

Article

# Corrosion Behavior of Pipeline Carbon Steel under Different Iron Oxide Deposits in the District Heating System

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**Abstract:** The corrosion behavior of pipeline steel covered by iron oxides ( $\alpha$ -FeOOH;  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ) was investigated in simulated district heating water. In potentiodynamic polarization tests; the corrosion rate of pipeline steel is increased under the iron oxide but the increase rate is different due to the different chemical reactions of the covered iron oxides. Pitting corrosion was only observed on the  $\alpha$ -FeOOH-covered specimen; which is caused by the crevice corrosion under the  $\alpha$ -FeOOH. From Mott-Schottky and X-ray diffraction results; the surface reaction and oxide layer were dependent on the kind of iron oxides. The iron oxides deposit increases the failure risk of the pipeline and localized corrosion can be occurred under the  $\alpha$ -FeOOH-covered region of the pipeline. Thus, prevention methods for the iron oxide deposit in the district pipeline system such as filtering or periodic chemical cleaning are needed.

**Keywords:** corrosion; polarization; iron oxide; Mott-Schottky; carbon steel

## 1. Introduction

A district heating (DH) system provides heat for inhabitants of large cities in an economical manner. Heat from heat and power generating plants and large heat sources is cheaper than heat produced in individual, low-power boiler rooms [1]. There are many merits to DH systems, including increased energy efficiencies, reduced life cycle costs, and elevated control over environmental impacts [2,3]. Additionally, the high efficiencies of DH systems decrease the emission of combustion products into the atmosphere. Because of these advantages, many countries such as Denmark, Russia, Finland, and Canada are developing DH systems, and the market share is reported to be approximately 50% [4,5]. Additionally, a DH system was introduced to Korea in 1987 and applied to various fields.

A DH system becomes more useful with more satellite and planned cities near each megalopolis. A DH system has a long stagnation period due to the construction of numerous urban housing facilities and infrastructure. Additionally, maintenance and improvement work are ongoing. During this period, the pipeline in the distribution part of the DH system is exposed to low temperature ( $\sim 40^\circ\text{C}$ ) water with little or no flow. The long stagnation condition has problems associated with corrosion such as deposits from solid particles (sand, debris, and iron oxides), ion conductivity, ferrous ions, and dissolved oxygen [6–9]. The deposits on the internal surface of a pipeline especially cause serious localized corrosion (such as pitting corrosion and crevice corrosion), which is identified as under deposit corrosion (UDC) [10–12].

UDC is unlike other corrosion forms, as the conditions, such as pH and concentration of the aggressive species, under the deposit are different from the conditions in regions without deposits. As a result, there will be galvanic corrosion between the areas under the deposit and the areas without

deposit [13–17]. Because of these properties, UDC is a serious problem in pipeline systems due to the potential for unexpected failure from localized damage. In order to prevent pipeline failure from UDC, it is important to investigate the mechanism of UDC. Jeannin et al. determined that the corrosion process of carbon steel differed according to the type of deposited minerals (silica, kaolinite, chlorite, and montmorillonite) [11]. Zhang et al. identified galvanic corrosion between the covered mixed deposit on the carbon steel and bare carbon steel (uncovered mixed deposit) in a gas filled environment [17]. However, the deposit is composed of not only minerals (clay and sand) but also corrosion products (iron oxide and carbonate etc.); this is because the corrosion products float in fluid, combine with each other, and are deposited under stagnant conditions. Therefore, the corrosion process under different corrosion product deposits is an important study.

The corrosion products can inhibit further corrosion by shielding the metal from the environment. However, there are cases where corrosion products accelerate corrosion [18]. The corrosion process can be dependent on the oxide film because the oxide is directly formed in close connection with the crystal of the metal while the deposit is stacked on the metal [19]. In this work, the corrosion behavior of carbon steel under different iron oxides, such as  $\alpha$ -FeOOH (goethite),  $\text{Fe}_3\text{O}_4$  (magnetite), and  $\text{Fe}_2\text{O}_3$  (hematite) was evaluated by electrochemical measurements and surface characterization. These iron oxides are usually produced on the pipeline surface in the DH system. The formation of these oxides depends on the presence of the oxygen in the water. The  $\text{Fe}_3\text{O}_4$  is generally formed in the de-aerated district water but  $\alpha$ -FeOOH and  $\text{Fe}_2\text{O}_3$  are generated in the aeration condition. Also, the damaged surface, which is mesas formed by corrosion, has been observed under the iron oxide. Thus, in this study, the influence of each oxide on the corrosion behavior is investigated for clear understanding of the UDC by iron oxides in the district heating system. Furthermore, the corrosion mechanism under different iron oxides was investigated to prevent unexpected corrosion and failure in the DH system from UDC.

## 2. Materials and Methods

### 2.1. Materials and Solution Preparation

The material used in this work was a pipeline carbon steel which is the standard material in the American society of testing and materials (ASTM A135). Table 1 lists the steel composition. Specimens were machined into 1 cm<sup>2</sup> square shapes and sealed with epoxy resin. Before the deposition process, the specimens were abraded with silicon carbide paper starting from 100- to 600-grit size, and then rinsed with deionized water and cleaned with ethanol.

**Table 1.** Chemical composition of tested pipeline steel (wt %).

C	Si	Mn	P	S	Fe
0.25	0.35	0.50	0.040	0.040	Balance

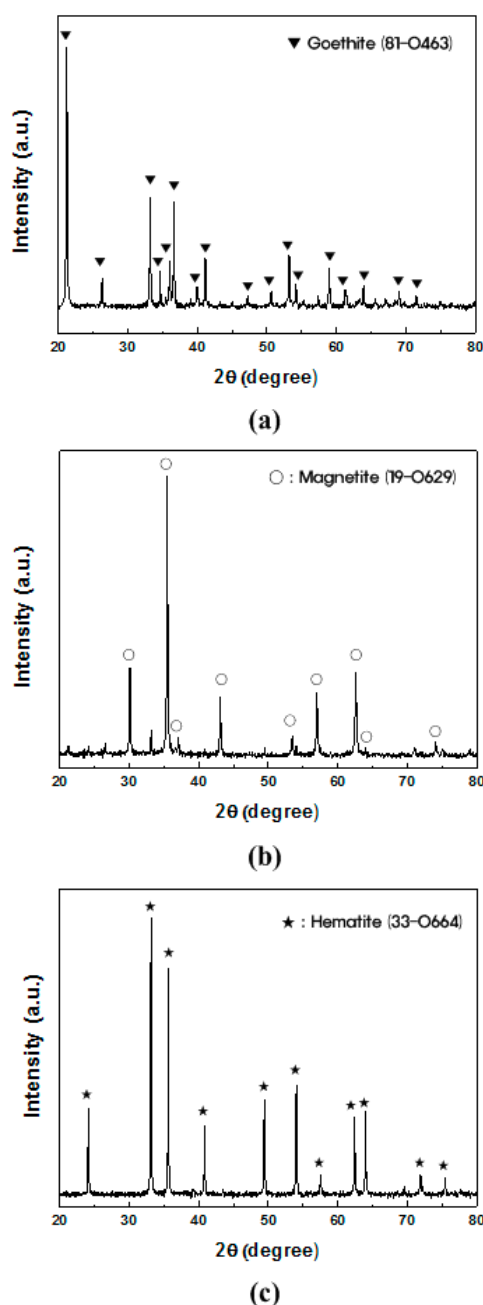
Table 2 lists the chemical composition of the simulated district heating water, which is based on actual district heating water over 10 years as measured in its stagnant condition. To adjust the chemical composition of the test solution, the pH was adjusted with a 0.1 M NaOH solution. Although the heating water was usually soft and pure, the detection of ferric ions ( $\text{Fe}^{3+}$ ) and chloride ions ( $\text{Cl}^-$ ) is attributed to the long stagnation condition [6]. Prior to testing, the solution was de-aerated by purging with  $\text{N}_2$  (99.999%) for 2 h because the DH system is blocked from the outside, i.e., it is a closed system so that the amount of dissolved oxygen is very low. The temperature is maintained at 40 °C using a constant-temperature water bath.

**Table 2.** Chemical composition of the simulated district heating water (mg/L).

pH	$\text{FeCl}_3$	$\text{NaNO}_2$	$\text{NaNO}_3$	$\text{NaCl}$
9.8	16.25	7.5	0.7	65.2

## 2.2. Deposition Process

The three iron oxides ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ) used in this study were purchased from SAMCHUN chemical corporation (Pyeongtaek-si, Korea). The powder X-ray diffraction analysis is shown in Figure 1 and the iron oxides were confirmed with the diffraction database. Because the powder-state iron oxides are difficult to deposit on the specimen, ethanol was mixed with the iron oxides. The specimen was covered with a rubber 'O' shaped ring (diameter: 3 cm, height: 3 mm) and then filled with iron oxide mixed with ethanol, which has the same thickness as the rubber ring, approximately 3 mm, to simulate the UDC environment. Before immersion in the test solution for the electrochemical tests, the deposit-covered specimen was dried in air for 30 minutes to vaporize the ethanol.



**Figure 1.** X-ray diffraction results of iron oxide powder used as deposit materials: (a)  $\alpha$ -FeOOH; (b)  $\text{Fe}_3\text{O}_4$ ; (c)  $\text{Fe}_2\text{O}_3$ .

### 2.3. Electrochemical Measurements

Electrochemical tests were conducted to evaluate the corrosion behavior and properties of the iron oxide deposits. A three-electrode electrochemical cell was constructed with the SPPS 38 carbon steel electrode, uncovered and covered with iron oxide deposits as the working electrode (WE), two pure graphite rods as the counter electrodes (CE), and a saturated calomel electrode (SCE) as the reference electrode (RE). In potentiodynamic polarization tests, the specimens were fully covered with iron oxide deposits (1 cm<sup>2</sup>), and a stainless steel rod covered with glass for preventing contact with the solution was used for the electric connection with the WE. The dynamic voltage (IR) drop was automatically compensated in the potentiostat because the simulated district heating water has low conductivity (347  $\mu\text{S}/\text{cm}$ ). The schematic of the three-electrode electrochemical cell used in this experiment is shown in Figure 2. Before potentiodynamic polarization tests, the working electrode was immersed in the test solution for 6 h until a steady state was reached, and the open-circuit potential (OCP) was obtained. Potentiodynamic polarization curves were measured by scanning the potential from  $-250\text{ mV}$  versus OCP to  $400\text{ mV}_{\text{SCE}}$  at a sweep rate of  $0.166\text{ mV}/\text{s}$ . The electrochemical impedance spectroscopy (EIS) was performed at the OCP with amplitude of  $10\text{ mV}$  at frequencies ranging from  $10,000$  to  $0.01\text{ Hz}$ .

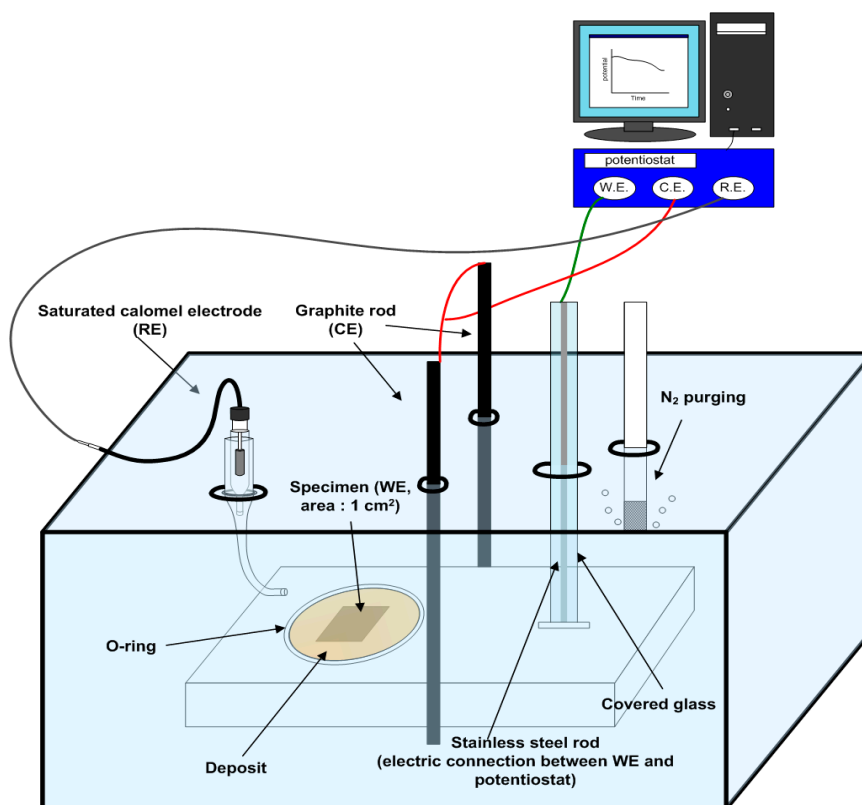


Figure 2. Schematic of three-electrode electrochemical cell used in this study.

To accelerate the corrosion process, potentiostatic tests were performed at an applied potential of  $-0.65\text{ mV}_{\text{SCE}}$ , slightly greater than the corrosion potential ( $E_{\text{corr}}$ ) of each specimen for 20 h. The fully deposit-covered specimens were evaluated to observe the corrosion process under the deposits. Additionally, to investigate the difference in corrosion behavior for covered and uncovered deposits, the deposit was designed to cover only half of the specimen. After potentiostatic tests, the iron oxide deposits and corrosion products on the carbon steel surface were removed and cleaned for 10 min in the cleaning solution containing 500 mL HCl (37% concentration), 3.5 g hexamethylenetetramine ( $\text{C}_6\text{H}_{12}\text{N}_4$ ), and distilled water to produce 1000 mL. The specimens were then rinsed in distilled water and dried with nitrogen gas.

To analyze the surface properties of uncovered and covered deposit specimens, Mott-Schottky measurements were performed with a PARSTAT 2263 (Princeton Applied Research, Oak Ridge, TN, USA). Before the Mott-Schottky measurements, each specimen was immersed in the test solution for 340 h. The Mott-Schottky plots were obtained by sweeping in the positive direction at a frequency of 1 kHz with an amplitude signal of 10 mV, a potential range of  $-0.7 V_{SCE}$  to  $0.1 V_{SCE}$ , and a potential step of 25 mV. All electrochemical tests were performed three times to ensure reproducibility.

#### 2.4. Surface Characterization

After the potentiostatic tests, the morphology (surface and cross-section) of the corroded specimens was observed using optical microscopy (OM). The specimen after potentiostatic test was cut by micro cutting machine, and then produced epoxy mounting. To clear observation of the damaged surface, the surface was cleaned by cleaning solution containing 500 mL HCl, 3.5 g hexamethylenetetramine ( $C_6H_{12}N_4$ ) and distilled water to make 1000 mL for 10 min. Additionally, to investigate the surface condition under the oxide deposits, the specimens were analyzed by X-ray diffraction (XRD, D8 Advanced, Bruker, Billerica, MA, USA) using Cu-K $\alpha$  radiation operated at 18 kW with a scanning speed of  $2^\circ/\text{min}$  after 340 h of immersion. Before the XRD analysis, the deposit on the specimens was removed by distilled water and dried with  $N_2$  gas to prevent additional oxidation. The XRD patterns were analyzed by the diffraction database.

### 3. Results

#### 3.1. Potentiodynamic Polarization Tests

Figure 3 shows the polarization curves in the form of  $I = f(E)$  and with the extrapolated Tafel slopes of a bare specimen and different iron oxides ( $\alpha\text{-FeOOH}$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ )-covered specimens after a 6 h immersion in the test solution at  $40^\circ\text{C}$ . All of the polarization curves showed active corrosion behavior. In the  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-FeOOH}$  cases, the current densities of cathodic and anodic polarization curves were increased compared to the bare specimen, and the corrosion potentials were negatively shifted. This indicates that the  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-FeOOH}$  deposits increased the cathodic and anodic reactions on the surface. Alternatively, in the case of  $\text{Fe}_2\text{O}_3$ , only the cathodic current density increased and the corrosion potential was not shifted.

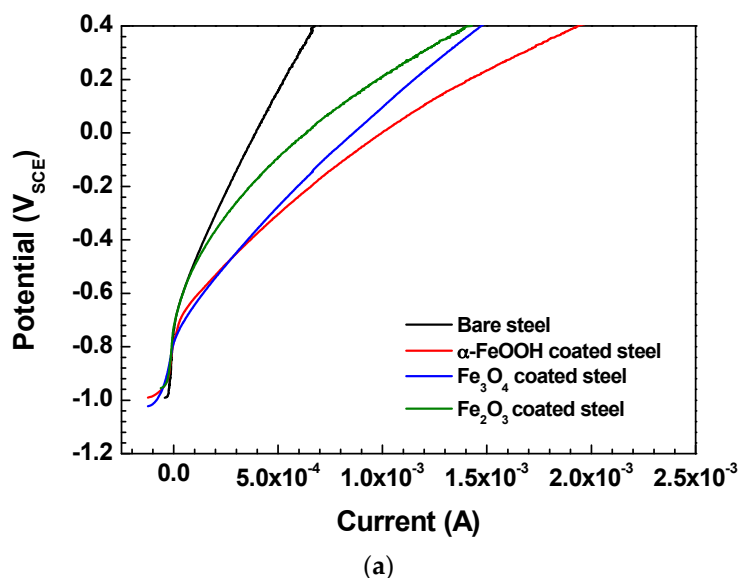
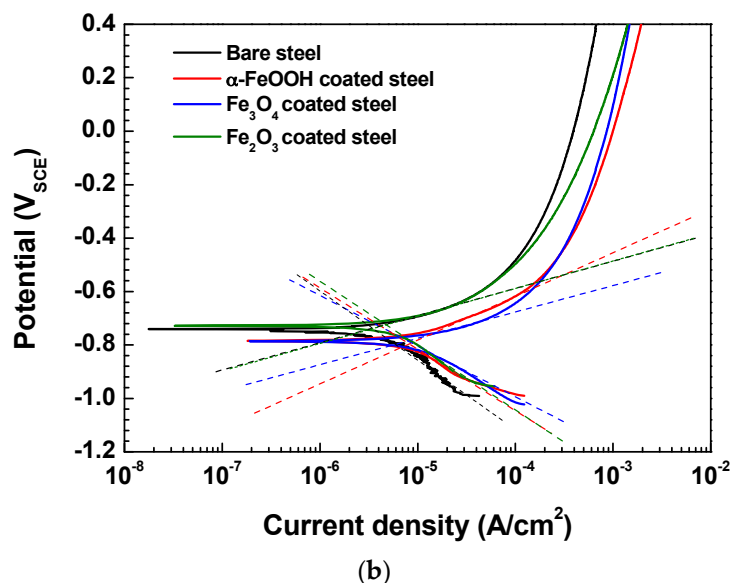


Figure 3. Cont.



**Figure 3.** (a) Polarization curves in the form of  $I = f(E)$  and (b) polarization curves with Tafel slopes of the specimens covered with different iron oxides ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ) and uncovered after 6 h of immersion in the simulated district heating water at 40 °C.

The corresponding kinetic parameters in the polarization curves, such as the corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ), polarization resistance ( $R_p$ ), and anodic and cathodic Tafel slopes ( $\beta_a$ ,  $\beta_c$ ), are listed in Table 3. The  $i_{\text{corr}}$  and  $E_{\text{corr}}$  values were different for the iron oxide-covered specimens, and  $i_{\text{corr}}$  was related to the corrosion rate according to Faraday's law:

$$\text{Corrosionrate (mm/yr)} = \frac{3.16 \times 10^8 \times i_{\text{corr}} \times M}{z \times F \times \rho} \quad (1)$$

where  $M$  is the molar mass of the metal (g/mol),  $z$  is the number of electrons transferred per metal atom,  $F$  is the Faraday's constant, and  $\rho$  is the density of the metal (g/cm<sup>3</sup>). Thus,  $i_{\text{corr}}$  was increased in all oxide-covered specimens, indicating the deposit state of the iron oxides increased the corrosion of the steel substrate. Also, the polarization resistance was calculated by the following equation [20]:

$$R_p = \frac{\beta_a \times \beta_c}{2.3 \times i_{\text{corr}} \times (\beta_a + \beta_c)} \quad (2)$$

**Table 3.** Electrochemical parameters of the polarization curves of the bare specimen and iron oxides ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ )-covered specimens in the simulated district heating water at 40 °C.

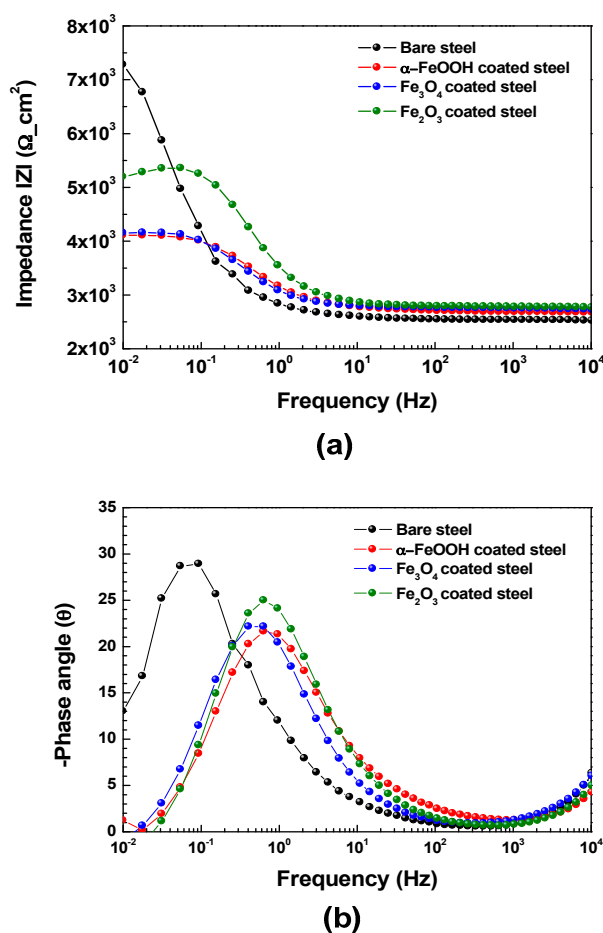
Specimen	$\beta_a$ (mV/Decade)	$\beta_c$ (mV/Decade)	$E_{\text{corr}}$ (mV <sub>SCE</sub> )	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_p$ ( $\Omega \cdot \text{cm}^2$ )	Corrosion Rate (mm/Year)
Bare	102 ± 3	−246 ± 12	−741 ± 5	3.876 ± 0.05	8088	0.045
$\alpha$ -FeOOH	122 ± 6	−215 ± 5	−775 ± 6	9.123 ± 0.03	3323	0.106
$\text{Fe}_3\text{O}_4$	99 ± 12	−202 ± 9	−786 ± 21	8.692 ± 0.1	3709	0.101
$\text{Fe}_2\text{O}_3$	105 ± 5	−265 ± 15	−735 ± 11	5.311 ± 0.09	6156	0.061

The  $i_{\text{corr}}$  and  $R_p$  are related to the corrosion resistance of the materials, and these were increased or decreased by the covered iron oxide, respectively. Consequently, it means that the corrosion reactions were affected by  $\text{Fe}_3\text{O}_4$  and  $\alpha$ -FeOOH deposits and the three iron oxide deposits ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ) affected the cathodic reactions [21–23]. The  $\beta_a$  and  $\beta_c$  were changed according to the kind

of covered iron oxides. In the case of  $\alpha$ -FeOOH, the  $\beta_a$  was increased while the  $\beta_c$  was decreased in comparison with the bare specimen. It indicates that the  $\alpha$ -FeOOH influenced the anodic and cathodic reactions on the steel surface. On the other hand, the  $\beta_a$  was not significantly changed and  $\beta_c$  was changed in the cases of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , meaning that the  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , mainly had an effect on the cathodic reaction than anodic reaction.

### 3.2. Electrochemical Impedance Spectroscopy (EIS)

Figure 4 presents the EIS results in the form of the Bode phase and impedance plots for specimens covered with different iron oxides ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}_2\text{O}_3$ ) and uncovered after 6 h immersion in the simulated district heating water at 40 °C. The Bode plot produces a more detailed explanation of the electrochemical frequency-dependent property than the Nyquist plot [24]. The high frequency spectra indicated local surface defect, whereas the low frequency spectra indicated the process within the film and at the metal/film interface [25]. The absolute impedance value of the specimen covered by iron oxides is less than that of the bare specimen. The absolute impedance value decreases in the following order:  $\alpha$ -FeOOH >  $\text{Fe}_3\text{O}_4$  >  $\text{Fe}_2\text{O}_3$  > bare, which is the same trend as the corrosion current density in the potentiodynamic polarization tests. Additionally, the phase angle maximum decreased in the same order:  $\alpha$ -FeOOH >  $\text{Fe}_3\text{O}_4$  >  $\text{Fe}_2\text{O}_3$  > bare, and the shoulder on the phase angle curve of the bare pipe shifted to a lower frequency. The results were due to inhomogeneity or porosity in the surface film [26], indicating that the surface film deteriorates after being covered with iron oxides, especially in the case of the  $\alpha$ -FeOOH-covered specimen.



**Figure 4.** Bode plots of (a) impedance and (b) phase angle vs. frequency for specimens covered with different iron oxides ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ) and uncovered after 6 h of immersion in the simulated district heating water at 40 °C.



Figure 5 shows the equivalent circuit to fit the results of the EIS tests. In this equivalent circuit, the  $R_s$  is the solution resistance, CPE1 (CPE: constant phase element) is the dielectric property of the film and water absorbed on the film,  $R_{film}$  is the electrical resistance resulting from the ionic path of the pores in the film, CPE2 is the capacitance generated by metal dissolution and the electric double layer, and  $R_{ct}$  is the resistance associated with metal dissolution. The CPE is applied in this equivalent circuit instead of a perfect capacitor to produce a more accurate fit and interpretation [27,28]. The impedance of CPE is expressed as:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (3)$$

where  $Y_0$  is the magnitude of CPE,  $j$  is the imaginary unit ( $j^2 = -1$ ),  $\alpha$  is the phase angle of CPE, and  $n = \alpha/(\pi/2)$ . The parameter  $n$  typically lies between 0.50 and 1.0, and CPE expresses an ideal capacitor at  $n = 1$ . The parameter  $n$  is often referred to as the frequency dispersion due to surface states like inhomogeneity [29,30] and roughness [31].

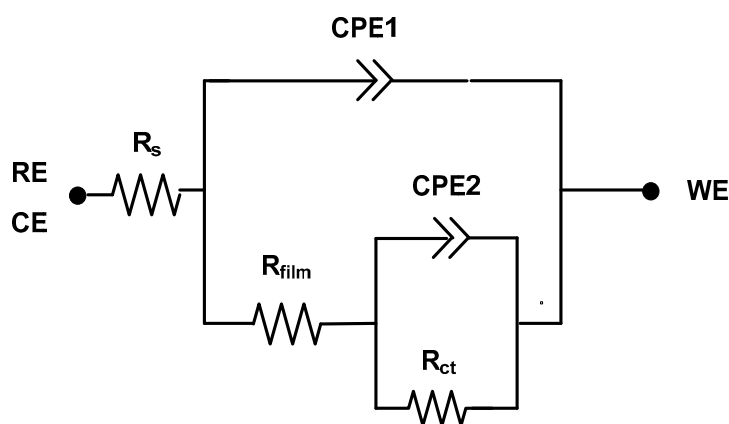


Figure 5. Equivalent circuit to fit the electrochemical impedance spectroscopy (EIS) data.

Some parameters extracted from the EIS data are listed in Table 4. To calculate the double layer capacitance ( $C_{dl}$ ), the following equation was used:

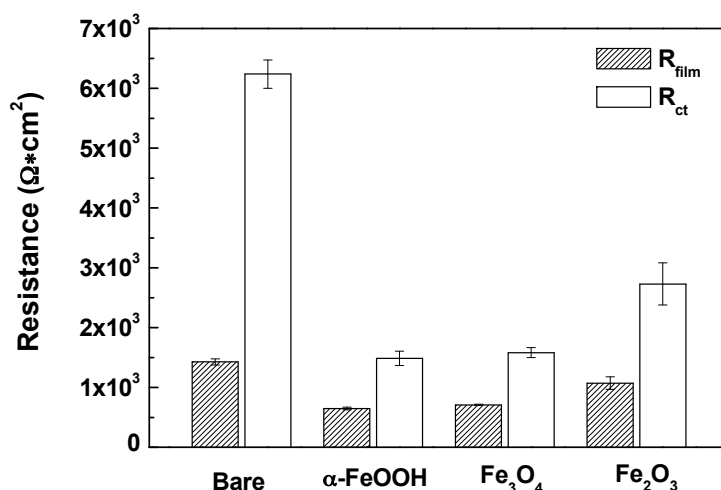
$$C_{dl} = Y_0(2\pi f_{max})^{n-1} \quad (4)$$

In Equation (4),  $C_{dl}$  is the double layer capacitance and  $f_{max}$  is the frequency at which the imaginary component of the impedance reaches the maximum value. The ZSimpwin program (v3.2, Princeton Applied Research, Oak Ridge, TN, USA) was used to fit the EIS data, which is presented in Table 4. Figure 6 shows the  $R_{film}$  and  $R_{ct}$  of the specimens.  $R_{film}$  and  $R_{ct}$  decreased for the iron oxide-covered specimens in the following order:  $\alpha$ -FeOOH >  $Fe_3O_4$  >  $Fe_2O_3$  > bare. The covered iron oxides had the lower corrosion resistance than bare specimen. Additionally, the  $n$  value in the case of  $\alpha$ -FeOOH was the lowest, indicating an unstable surface film due to pores and defects on the surface.

Table 4. Impedance parameters of bare specimen and iron oxides ( $\alpha$ -FeOOH,  $Fe_3O_4$  and  $Fe_2O_3$ )-covered specimens in the simulated district heating water at 40 °C.

Specimen	$R_s$ ( $\Omega \cdot cm^2$ )	$R_{film}$ ( $\Omega \cdot cm^2$ )	$n$	$C_{film}$ ( $\mu F \cdot s^{n-1} / cm^2$ )	$R_{ct}$ ( $\Omega \cdot cm^2$ )	$n$	$C_{dl}$ ( $\mu F \cdot s^{n-1} / cm^2$ )
Bare	2653 ± 158	1427 ± 52	0.98 ± 0.01	53 ± 5	6237 ± 236	0.88 ± 0.01	582.2 ± 22
$\alpha$ -FeOOH	2712 ± 72	648 ± 23	0.72 ± 0.05	19 ± 3	1485 ± 118	0.83 ± 0.01	621.8 ± 8
$Fe_3O_4$	2759 ± 123	709 ± 11	0.78 ± 0.02	220 ± 6	1582 ± 85	0.83 ± 0.02	889.6 ± 56
$Fe_2O_3$	2788 ± 201	1071 ± 105	0.84 ± 0.01	151 ± 11	2730 ± 351	0.86 ± 0.02	782.5 ± 78





**Figure 6.**  $R_{film}$  and  $R_{ct}$  of the specimens covered with different iron oxides ( $\alpha$ -FeOOH, Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>) and uncovered after 6 h immersion in the simulated district heating water at 40 °C.

### 3.3. Potentiostatic Tests

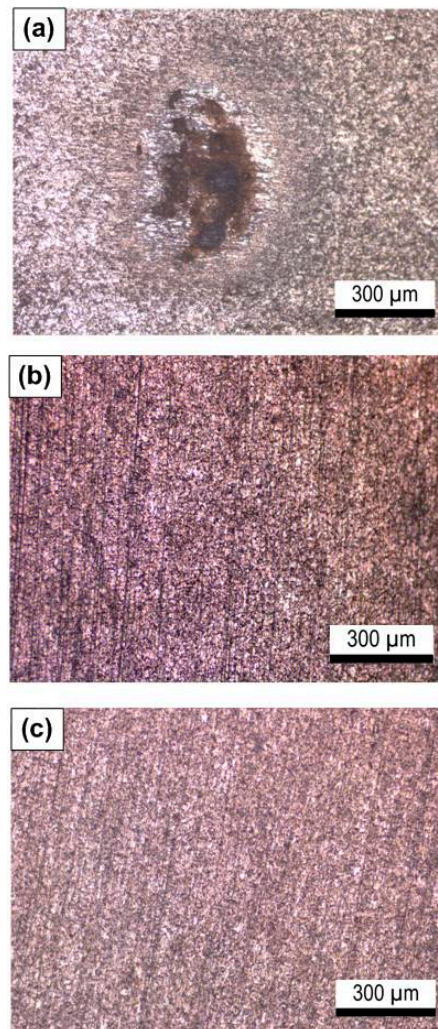
Potentiostatic tests were conducted to investigate the corrosion behavior of the iron oxide-covered specimens. Additionally, to identify galvanic corrosion between covered and uncovered specimens, half of the specimen was covered with deposit. Figure 7 shows the specimen covered iron oxides after potentiostatic tests under  $-650 \text{ mV}_{SCE}$  for 20 h in the test solution at 40 °C. As shown in Figure 7a, significant pitting was observed on the  $\alpha$ -FeOOH-covered specimen and the size of the pits ranged from 150 to 300  $\mu\text{m}$ . However, as shown in Figure 7b,c, pitting was not observed on the Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>-covered specimens. Figure 8 shows the cross section of the  $\alpha$ -FeOOH-covered specimen after the potentiostatic test. As shown in Figure 8, pitting was observed on the  $\alpha$ -FeOOH-covered specimen and the depth of the pitting was approximately 170  $\mu\text{m}$ . This indicates that the corrosion behavior was different in the  $\alpha$ -FeOOH, Fe<sub>3</sub>O<sub>4</sub>, and Fe<sub>2</sub>O<sub>3</sub> cases.

Figure 9 shows the boundary of the specimens with covered (left side) and uncovered (right side) deposits after potentiostatic tests under  $-650 \text{ mV}_{SCE}$  for 20 h at 40 °C. In Figure 9a,b, the corrosion was accelerated at the boundary of the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>-covered specimens, which was caused by more negative corrosion potential than the bare specimen, i.e., a galvanic effect. Alternatively, the boundary between the Fe<sub>2</sub>O<sub>3</sub>-covered and uncovered did not show accelerating corrosion behavior as shown in Figure 9c, which could be due to the absence of the corrosion potential difference [17,32–34]. In the cross-sectional view of the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>-covered specimens in Figure 10, obvious corrosion acceleration was observed. These results indicate that the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub> deposits can cause galvanic corrosion under stagnant conditions, while the Fe<sub>2</sub>O<sub>3</sub> deposit did not cause a galvanic effect.

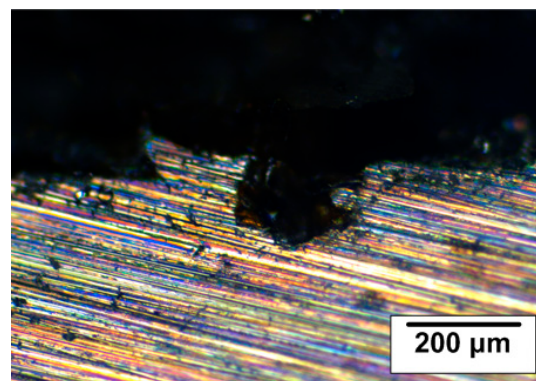
### 3.4. Surface Characterization

Figure 11 shows the XRD results for the iron oxide-covered and uncovered specimens in the test solution for 340 h at 40 °C. In the Fe<sub>3</sub>O<sub>4</sub>-covered specimen, Fe and a few Fe<sub>3</sub>O<sub>4</sub> peaks were observed. Similarly, in the case of the Fe<sub>2</sub>O<sub>3</sub>-covered specimen, Fe, Fe<sub>2</sub>O<sub>3</sub>, and a few Fe<sub>3</sub>O<sub>4</sub> peaks were observed. The Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> deposits did not influence the formation of a thick surface film on the steel substrate. Even though the Fe<sub>3</sub>O<sub>4</sub> peaks were observed in the Fe<sub>2</sub>O<sub>3</sub> case, the Fe<sub>3</sub>O<sub>4</sub> peaks overlapped with the Fe<sub>2</sub>O<sub>3</sub>-peaks and the intensity was insignificant. Thus, Fe<sub>3</sub>O<sub>4</sub> was formed under the Fe<sub>2</sub>O<sub>3</sub>-covered state but the formation and reaction activities were too small. However, in the cases of  $\alpha$ -FeOOH-covered and bare specimens, Fe<sub>3</sub>O<sub>4</sub> diffraction peaks were observed. These results indicate that Fe<sub>3</sub>O<sub>4</sub> is the main surface film on the bare state in the test environment, and  $\alpha$ -FeOOH

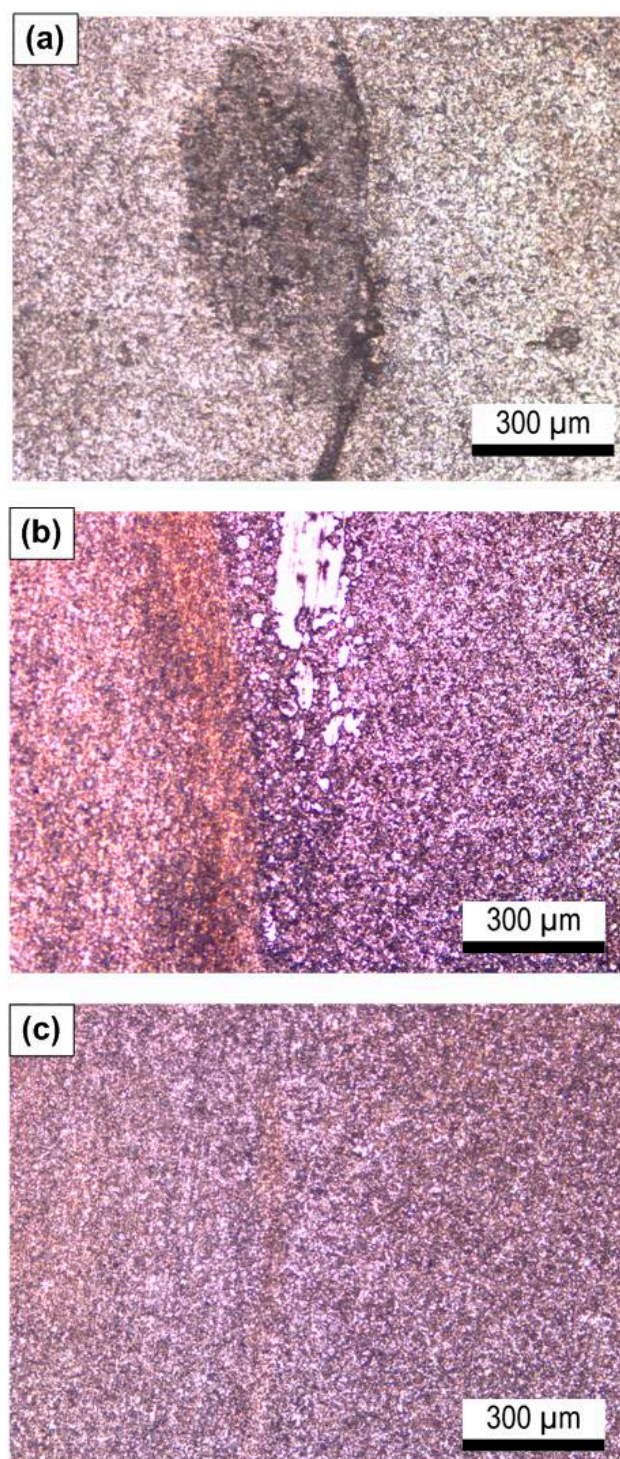
influences the formation of the  $\text{Fe}_3\text{O}_4$  surface film on the steel substrate compared to the  $\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  cases.



**Figure 7.** Optical microscope images of the specimens covered with (a)  $\alpha\text{-FeOOH}$ , (b)  $\text{Fe}_3\text{O}_4$  and (c)  $\text{Fe}_2\text{O}_3$  iron oxide deposits, after potentiostatic tests under  $-650 \text{ mV}_{\text{SCE}}$  for 20 h in the simulated district heating water at  $40^\circ\text{C}$ .

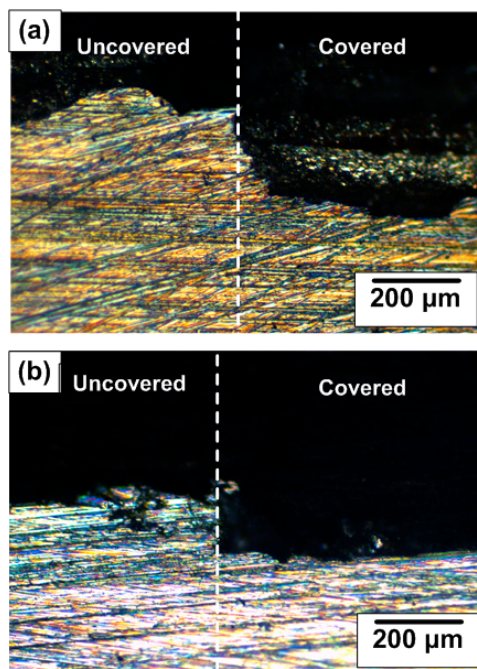


**Figure 8.** Cross-sectional image of the  $\alpha\text{-FeOOH}$ -covered specimen after potentiostatic tests under  $-650 \text{ mV}_{\text{SCE}}$  for 20 h in the simulated district heating water at  $40^\circ\text{C}$ .

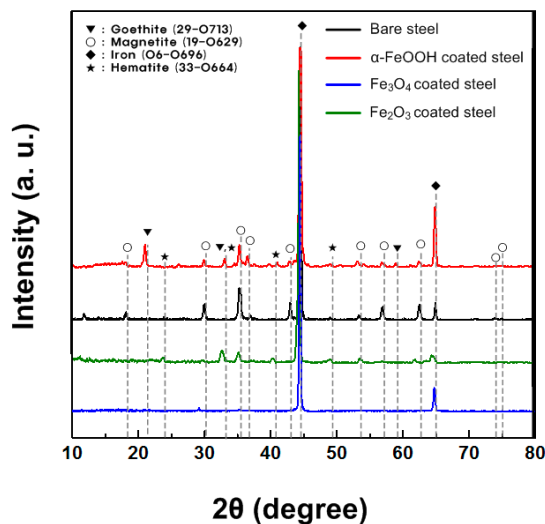


**Figure 9.** Optical microscope images of boundary covered (left side) and uncovered (right side) (a)  $\alpha$ -FeOOH, (b)  $\text{Fe}_3\text{O}_4$  and (c)  $\text{Fe}_2\text{O}_3$  iron oxides deposit, after potentiostatic tests under  $-650 \text{ mV}_{\text{SCE}}$  for 20 h in the simulated district heating water at  $40^\circ\text{C}$ .





**Figure 10.** Cross-sectional images of the boundary of covered and uncovered (a)  $\alpha$ -FeOOH, (b)  $\text{Fe}_3\text{O}_4$  iron oxides deposit, after potentiostatic tests under  $-650 \text{ mV}_{\text{SCE}}$  for 20 h in the simulated district heating water at  $40^\circ\text{C}$ .



**Figure 11.** X-ray diffraction (XRD) spectra for the specimens covered with iron oxides and uncovered which were immersed in the simulated district heating water for 340 h at  $40^\circ\text{C}$  ( $\nabla$ : goethite,  $\alpha$ -FeOOH;  $\blacklozenge$ : iron, Fe;  $\circ$ : magnetite,  $\text{Fe}_3\text{O}_4$ ;  $\star$ : hematite;  $\text{Fe}_2\text{O}_3$ ).

### 3.5. Mott-Schottky Tests

It is well known that there is a relationship between the surface film properties related to the semiconducting behavior of a surface film and the corrosion behavior of materials [35,36]. These properties and behavior can be investigated by analyzing the curves of a Mott-Schottky plot. Thus, the surface film properties of a steel substrate under iron oxide deposits ( $\alpha$ -FeOOH,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ) were investigated using a Mott-Schottky plot based on measurements of the electrode capacitance as a function of the electrode potential ( $E$ ). It was assumed that the capacitance of the space-charge was much less than that of the Helmholtz layer, and thus the electrode capacitance was equal to  $C$ .

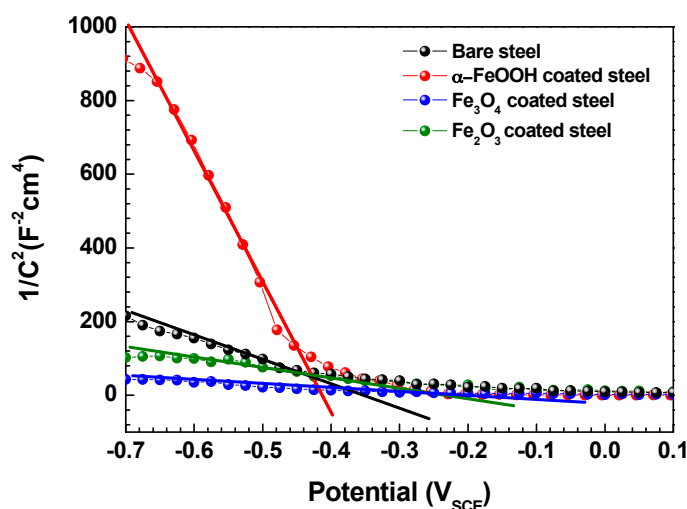
According to Mott-Schottky theory, the space-charge capacitance and  $n$ -type and  $p$ -type semi-conductors are given by Equations (5) and (6), respectively:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 e N_D} \left( E - E_{FB} - \frac{kT}{e} \right) \quad (5)$$

$$\frac{1}{C^2} = -\frac{2}{\epsilon\epsilon_0 e N_A} \left( E - E_{FB} - \frac{kT}{e} \right) \quad (6)$$

where  $\epsilon$  denotes the relative dielectric constant of the layer,  $\epsilon_0$  is the permittivity of a vacuum ( $8.8542 \times 10^{-14}$  F/cm),  $e$  is the absolute value of the electron charge ( $1.6029 \times 10^{-19}$  C),  $k$  is the Boltzmann constant ( $1.389 \times 10^{-23}$  J/K),  $T$  is the absolute temperature,  $E_{FB}$  is the flat band potential that can be obtained from the extrapolation of  $1/C^2$  to 0  $V_{SCE}$ , and  $N_D$  and  $N_A$  are the donor and acceptor densities, respectively, which can be determined from the slope of the experimental  $1/C^2$  versus applied potential [37–39].

Figure 12 shows the Mott-Schottky plots for the iron oxide-covered and uncovered specimens immersed in the test solution for 340 h at 40 °C. The slope of the Mott-Schottky diagram is negative, indicating  $p$ -type semiconducting behavior of the surface films in all conditions. In the iron oxides, the  $Fe_2O_3$  and  $\alpha$ -FeOOH indicate the  $n$ -type property whereas the  $Fe_3O_4$  has  $p$ -type property [35]. It means that the  $Fe_3O_4$  is mainly formed on the surface in all conditions. According to Equation (3), acceptor density ( $N_A$ ) can be determined from the slope of the experimental  $1/C^2$  versus  $E$  plots, i.e., more negative slope in Mott-Schottky plot suggests the decrease of acceptor density. Thus, the decrease of  $N_A$  was observed according to the following order:  $\alpha$ -FeOOH < bare <  $Fe_2O_3$  <  $Fe_3O_4$ . The donor and acceptors in oxide layers are defects consisted of cation vacancies, anion vacancies and cation interstitials. Cation vacancies yielding  $p$ -type character acts as the doping element which prevents migration of cation from the metal surface and penetration of harmful anions such as  $Cl^-$ ,  $F^-$  and  $SO_4^{2-}$  [36,40]. Thus, the semi-conductive properties of the oxide layer depend on the kind of oxide and the concentration of cation or anion vacancies. Although the increase of the  $N_A$  is related to the more disordered oxide layer and susceptible to corrosion in the passivity materials, this interpretation is not adequate in this study because the oxide layer was almost not formed on the  $Fe_2O_3$  and  $Fe_3O_4$  as shown in XRD results, and localized corrosion was only observed in the case of  $\alpha$ -FeOOH-covered specimen. It is therefore the  $\alpha$ -FeOOH on the surface and  $Fe_3O_4$  formed beneath the  $\alpha$ -FeOOH have an effect on the pitting corrosion.



**Figure 12.** Mott-Schottky plots for iron oxides-covered and uncovered specimens immersed in the simulated district heating water for 340 h at 40 °C.

The thickness ( $W$ ) of the space-charge layer, which is the surface film at a film formation potential, can be calculated by [41]:

$$W = \left( \frac{2\epsilon\epsilon_0}{eN_A} \right)^{\frac{1}{2}} \left( E_f - E_{FB} - \frac{kT}{e} \right)^{\frac{1}{2}} \quad (7)$$

In this equation,  $E_f$  is the film formation potential, and the other parameters have the same meanings as those in Equation (5). The film thickness ( $W$ ) of space-charge layer is proportional to  $1/C^2$  according to the following equation, obtained using Equations (6) and (7):

$$W = \epsilon\epsilon_0 \left( \frac{1}{C^2} \right)^{\frac{1}{2}} \quad (8)$$

Thus,  $W$  is increased in the following order:  $\alpha$ -FeOOH > bare > Fe<sub>2</sub>O<sub>3</sub> > Fe<sub>3</sub>O<sub>4</sub>. This indicates that the iron oxide deposits are not considered a surface film.

## 4. Discussion

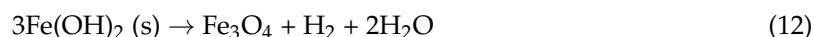
### 4.1. Surface Reaction under the Iron Oxide Deposits

The potentiodynamic polarization curves indicated a negative shift in the corrosion potential and an increase in the cathodic and anodic reactions on the iron oxide-covered specimens. The negative shift in the corrosion potential in the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>-covered specimens means that the increase in the anodic reaction area was due to the surface reaction from the Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -FeOOH [42]. Additionally, the cathodic and anodic reactions for the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>-covered specimens increased. Therefore, the oxide deposit does not act as a surface barrier of the substrate, which is due to the porous properties of iron oxide particles [43].

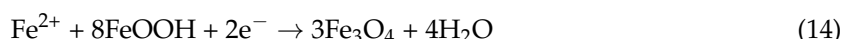
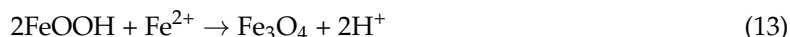
The following anodic and cathodic reactions occur on the steel substrate under the test solution conditions (de-aeration and pH 10). Equation (9) is the anodic dissolution and Equation (10) is the cathodic reaction in an alkaline solution under the de-aeration condition [44]:



Additionally, the Fe<sub>3</sub>O<sub>4</sub> formation reactions occurred as shown in the XRD results according to the following Equations [45,46]:

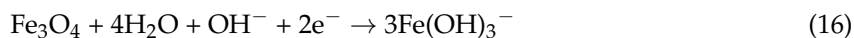
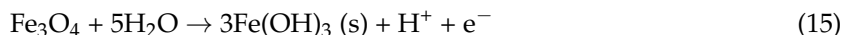


However, these surface film formation reactions are affected by the iron oxide deposits ( $\alpha$ -FeOOH, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>) on the substrate. Under the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>-covered specimens, the following cathodic and anodic reactions can occur. Under the  $\alpha$ -FeOOH deposit, the following reactions occurred on the steel substrate [47–50]:



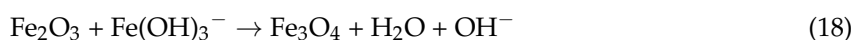
The reduction reaction of  $\alpha$ -FeOOH occurred and due to these reduction reactions, the cathodic reaction was increased as shown by the polarization curve. In addition, with the increase in  $\alpha$ -FeOOH reduction reactions, more Fe<sup>2+</sup> ions were required to satisfy the equilibrium of Equations (13) and (14) such that the anodic dissolution of Equation (9) was increased simultaneously, as shown by the increase in the anodic reaction in the polarization curve. Based on these reactions, the formation of Fe<sub>3</sub>O<sub>4</sub> can occur under the  $\alpha$ -FeOOH deposit.

Under the  $\text{Fe}_3\text{O}_4$  deposit, the following reactions can occur on the substrate [44,50,51]:



Equations (15) and (16) indicate the oxidation and reduction of  $\text{Fe}_3\text{O}_4$  with water and hydroxide ions in the test solution, respectively. These oxidation and reduction reactions of  $\text{Fe}_3\text{O}_4$  are indicated by the increase in anodic and cathodic reactions in the polarization curve. Additionally, the  $\text{Fe}_3\text{O}_4$  formation reaction on the substrate was obstructed because the  $\text{Fe}_3\text{O}_4$  deposit existed on the substrate, which restricts the formation of  $\text{Fe}_3\text{O}_4$  as a surface film on the substrate.

Under the  $\text{Fe}_2\text{O}_3$  deposit, the following reaction occurs on the substrate [51,52]:



Hematite,  $\text{Fe}_2\text{O}_3$ , is the final oxidation product among the iron oxides [53]. Thus, reduction reaction, Equation (17), occurs; this increases only cathodic reaction of the  $\text{Fe}_2\text{O}_3$ -covered specimen, as indicated in the polarization curve. The formation of  $\text{Fe}_3\text{O}_4$  under the  $\text{Fe}_2\text{O}_3$  deposit can be induced by Equation (18), but the reaction is limited due to the multiple reaction steps of  $\text{Fe}(\text{OH})_3^-$ . Thus, the formation of  $\text{Fe}_3\text{O}_4$  under the  $\text{Fe}_2\text{O}_3$  deposit is difficult.

The above reaction results were confirmed by Mott-Schottky and XRD analysis. In the Mott-Schottky results, the  $p$ -type semiconducting property and film thickness increased in the following order:  $\alpha\text{-FeOOH} > \text{bare} > \text{Fe}_2\text{O}_3 > \text{Fe}_3\text{O}_4$ . Additionally,  $\text{Fe}_3\text{O}_4$ , which has  $p$ -type semiconducting properties [54], was primarily formed on the  $\alpha\text{-FeOOH}$ -covered and bare specimens, as shown in the XRD analysis results. The results indicate that different reactions on the surface caused by iron oxide deposits affect the formation of  $\text{Fe}_3\text{O}_4$  on the surface. In addition, the semiconducting property of the iron oxide deposits, which means  $\alpha\text{-FeOOH}$  and  $\text{Fe}_2\text{O}_3$  are  $n$ -type and  $\text{Fe}_3\text{O}_4$  is  $p$ -type, was not observed in the Mott-Schottky results [36,55]. This implies that the iron oxide deposit on the specimen could not be analyzed by the Mott-Schottky measurement because the iron oxide deposits did not act as a surface film or barrier but rather as a reactant similar to a catalyst on the surface.

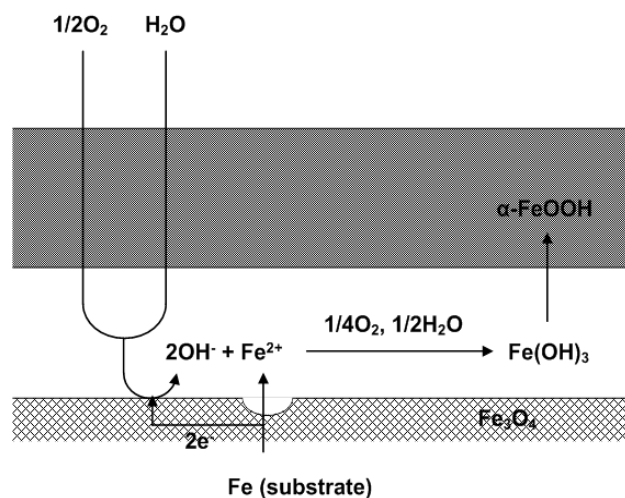
#### 4.2. Mechanism of Different Corrosion Behavior under the Iron Oxide Deposits

In the potentiostatic tests, uniform corrosion behavior was indicated in all conditions, except the  $\alpha\text{-FeOOH}$ -covered specimen. Pitting corrosion only occurred under the  $\alpha\text{-FeOOH}$ -covered specimen. Uniform corrosion under the iron oxide deposits occurs due to the diffusion of external factors such as water and anions in the test solution, which were associated with porous properties of iron oxides that were revealed by the EIS and Mott-Schottky tests [56]. Under the  $\alpha\text{-FeOOH}$ , pitting corrosion was observed, indicating that the cathode and anode areas were separated on the substrate.

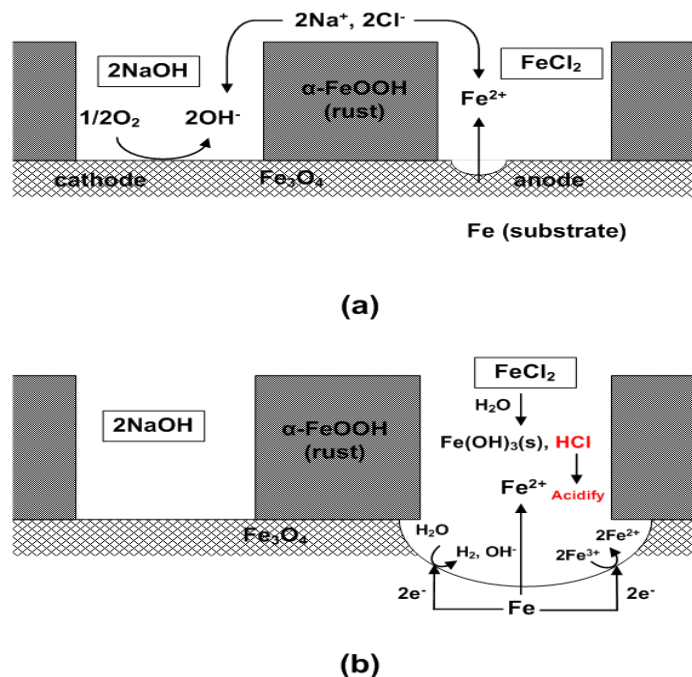
Localized corrosion of steel can occur due to rust on the steel surface [18]. Two types of localized corrosion such as the UDC and the crevice corrosion were observed in this study. The rust on the steel and iron at the initial stage of corrosion is generally composed of  $\text{Fe}(\text{OH})_3$ ,  $\alpha\text{-FeOOH}$ , and  $\text{Fe}_3\text{O}_4$  from each transformation. The rust is visualized schematically in Figure 13.  $\text{Fe}(\text{OH})_3$  was transformed into  $\alpha\text{-FeOOH}$  and then  $\alpha\text{-FeOOH}$  was transformed into  $\text{Fe}_3\text{O}_4$ , as described by Equations (11) and (12). Based on these reactions, porous defects such as cracks and voids were developed in the rust layer, and the outside environment reaches the metal. The corrosion in these defects initiates a reaction, but the  $\text{Fe}^{2+}$  and  $\text{OH}^-$  ions cannot react directly because the remaining  $\alpha\text{-FeOOH}$  rust obstructs their direct reaction. Due to these separated reactions,  $\text{FeCl}_2$  and  $\text{NaOH}$  are formed in the anode and cathode regions, respectively. Acidification occurs due to the  $\text{FeCl}_2$  in the anode region when the anode dissolution is accelerated. This corrosion under the thick rust layer can be considered crevice corrosion [19]. Figure 14 shows the crevice corrosion process under the  $\alpha\text{-FeOOH}$  rust layer. Localized



corrosion occurred under the  $\alpha$ -FeOOH-covered specimen, even though the passive behavior was not observed on the polarization curve.



**Figure 13.** Schematic of the rust film formed on the steel at the initial stage of corrosion. Reproduced with permission from [18]. Copyright Elsevier, 2008.



**Figure 14.** Mechanism of (a) crevice corrosion and (b) corrosion under the  $\alpha$ -FeOOH rust.

## 5. Conclusions

(1) In the potentiodynamic polarization results,  $i_{\text{corr}}$  increased in all deposit-covered specimens, which means that the corrosion reaction increased due to the deposit. The  $\alpha$ -FeOOH and  $\text{Fe}_3\text{O}_4$ -covered specimens demonstrate a negative shift in the corrosion potential and an increase in the number of anodic and cathodic reactions, and the  $\text{Fe}_2\text{O}_3$ -covered specimen only increased the cathodic reaction.

(2) Pitting corrosion was only observed on the  $\alpha$ -FeOOH-covered specimen, while uniform corrosion was observed on the others. This occurs due to a crevice corrosion phenomenon, which occurs via localized corrosion under the  $\alpha$ -FeOOH rust layer on the steel substrate. Additionally,

the corrosion at the boundary between deposit-covered and uncovered pipe was observed on the  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub> due to the galvanic effect.

(3) The Mott-Schottky and XRD analyses revealed that surface reactions differ according to the kind of iron oxide deposited, which influences the formation of surface film and the reaction rate of anode and cathode sites.

Based on this study, the iron oxides covered as a deposit on the steel substrate had a negative effect on the corrosion in district heating water.  $\alpha$ -FeOOH can lead to localized corrosion, which causes failure in the early stage. Thus, stagnant condition prevention and floating matter filtration are important tasks for maintaining the pipeline. It would be helpful to purge with nitrogen to maintain a minimum flow rate rather than to fill the pipe with water during downtimes.

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**Author Contributions:** Jung-Gu Kim conceived and designed the experiments; Yong-Sang Kim performed the experiments; Jung-Gu Kim and Yong-Sang Kim analyzed the data; Jung-Gu Kim contributed reagents/materials/analysis tools; Yong-Sang Kim wrote the paper.

**Conflicts of Interest:** The authors declare no conflict of interest.

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