}$) and was visually confirmed by SEM analysis. This study showed that the corrosion thickness using the EQCM method can be performed relatively quickly and easily, but the accurate calculation of the

corrosion thickness using the EQCM method has limitations in an environment where both deposition and dissolution of corrosion products occur.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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