Influence of Soil Particle Size, Covering Thickness, and pH on Soil Corrosion of Carbon Steel

Ryo HIRATA,¹* Waka YONEMOTO,² Azusa OOI,¹ Eiji TADA¹ and Atsushi NISHIKATA¹

1) Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo, 152-8552 Japan.
2) Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology. Now at Canon Inc., 70-1, Yanagicho, Saiwai-ku, Kawasaki, Kanagawa, 212-8602 Japan.

(Received on April 30, 2020; accepted on June 29, 2020; J-STAGE Advance published date: September 2, 2020)

The effects of environmental factors, such as particle size, covering depth, and pH, on the corrosion behavior of carbon steel in silica sand filled with a 3% NaCl solution were investigated by electrochemical impedance spectroscopy (EIS) and polarization measurements.

The corrosion rate initially decreased with the decrease in the oxygen concentration near the steel surface, which was a result of the consumption of the dissolved oxygen during the corrosion reaction. The corrosion rate became constant at approximately 10 μm y⁻¹ regardless of the particle size and covering thickness. At the steady state, both the anodic reaction (iron dissolution) and cathodic reaction (oxygen reduction) appeared to be suppressed by the formation of an oxide film on the steel surface. In the silica sand filled with non-buffer and buffer solutions of pH 3–6, the corrosion rate was initially significantly enhanced by the hydrogen ions (H⁺). The period of the enhancement depended on the buffering capacity. However, the corrosion rate was subsequently independent of the pH due to the neutralization of the solution in the vicinity of the steel surface.

KEY WORDS: soil corrosion; electrochemical impedance spectroscopy; corrosion monitoring; polarization method.

1. Introduction

Underground steel structures in Japan are generally designed with a 1 mm “corrosion allowance” in 50 years, which is based on the results of exposure tests performed in the past.¹ Nevertheless, there are numerous potential risks linked to uniform design. The environmental factors of the soil vary depending on the region and thus, the corrosion rates change accordingly. Due to the recent problems of aging infrastructure and the demand for resource and energy saving, rationalization of steel design considering soil environment is required. Furthermore, the corrosion prevention standards have not been sufficiently established overseas (e.g. Southeast Asia). Hence, establishing an evaluation method for standardization is a key issue for the overseas development of steel materials.

Soil corrosion has been extensively studied for many years; however, there are numerous environmental factors that are thought to affect corrosion. The interactions between these factors are complex; therefore, comprehensive understanding of the soil corrosion processes and establishment of a corrosion model have not been reported.²³ Soil environmental factors include pH, water content, particle size, covering thickness, anions, such as Cl⁻ and SO₄²⁻, temperature, and microorganisms. In the soil environment, convection is suppressed by the presence of soil particles; therefore, the mass transfer of oxidizing agents and corrosion products is more restricted than in aqueous solutions. Among the environmental factors, pH, water content, particle size, and covering thickness affect the amount or mass transfer of oxidizing agents, such as oxygen and hydrogen ions, to a large extent and are considered to have a significant effect on the corrosion reaction.

The key studies on the topic of soil corrosion include long-term exposure tests on steel pipes in various soils by the National Bureau of Standards (NBS) in the USA³ as well as evaluation of the exposure of steel piles by the Kozai Club in Japan.¹ In addition, many studies on the correlation between corrosion rates and individual environmental factors have been carried out by employing laboratory level exposure tests and electrochemical measurements.⁴⁻¹¹ Kasahara et al. have previously determined the existence of...
a proportional relation between the polarization resistance of mild steel, $R_p$, measured in various soils and the corrosion current density, $i_{corr}$, obtained from the corrosion mass loss.\textsuperscript{4)} Based on this result, it is assumed that similarly to the case of aqueous solutions, the corrosion rate of steel in soil can be estimated using the Stern-Geary’s equation.\textsuperscript{12)} Consequently, it is possible to monitor the corrosion rate of carbon steel in soil by applying the electrochemical impedance spectroscopy (EIS) method, which can accurately determine $R_p$ or charge transfer resistance $R_{ct}$ in soil corrosion.

In this study, the soil environmental factors affecting the corrosion behavior of carbon steel, in particular, particle size, covering thickness, and pore water pH, were investigated by corrosion monitoring utilizing EIS method with a two electrode cell system.\textsuperscript{13–16)} Furthermore, the diffusion coefficient for oxygen in the soil was determined by a polarization measurement. The mechanism of soil corrosion is discussed based on these obtained results.

2. Experimental Methods

2.1. Electrochemical Impedance Spectroscopy (EIS)

The EIS measurement was carried out using a two-electrode cell, in which two carbon steel plates (SM490A, 10 mm $\times$ 5 mm $\times$ 4.5 mm) were embedded in parallel in an epoxy resin at 2 mm intervals. Table 1 shows the chemical composition of the specimen. Prior to the measurement, the electrode surface was wet-polished to #2000 using the SiC abrasive paper and ultrasonically cleaned in ethanol. Figure 1(a) shows the schematic diagram of the electrochemical cell used for the EIS measurement. Artificial soil was prepared by mixing the commercial silica sand (Marutou Co., Ltd., Japan) of different particle sizes and a 3% NaCl solution.

The resulting soil was subsequently poured into the cell. In all the experiments, the solution layer was positioned approximately 10 mm above the top of the soil. EIS was measured using a potentiostat (1287A; Solartron Analytical, UK) in the frequency range of 100 kHz to 1 mHz and a potential amplitude of 10 mV.

For the investigation of the effects of soil particle size, covering thickness (defined as the distance from the electrode surface to the top of the soil), and pH, the soil factors were changed as follows. Firstly, to investigate the effect of the soil particle size, the covering thickness was fixed at 50 mm and the silica sand particle size was changed to 1 000, 100, 10, and 1 μm. Subsequently, to evaluate the covering thickness, the particle size was kept constant at 100 μm, while the covering thickness was changed to 50, 30, and 10 mm. In the experiments, a 3% NaCl solution without pH adjustment was utilized as the electrolyte. Finally, to investigate the effect of the soil pH, the pH of a 3% NaCl solution was adjusted to 3, 4, 5, and 6 using HCl solution. The solutions were used with the silica sand with the particle size of 100 μm and a covering thickness of 50 mm. In addition, to examine the effect of the pH buffer capacity, a 3% NaCl solution was adjusted to pH 6 with a mixed solution of 0.2 M Na$_3$HPO$_4$/0.2 M NaH$_2$PO$_4$. To adjust it to pH 3, a mixed solution of 0.2 M H$_3$PO$_4$/0.2 M NaH$_2$PO$_4$ was used.

2.2. Cathodic Polarization Measurement

To investigate the oxygen reduction behavior in the silica sand, the cathodic polarization curve was measured by utilizing the potentiodynamic and potentiostatic methods employing an electrochemical unit (VSP; Bio-Logic). In the potentiodynamic method, a three-electrode cell (Fig. 1(b)) was employed to reduce the IR drop because of a relatively large current, whereas in the potentiostatic method, a two-electrode cell (Fig. 1(c)) was used.

In the potentiodynamic method, a carbon steel plate (SM490A, 10 mm $\times$ 10 mm $\times$ 4.5 mm) and a silver plate (3 mm $\times$ 10 mm $\times$ 5 mm) were embedded in the epoxy resin, which acted as working and reference electrodes, respectively. The distance between the two electrodes was set at 2 mm. Moreover, a Pt wire acted as the counter electrode. The Ag/AgCl reference electrode was fabricated according to the following procedure. The surface of the silver and carbon steel embedded in the epoxy resin was wet-polished to #2000 using a SiC polishing paper. After coating just the carbon steel surface with an adhesive tape, the silver was coated with a solution of 0.2 M Na$_3$HPO$_4$/0.2 M NaH$_2$PO$_4$. To adjust it to pH 3, a mixed solution of 0.2 M H$_3$PO$_4$/0.2 M NaH$_2$PO$_4$ was used.
anodized in a 1 M HCl solution at a constant current of 0.4 mA cm$^{-2}$ for 5–30 min to form AgCl on the Ag electrode. Subsequently, the electrode surfaces were ultrasonically cleaned after peeling the tape off. The potential difference between the Ag/AgCl reference electrode and the commercial Ag/AgCl/saturated KCl reference electrode (SSE) was +50 mV (vs. SSE) in a 3% NaCl solution. This measured potential difference was maintained before and after the polarization measurement. In the present study, all electrode potentials were converted to the SSE standard. Silica sand with a particle size of 1 000, 100, 10, and 1 μm was used as the artificial soil, and the covering thickness was kept constant at 30 mm. A 3% NaCl solution was added up to a height of approximately 20 mm from the top surface of the soil, and counter electrode was installed in the solution layer above the soil. Open circuit potential (OCP) was measured for 30 min, and then the cathodic polarization was performed at a potential scanning rate of 0.5 mV s$^{-1}$. The scanning range of OCP was approx. −1.1 V.

In the potentiostatic method, the same carbon steel plate as in the potentiodynamic method was employed as the working electrode. The inside of the O-ring was defined as the test area of the sample electrode (7.7 cm$^2$), as shown in Fig. 1(c). The potentiostatic polarization measurement was performed utilizing a two-electrode cell with the Ag/AgCl electrode prepared analogously to the method described for the potentiodynamic method. The measurement was carried out with the covering thickness of 50, 30, 10, and 5 mm using silica sand with the particle size of 1 000, 100, 10, and 1 μm as the artificial soil. A 3% NaCl solution was added to the top of the soil. The polarization potential was −0.80 V vs. SSE, which is the diffusion limiting current region of oxygen.

3. Results

3.1. EIS Characteristics of Carbon Steel in Silica Sand

The typical EIS results measured using artificial soil are displayed as a Bode plot in Fig. 2. The EIS changes with time measured in silica sand with a particle size of 100 μm and a covering thickness of 10 mm. The EIS characteristics of the other evaluated particle sizes were nearly identical. Moreover, the solution resistance, $R_{\text{sol}}$, which appeared on the high frequency side, exhibited a constant value, regardless of the changes in time. On the other hand, the sum of the charge transfer resistance, $R_{\text{ct}}$, as well as the value of $R_{\text{sol}}$ on the low frequency side, increased with time at the beginning of the test, and then became constant. In addition, immediately after the start of the experiment (day 0), in the low frequency range below $10^{-2}$ Hz, the diffusion impedance was observed. However, after one day, the value of $R_{\text{ct}}$ increased and the diffusion impedance completely diminished. Figures 3(a) and 3(b) demonstrate the equivalent circuits of the steel/silica sand interface with and without diffusion, respectively. CPE denotes the constant phase element, whereas W is the Warburg impedance. CPE is a parameter, which expresses the deviation from ideal behavior of the capacitor. In this case, the capacitance of the capacitor corresponds to the electric double layer capacitance $C_{\text{dl}}$.

The reciprocal of the charge transfer resistance ($R_{\text{ct}}^{-1}$) is proportional to the corrosion current density $i_{\text{corr}}$, as shown in Eq. (1).\cite{12,17}

$$i_{\text{corr}} = k / R_{\text{ct}} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cd -1

Fig. 2. Bode diagram of carbon steel in silica sand filled with a 3% NaCl solution (particle size: 100 μm, covering thickness: 10 mm). (Online version in color.)

Fig. 3. Equivalent circuits (a) with and (b) without diffusion impedance. $R_{\text{sol}}$: solution resistance, $R_{\text{ct}}$: charge transfer resistance, W: Warburg impedance, CPE: constant phase element.

3.2. Influence of the Soil Environment Factors on the Soil Corrosion Rate

3.2.1. The Effects of Particle Size

The changes in $R_{\text{ct}}^{-1}$ with time for carbon steel in silica sands of the various particle sizes are shown in Fig. 4. In this study, $R_{\text{ct}}^{-1}$ was used as an index of the corrosion rate. The demonstrated results relate to the covering thickness of...
50 mm; however, the same tendency was observed when the covering thickness was 10 mm and 30 mm. The $R_{ct}$ of carbon steel decreased with time and became nearly constant after several days. The comparison of the $R_{ct}$ values after 15 days revealed that all $R_{ct}$ values were in the range of $5 \times 10^{-5}$ to $10^{-4} \, \Omega^{-1} \, \text{cm}^{-2}$, even when the particle size was increased by three orders of magnitude, i.e., from 1 μm to 1 mm. Thus, it can be concluded that the particle size does not affect the soil corrosion rate. Based on $R_{ct} = 5.0 \times 10^{-5} \, \Omega^{-1} \, \text{cm}^{-2}$, the $i_{corr}$ calculated using Eq. (1) is approximately 1 μA cm$^{-2}$ (thickness loss: approx. 10 μm y$^{-1}$).

3.2.2. The Effects of Soil Covering Thickness
The changes in $R_{ct}$ with time for carbon steel in silica sand when the covering thickness was 10, 30, and 50 mm are demonstrated in Fig. 5. Similarly to Fig. 4, the $R_{ct}$ decreased with time and became constant after several days. Furthermore, as illustrated in Fig. 6, the corrosion rate under steady-state (15 days) exhibited a nearly identical value ($5.0 \times 10^{-5} \, \Omega^{-1} \, \text{cm}^{-2}$) regardless of the covering thickness.

3.2.3. The Effects of Pore Water pH
Changes in the value of $R_{ct}$ for carbon steel with time without buffer capacity are shown in Fig. 7. As it can be seen, the $R_{ct}$ decreased with time in all cases. Initially, at pH = 3, $R_{ct}$ was larger than at other pH values; however, it declined to nearly the same value ($5.0 \times 10^{-5} \, \Omega^{-1} \, \text{cm}^{-2}$) on the 15th day.

The comparison of the $R_{ct}$ values in the presence of the phosphate buffer solution or non-buffer solution (hydrochloric acid) is illustrated in Fig. 8. During the first few days of the test, both solutions at pH = 3 and 6 exhibited higher $R_{ct}$ in the buffered silica sand. This is because even when the H$^+$ ions are consumed by the corrosion reaction, more protons are supplied from the phosphate; thus, the pH at the carbon steel/solution interface is maintained. On the other hand, in the case of silica sand in the absence of pH buffering, the supply of H$^+$ to the metal surface is only a result of the diffusion from the outside of the silica sand. Consequently, the H$^+$ diffusion process becomes the rate-determining step of the corrosion reaction and the corrosion rate decreases with time, which is analogous to the case where oxygen acts as the oxidant. Nonetheless, despite the initial presence of the buffering capacity, the pH buffering of the phosphate near the carbon steel/silica sand interface is lost over time. As demonstrated in Fig. 9, the corrosion rate eventually declines to the same extent as the solution without the buffering capacity at steady-state. This is because unlike in the case of aqueous solutions, there is no convection in the soil.

From above results, it was clarified that the pH value
and pH buffer capacity of the soil pore water affect the initial stage of steel corrosion. In real soil, they may differ depending on the type of soil. It is necessary to examine by long-term monitoring how long the buffer capacity lasts in actual soil.

3.3. Cathodic Polarization Behavior of Carbon Steel in Soil

3.3.1. Potentiodynamic Polarization

Figure 10 illustrates the cathodic polarization curves of carbon steel in a 3% NaCl solution and in artificial soil (particle size 1,000, 100, 10 μm, covering thickness 30 mm) saturated by the same solution. In the cathodic polarization curve in an aqueous solution, the diffusion limiting current density \( i_d \) resulting from the reduction reaction of dissolved oxygen expressed by Eq. (2), appears from the immersion potential to approximately \(-1.05 \) V. Upon further polarization, the current resulting from the water reduction reaction expressed by Eq. (3) is observed.

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 4\text{OH}^- \quad \text{(2)} \\
2\text{H}_2\text{O} + 2\text{e}^- & \rightarrow \text{H}_2 + 2\text{OH}^- \quad \text{(3)}
\end{align*}
\]

The value of \( i_d \) can be obtained according to Fick’s first law using the following equation:

\[
i_d = -4FD_0C_0 / \delta \quad \text{(4)}
\]

where, \( F \) is the Faraday constant, \( D_0 \) denotes the diffusion coefficient of oxygen, \( C_0 \) is the dissolved oxygen concentration in the bulk aqueous solution, and \( \delta \) is the thickness of the steady-state diffusion layer.

In the silica sand, the reduction current of oxygen and water was confirmed using the same method as for the aqueous solution. However, compared with the cathodic polarization curve in the aqueous solution, the reduction current of oxygen is potential-dependent and exhibits a small value. This is thought to be due to the difference between the diffusion layer formed in the aqueous solution and in the soil. In a stationary aqueous solution, the thickness of the steady diffusion layer is about 0.01–0.1 mm under a natural convection.\(^{19}\) On the other hand, in soil, the convection is restricted by the presence of solid soil particles; therefore, the oxygen-diffusion layer is thought to grow to the covering thickness. Consequently, the oxygen reduction current in the silica sand is much smaller than that in the aqueous solution. Subsequently, to determine the diffusion coefficient of oxygen in the silica sand, the potentiostatic polarization was performed at \(-0.8 \) V vs. SSE.

3.3.2. Potentiostatic Polarization

The decay curves of the reduction current \( (i_{-0.8V}) \) with time at \(-0.8 \) V in a 3% NaCl solution and in the silica sand are demonstrated in Fig. 11. The insert shows the graph for the silica sand with magnified vertical axis. It is noteworthy that the \( i_{-0.8V} \) value decreases with time until reaching a constant value. It is suspected that the current in the aqueous solution oscillates due to the changes in the convection conditions in the solution resulting from the temperature fluctuation. Moreover, in the silica sand, the growth of the diffusion layer to the covering thickness takes about 2 to 3 days to reach the steady-state, whereas the steady-state is achieved more rapidly in the case of the aqueous solution.
In addition, the value of \( i_{-0.8V} \) in the silica sand was approximately an order of magnitude smaller than that in the aqueous solution. In the case of the largest silica sand (1 000 μm diameter), current oscillations were observed after approx. 0.17 day (4 hour). The oscillations may be attributed to the presence of convection in each pore water. Therefore, the data for the particle size of 1 000 μm are excluded from the analysis of oxygen diffusion.

The changes in \( i_{-0.8V} \) with time for the carbon steel when the covering thickness was changed from 5 to 50 mm are displayed in Fig. 12. Similarly to the observations in Fig. 11, \( i_{-0.8V} \) attenuated with time and became constant after a few days. When the covering thickness of the silica sand increased, the value of \( i_{-0.8V} \) decreased and the time to reach the steady value increased. This indicates that the oxygen-diffusion layer grows in the direction perpendicular to the electrode surface (in the direction of the covering thickness). The relation between the reciprocal of the covering thickness (\( d^{-1} \)) and the steady-state value of \( i_{-0.8V} \) (\( i_{-0.8V(s)} \)) is illustrated in Fig. 13. It can be seen that \( i_{-0.8V(s)} \) increased with an increase in \( d^{-1} \) (decrease in the covering thickness) at any particle size. Moreover, with a particle size of 100 μm, \( i_{-0.8V(s)} \) is a straight line passing through the origin and exhibits a proportional relation to \( d^{-1} \). This means that the covering thickness \( d \) is equal to the thickness of the steady state diffusion layer \( \delta \) in Eq. (4). Conversely, the proportional relation is not observed for the particle sizes of 10 μm and 1 μm. If the particles are closely packed at all particle sizes, the apparent \( D_O \) should not depend on the particle size, as the total pore water volume is equal under the conditions of constant covering thickness.

4. Discussion

Based on the obtained experimental results, the corrosion mechanism (in neutral environment) of carbon steel in the silica sand filled with a 3% NaCl solution is discussed in detail in the following sections.

4.1. Initial Stage of Soil Corrosion

It is clearly demonstrated in Figs. 5 and 6 that the cor-
4.2. Soil Corrosion in the Steady-state

As it is evident from Figs. 4 and 5, the corrosion rate, \( R_{\text{cor}} \), decreases for the first few days, and then becomes constant at approximately \( 5 \times 10^{-5} \ \Omega^{-1} \ \text{cm}^{-2} \) (\( i_{\text{cor}} \approx 1 \ \mu\text{A cm}^{-2} \)). If the corrosion of carbon steel is assumed to continue to proceed under the diffusion control of oxygen in the steady state, the oxygen-diffusion layer grows to the covering thickness of the soil because there is no convection in the pore water of the soil. From the apparent diffusion coefficient of oxygen obtained by the potentiostatic cathodic polarization (Fig. 13), the net diffusion limiting current \( i_d \) (not including the reduction current of water) of oxygen was calculated to be \( 0.46 \ \mu\text{A cm}^{-2} \), \( 0.15 \ \mu\text{A cm}^{-2} \), and \( 0.09 \ \mu\text{A cm}^{-2} \) at 10 mm, 30 mm, and 50 mm of the covering thickness, respectively. Assuming that the corrosion reaction is controlled by the diffusion of oxygen through the soil in the steady-state, the corrosion rate should be equal to the above \( i_d \) values. However, the steady-state corrosion rate (approximately \( 1 \ \mu\text{A cm}^{-2} \)) estimated from EIS was larger than the values of \( i_d \). Therefore, the oxygen-diffusion layer did not grow to the covering thickness under the employed experimental conditions. This is also confirmed from the fact that the corrosion rate of carbon steel did not depend on the covering thickness (Fig. 6).

Another corrosion mechanism involves the transit of the corrosion reaction of carbon steel from the reaction with oxygen (Eq. (2)) to the reaction with water (Eq. (3)). Generally, the oxygen reduction reaction is controlled by the oxygen-diffusion step, while the water reduction reaction is controlled by the charge transfer step. Namely, in the reaction with oxygen, the corrosion rate of carbon steel decreases with time; however, when it decreases to a certain degree, the reaction with water becomes the main reaction and the corrosion rate becomes constant. To confirm this, the polarization curves of carbon steel were measured in the silica sand after the soil corrosion reached a steady-state. Figure 14 illustrates the polarization curves of carbon steel measured by the three-electrode cell shown in Fig. 1(b) after 7 days of exposure (steady-state). The polarization curve immediately after soil burial is also shown. To avoid the influence of the mutual polarization, the anodic and cathodic polarization curves were measured using separate electrodes. The anodic polarization curve was measured from \( E_{\text{cor}} \) to the noble direction, while the cathodic polarization curve was measured from \( E_{\text{cor}} \) to the less noble direction at a 0.5 mV s\(^{-1}\) scanning rate. Suppression can be seen for both the cathodic reaction represented by Eqs. (2) and (3) and the anodic reaction shown in Eq. (5).

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{..................................} \quad (5)
\]

Even after 7 days, the oxygen reduction waves (\( E_{\text{cor}} \approx -0.9 \ \text{V} \)) were clearly observed, although the current value was small. It appears that the carbon steel corrosion has not yet been fully transferred from the reaction with oxygen to the reaction with water.

As indicated in Fig. 14, in the steady-state, the oxygen reduction is strongly suppressed, and the reduction current displays potential dependence. The reduction reaction of oxygen seems to be mixed-controlled (charge-transfer/diffusion) instead of diffusion-controlled. The suppression can be attributed to not only oxygen consumption due to corrosion but also the formation of an iron oxide film on the surface of the carbon steel. The surface morphology of the carbon steel exposed in the silica sand for 7 days is shown in Fig. 15(a). It can be clearly seen that the entire surface was covered with a thin oxide film. The cathodic polarization curve of the exposed carbon steel was measured in an aerated 3% NaCl solution, and is shown in Fig. 16. For comparison, the cathodic polarization curve of the as-polished carbon steel is also shown. It was confirmed that the oxygen reduction reaction was significantly suppressed on the carbon steel surface covered with the thin oxide film.

Thus, in the present work, a corrosion mechanism model considering the corrosion products (iron oxide film) is proposed. In the initial stage of corrosion (within approx. 7 days), the rate of the charge transfer of the oxygen reduction reaction is sufficiently higher than the diffusion rate; therefore, the corrosion of carbon steel proceeds by the diffusion-controlled reduction of oxygen in the silica sand, resulting in the growth of the diffusion layer. Consequently, the corrosion rate of carbon steel decreases with time. Concurrently, the dissolved Fe ions accumulate at the carbon steel/silica sand interface and iron thin oxide film forms on the surface, leading to the suppression of the cathodic (Eq. (2)) and anodic (Eq. (5)) reactions. Moreover, the growth of the diffusion layer becomes slower and reaches.
a quasi-steady-state. On the other hand, on the carbon steel electrode without the oxide film under cathodic polarization (Fig. 15(b)), as described in Section 3.3, the oxygen reduction reaction continues to proceed under diffusion control in the steady state because it is not suppressed by the oxide film.

5. Conclusions

Using silica sand filled with a 3% NaCl solution as an artificial soil, the corrosion of carbon steel was electrochemically investigated in the covering thickness range of 5 to 50 mm. The main conclusions that can be drawn are as follows.

(1) It was determined that the electrochemical impedance characteristics of carbon steel in the artificial soil can be represented by a simple equivalent circuit, in which soil resistance is connected in series to a parallel circuit of the charge transfer resistance and CPE corresponding to electric double layer capacitance.

(2) The corrosion rate of carbon steel decreased with time and reached a quasi-steady-state after several days. The corrosion rate in the quasi-steady-state was approximately 10 μm year⁻¹, irrespective of the particle size and covering thickness of the silica sand. The initial decrease in the corrosion rate was caused by the consumption of oxygen at the carbon steel/soil interface by the corrosion reaction. After that, the corrosion rate was further reduced by the formation of a thin oxide film on the surface, and eventually reached a constant value.

(3) The corrosion of carbon steel was promoted by H⁺ when the pH of the soil was lowered. The duration of the promotion was determined to depend on the strength of the soil pH buffering capacity. However, even in the case of strong pH buffering properties, it was found that the corrosion rate eventually decreased to the same level as that of the neutral environment.

(4) The potentiostatic polarization measurement was conducted in the silica sand with a particle size of 100 μm, and the apparent oxygen-diffusion coefficient of 4.6 × 10⁻⁶ cm² s⁻¹ was obtained.

Acknowledgments

This research was supported by The Iron and Steel Institute of Japan, “Elucidation of Soil Corrosion Mechanism of Iron and Steel Materials” Study Group.

REFERENCES