

Effect of pH on External Surface Corrosion of Stainless Steel Pipes for Hot Water Supply Systems

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Abstract

This study investigates the effect of pH on the occurrence of external corrosion in stainless steel pipes used for hot-water supply systems. Leaching tests of coating materials revealed that the solution pH decreased to approximately 2.0 within four months, indicating significant acidification due to released components. Corrosion behavior was evaluated using corrosion potential measurements, surface observations, and anodic polarization measurements. The polarization potential increased with decreasing pH for both plate and pipe specimens. Scanning electron microscope (SEM) observations showed no significant surface changes for plate specimens before and after testing, whereas pipe specimens exhibited pronounced grain boundary development, particularly under higher pH conditions. Anodic polarization measurements demonstrated that plate specimens maintained stable passive behavior regardless of pH. By contrast, pipe specimens exhibited stable passivity at pH 1.5, while fluctuations in passive current density were observed at pH 2.0 and 3.0, suggesting instability of the passive film. These findings indicate that corrosion behavior is strongly dependent on pH, with pipe specimens being more susceptible than plate specimens. The enhanced susceptibility of the pipe specimens is attributed to tensile stress introduced during the forming process, which promotes grain boundary widening and facilitates localized corrosion. Overall, the results highlight the critical role of solution pH in determining the corrosion resistance of stainless-steel piping systems.

Keywords

Stainless Steel, Corrosion, Chloride, Hot Water Supply System

1. Introduction

For hot-water supply systems in building services, stainless-steel pipes are commonly supported using resin-coated dip-type support fittings in which polyvinyl chloride (PVC) is frequently used as a coating material. Corrosion has been reported in stainless steel pipes in contact with these dip-coated supporting fittings, particularly in high-temperature regions exceeding 60°C, whose conditions are adopted for Legionella control, and in environments with high ambient relative humidity [1]-[3]. This corrosion is considered to be localized corrosion caused by the leaching of components, such as hydrogen chloride, from the coating resin of the dip-coated support fittings [4] and [5]. Furthermore, it is believed that stress corrosion cracking (SCC) subsequently occurs, is initiated at these corroded sites, and is promoted by residual stress in the pipes.

We investigated corrosion on the external surface of stainless-steel pipes influenced by leaching components from dip-coated support fittings, and the occurrence of corrosion acting as initiation sites of cracking when coating resins with different thermal resistance properties were used [6]-[9]. The corrosion of stainless-steel pipes was promoted by chloride ions leached from the coating resin of the support fittings. Additionally, calcium and zinc species released from the resin reduced the corrosion resistance of stainless-steel pipes [10] and [11].

In this study, we investigated the effect of pH on the occurrence of external surface corrosion in stainless-steel pipes, which act as initiation sites for SCC.

2. Method

2.1. Material

The pH measurements were conducted every five days using a pH combination electrode (Thermo Scientific, Orion 8172BNWP). Two types of specimens were used in this study: JIS G 4305 (2021) SUS304 TPD-L stainless steel pipes (100 mm in length, 15.88 mm in width, and 0.8 mm in thickness; hereafter referred to as “pipe specimens”) and JIS G 3448 SUS304 stainless steel plates (100 mm in length, 15 mm in width, and 0.5 mm in thickness; hereafter referred to as “plate specimens”). Prior to testing, all the specimens were degreased with acetone and thoroughly rinsed with de-ionized water.

2.2. Test Solution

The test solutions were prepared by adjusting the pH to 1.5, 2.0, and 3.0 using hydrochloric acid. Sodium chloride was then added to achieve a chloride ion concentration of 1800 ppm, corresponding to that of the solution at pH 1.5.

2.3. Measurement of pH Changes Induced by Leaching of Components from the Coating Resin of Dip-Coated Support Fittings

The coating resin of dip-coated support fittings with a heat resistance temperature of 60°C was cut into pieces of approximately 5 mm × 5 mm × 0.8 mm in size. The surfaces of the cut resin samples were cleaned with 2-propanol before testing. A total of 12 g of resin was placed in a 50 mL centrifuge tube (Labcon North America, polypropylene, metal-free type). Subsequently, 10 mL of deionized water was added to the tube, which was then sealed and kept at 80°C under static conditions. The pH of the solution was monitored over a period of four months. The chloride, calcium, and zinc concentrations in the test solutions were monitored monthly using an inductively coupled plasma optical emission spectrometer (ICP-OES, Horiba, ULTIMA2). In this experiment, sequential sampling approach was adopted to monitor temporal changes in both the solution chemistry and specimen condition.

Specifically, four independent test systems (containers) were initiated simultaneously under identical environmental conditions.

After 1 month, measurements were performed for all four test systems, and the mean value was calculated from $n = 4$ independent samples. After 2 months, one test system had been terminated for sampling; therefore, measurements were obtained from the remaining three systems, and the mean value was calculated from $n = 3$. After 3 months, measurements were obtained from the remaining two systems ($n = 2$). After 4 months, the final remaining system was measured, resulting in $n = 1$.

Thus, during the early and intermediate stages of the immersion test (1 - 3 months), data reproducibility was ensured by calculating mean values from multiple independent test systems. This experimental design enabled time-resolved monitoring while minimizing disturbance to the remaining specimens and test solutions.

2.4. Corrosion Potential Measurement

A schematic of the test apparatus is illustrated in **Figure 1**. A 50 mL centrifuge tube was used as the test vessel. The test solution was added to a final volume of 25 mL and stirred at 300 rpm at room temperature instead of 60°C because of limitations associated with the experimental setup. Furthermore, this test was conducted under open-air conditions to evaluate the changes in the corrosion potential of a stainless-steel pipe or plate in the test environment. For the stainless-steel pipe specimens, the pipe ends were sealed with a silicone stopper to prevent ingress of the test solution, and measurements were performed on the external surface of the pipe. The immersion period was set to 14 days, and the corrosion potential was measured over time. The corrosion potentials were measured using a digital multimeter (Keysight: 34070 A). A saturated KCl Ag/AgCl (SSE) reference electrode was used in this study. The test area measured 3 cm². The measurements were

performed in triplicates. After testing, the surfaces of the specimens were examined using a digital microscope (KEYENCE: VHX-5000) and an SEM (JEOL: JSM-IT810).

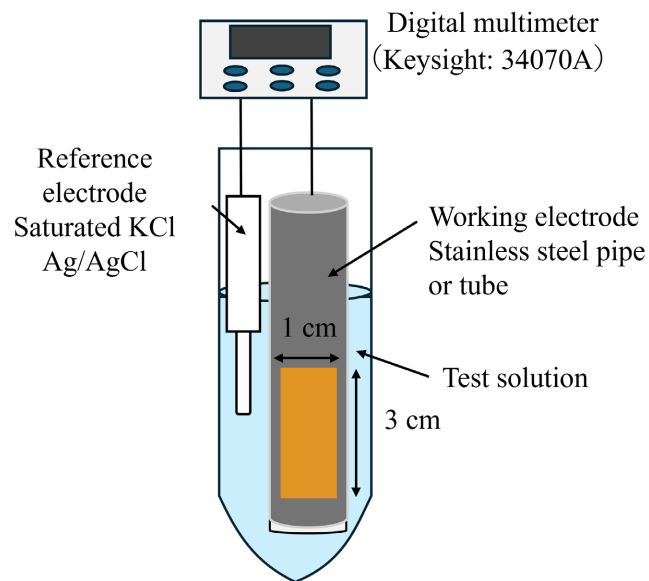


Figure 1. Schematic of corrosion potential measurement apparatus.

2.5. Anodic Polarization Curve Measurement

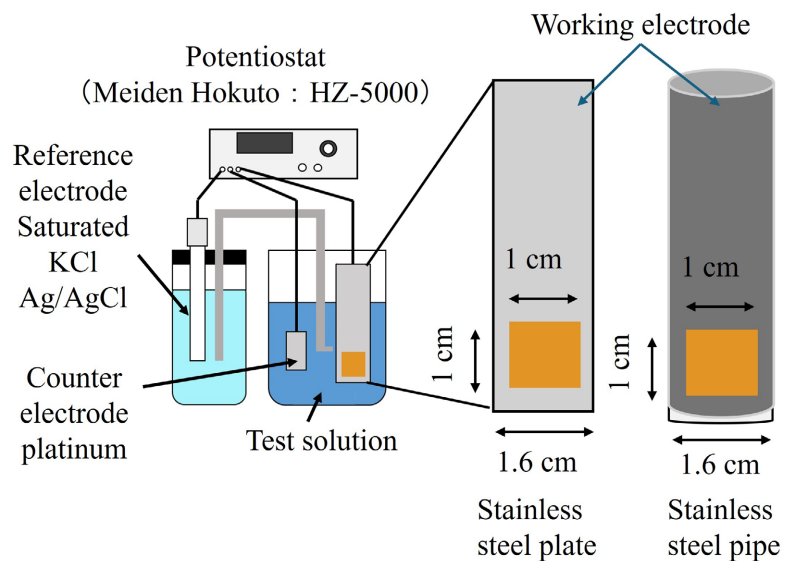


Figure 2. Schematic of anodic polarization curve measurement apparatus.

A schematic of the test apparatus is shown in **Figure 2**. A 500 mL beaker was used as the test vessel. The test solutions were prepared in a total volume of 500 mL. All measurements were conducted under open-air conditions and at room temperature because the experimental apparatus was not equipped for measurements at 60°C. Polarization curves were obtained using a potentiostat (Meiden

Hokuto: HZ-5000) at a scan rate of 20 mV min^{-1} . A stainless-steel pipe or plate served as the working electrode, a saturated KCl Ag/AgCl electrode (SSE) was used as the reference electrode, and a Pt electrode was employed as the counter electrode. For the stainless-steel pipe specimens, the pipe ends were sealed with a silicone stopper to prevent ingress of the test solution, and measurements were performed on the external surface of the pipe. The area of the exposed electrode was fixed at 1 cm^2 . All measurements were performed in triplicates.

3. Results and Discussion

3.1. pH Changes Induced by Leaching of Components from the Coating Resin of Dip-Coated Support Fittings

Figure 3 shows the results of the ICP analysis. Concentrations of chloride, zinc, and calcium in the test solutions are shown from left to right. The concentrations of all components increased due to leaching during the first two months, after which they stabilized at approximately constant values.

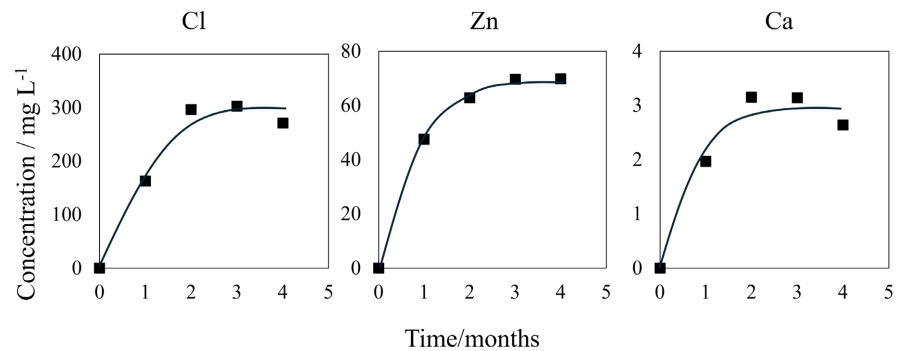


Figure 3. Temporal variation of chloride (left), zinc (center), and calcium (right) concentrations during leaching from the coating resin.

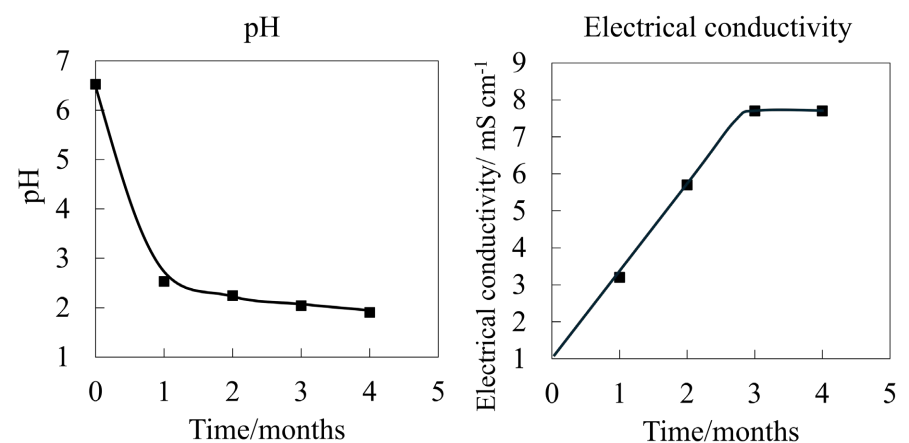


Figure 4. Temporal variation of pH (left) and electrical conductivity (right) during leaching from the coating resin.

Figure 4 shows the temporal variations in the pH and electrical conductivity

measured monthly. The pH variation is shown on the left, and the variation in electrical conductivity is shown on the right. The pH decreased rapidly immediately after the start of the test, reaching approximately 2.5 after one month. Thereafter, the pH gradually decreased further, reaching approximately 2.0 after four months. The electrical conductivity exhibited a similar trend, increasing continuously from the beginning of the tests. They reached a peak after three months, after which they remained nearly constant. These results indicate that the components leached from the coating resin caused the pH of the solution to decrease to approximately 2.0. Based on these findings, the pH values for the corrosion potential and anodic polarization curve measurements were determined.

3.2. Corrosion Potential Results

Figure 5 shows the results of the corrosion potential measurements over time on the horizontal and vertical axes. The left panel shows the plate specimens, and the right panel shows the pipe specimens. The red, blue, and black curves correspond to the pH values of 1.5, 2.0, and 3.0, respectively.

For all plate specimens, the polarization potential initially decreased immediately after the start of the test, followed by a gradual increase after approximately three days. The polarization potentials eventually stabilized at around 0.23 V (pH 1.5), 0.19 V (pH 2.0), and 0.15 V (pH 3.0).

In case of the pipe specimens, at pH 1.5 and 2.0, the potential increased sharply immediately after the start of the test and then stabilized at approximately 0.35 V and 0.31 V, respectively. By contrast, at pH 3.0, the polarization potential initially decreased and subsequently stabilized at approximately 0.27 V.

These results indicate that the polarization potential increased with decreasing pH. Additionally, the pipe specimens exhibited higher potentials than the plate specimens under all the tested conditions.

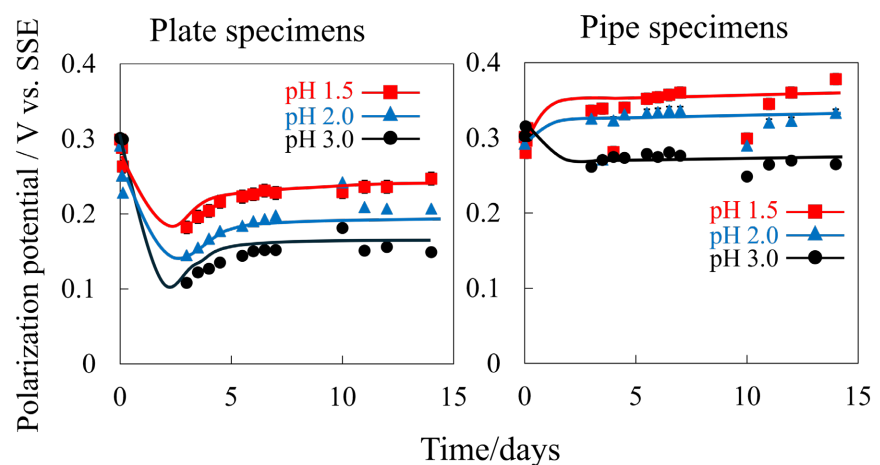


Figure 5. Temporal variation of polarization potential of plate specimens (left) and pipe specimens (right) at several pH conditions.

Figure 6 and **Figure 7** show digital microscope images of the specimen surfaces

before and after the corrosion potential measurements. For both the plate and pipe specimens, the surface conditions before and after the measurements at pH 1.5, 2.0, and 3.0, were compared. The results did not show evident corrosion products on any of the specimen surfaces under the experimental conditions.

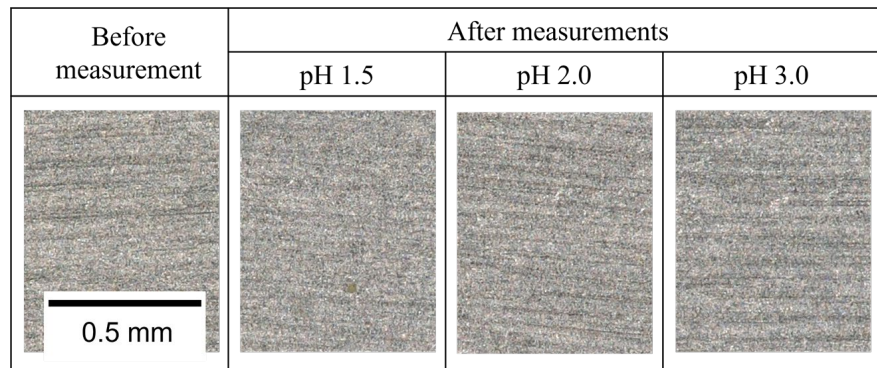


Figure 6. Digital microscope images of the plate specimen surface before and after measurements at pH 1.5, 2.0 and 3.0.

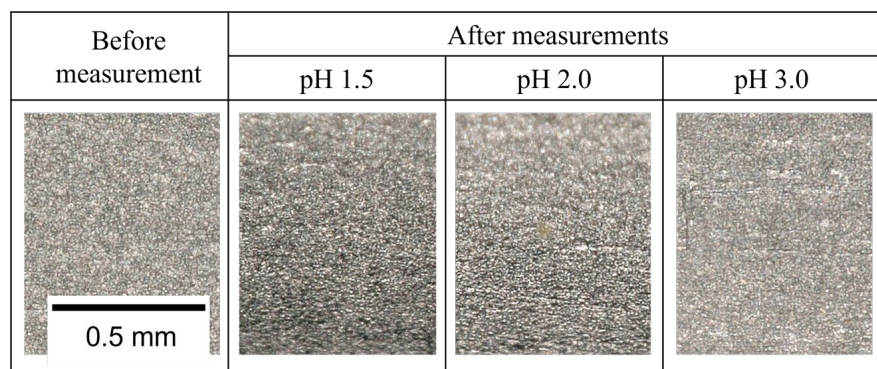


Figure 7. Digital microscope images of the pipe specimen surface before and after measurements at pH 1.5, 2.0 and 3.0.

Figure 8 and **Figure 9** show the SEM images of the stainless-steel surfaces before and after the measurements. The surface conditions of both plate and pipe specimens before and after measurements at pH 1.5 and pH 3.0 are presented.

For the plate specimens, no significant differences were observed between the surfaces before and after measurement.

By contrast, the pipe specimens exhibited significant changes in the grain boundaries after the measurements. Compared with the surface before measurement, the specimen measured at pH 1.5 showed a widening of the grain boundaries. A further increase in the shadowed regions was observed in the specimen measured at pH 3.0, suggesting that the grain boundary grooves became deeper.

Furthermore, a comparison of the plate and pipe specimens revealed that the grain boundaries were generally wider in the pipe specimens. This difference was attributed to the tensile stress introduced on the pipe surface during the forming process, as the pipe was manufactured by bending the plate material.

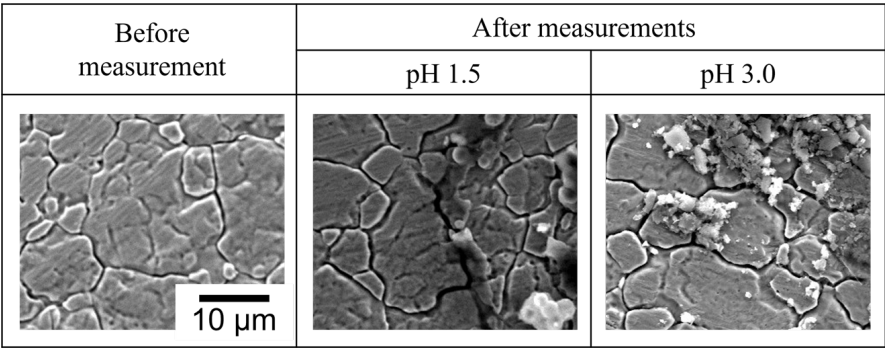


Figure 8. Scanning electron microscope images of the plate specimen surface before and after measurements at pH 1.5 and 3.0.

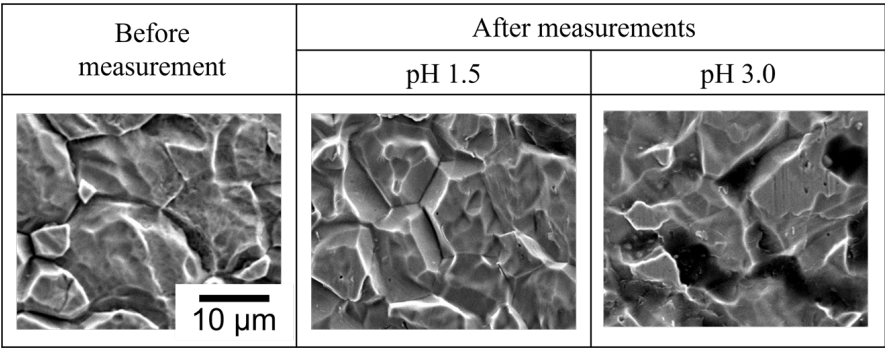


Figure 9. Scanning electron microscope images of the pipe specimen surface before and after measurements at pH 1.5 and 3.0.

3.3. Anodic Polarization Curves

Figure 10 shows the results of the anodic polarization measurements. For the plate specimens, a sharp increase in current density was observed at approximately -0.15 V for all pH conditions. The current density then remained nearly constant up to around 0.35 V, after which it increased again.

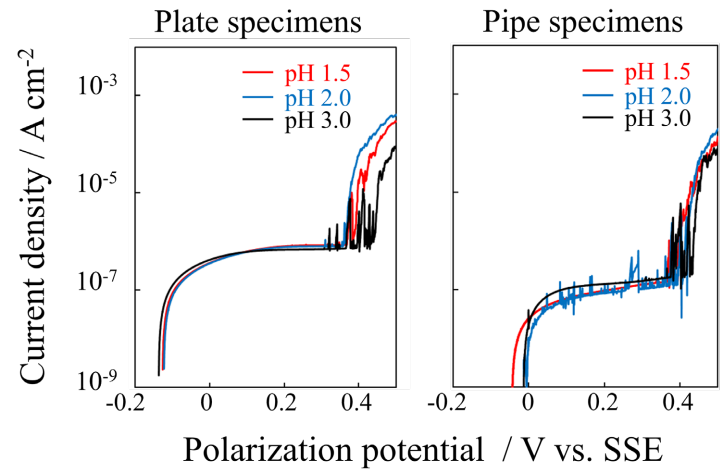


Figure 10. Anodic polarization curve of the plate specimens (left) and pipe specimens (right) at pH 1.5, 2.0 and 3.0.

For the pipe specimens, the current density increases sharply from approximately 0 V, followed by a region of nearly constant current density up to approximately 0.35 V, and then further increase again at higher potentials. The region where the current density remained nearly constant corresponded to the passive current density. At pH 2.0 and 3.0, fluctuations in the current density, characterized by spike-like variations, were observed within the passive region.

These results indicate that the onset potential for passivation was lower in the plate specimens than in the pipe specimens. Additionally, a gradual increase in the passive current density was observed under all measurement conditions.

3.4. Discussion

The effect of pH on the corrosion behavior of the pipe specimens was investigated. Stainless-steel pipes are generally fabricated using bending plate materials, followed by welding. As introduced by the SEM observations presented earlier, tensile stress was likely introduced to the outer surface of the pipe, resulting in a tendency for the grain boundaries to widen. This structural feature may facilitate the exposure of fresh metal surfaces at the grain boundaries.

In the solution at pH 1.5, the pre-existing oxide film on the pipe surface was likely removed. Consequently, a relatively uniform passive film could be formed on the stainless-steel surface. This interpretation is supported by the anodic polarization results, in which a wide potential range exhibiting a gradual increase in current density was observed under the pH 1.5 condition for the pipe specimens.

By contrast, in the solution at pH 3.0, the original oxide film remained partially intact. Consequently, the formation of a uniform passive film was difficult to achieve. Under such conditions, the residual oxide film can act as a cathodic site, whereas regions where the oxide film has been removed and fresh surfaces are exposed act as anodic sites, leading to localized electrochemical heterogeneity. This may promote localized corrosion in the anodic regions. Consistent with this interpretation, SEM observations showed that the grain boundary widening progressed more deeply at pH 3.0 condition than at pH 1.5 condition.

Based on these findings, the stability of the passive film and the corrosion morphology on the outer surface of stainless-steel pipes are strongly influenced by the pH value of the solution.

4. Conclusions

We investigated the effect of pH on the occurrence of external corrosion in stainless-steel pipes used in hot-water supply systems.

Leaching measurements of the coating material showed that the solution pH decreased to approximately 2.0 within four months after the start of the measurements.

According to corrosion potential measurements, the polarization potential increased with decreasing pH. The SEM observations revealed no significant surface changes before and after the measurement of the plate specimens. By contrast, the

pipe specimens exhibited a more pronounced grain boundary development, particularly under higher pH conditions.

Anodic polarization measurements indicated that the plate specimens exhibited passive current density regardless of the pH value. By contrast, the pipe specimens showed stable passive behavior at pH 1.5, whereas fluctuations in the passive current density were observed at pH 2.0 and 3.0.

Overall, pH-dependent corrosion behavior was confirmed for both the plate and pipe specimens, with a more pronounced effect observed in the pipe specimens.

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Conflicts of Interest

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

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