

Article

Time-Dependency in the Corrosion Process of Reinforced Concrete Subjected to a Chloride Solution

Sangki Park , Dong-Woo Seo  and Jaehwan Kim * 

Department of Structural Engineering Research, Korea Institute of Civil Engineering and Building Technology, 283 Goyangdae-ro, Goyang-si 10223, Gyeonggi-do, Republic of Korea; skpark@kict.re.kr (S.P.); dwseo@kict.re.kr (D.-W.S.)

* Correspondence: jaehwankim@kict.re.kr

Abstract: The corrosion of steel in reinforced concrete exposed to marine environments or winter de-icing poses a significant threat. However, evaluation of it is challenging due to variables such as environmental conditions and concrete properties. Many studies in concrete engineering have introduced a performance-based approach, evaluating structures with experimental data by considering the environmental conditions. Electrochemical techniques, including half-cell potential (HP), electrochemical impedance spectroscopy (EIS), and galvanostatic pulse (GP), are widely used for studying steel corrosion in concrete. Despite the widespread use, corrosion measurements have still limitations due to ambiguous impedance results from concrete presence, equipment sensitivity, and analysis flexibility. The corrosion of steel in chloride-laden concrete was assessed in well-controlled laboratory conditions using EIS and GP before field application. The results showed that measured values for corrosion parameters were consistent with each other (within 10% discrepancy). Corrosion initiation times varied from 171 to 319 days depending on the techniques, the differences attributed to measurement periods, and the condition of the steel. In addition, it was confirmed that the corrosion potential for HP was significantly correlated with the time constant for GP. This study demonstrated these techniques to improve both the understanding of the corrosion process and the accuracy of the calculated corrosion rate.

Keywords: electrochemical impedance spectroscopy; galvanostatic pulse technique; chloride; steel; corrosion



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1. Introduction

Reinforced concrete (RC) is widely used worldwide owing to its durability and structural integrity, particularly in infrastructures requiring a prolonged service life [1]. The durability of RC can be ensured by improving the quality of the cover concrete with a denser pore structure and with the formation of a passive film on the steel embedded in the concrete through the concrete alkalinity [2,3]. However, preventing steel corrosion remains the primary challenge in ensuring a long service life of RC.

Steel corrosion is commonly influenced by the environment; steel is exposed to extreme environmental conditions that cause corrosion in RC, leading to the breakdown of the passive film formed on the reinforcement surface. This could be attributed to either carbon dioxide or chlorides. Steel corrosion can have serious effects on RC structures, such as a reduced effective thickness of steel, a reduced load-carrying capacity of the structure, and the formation of corrosion byproducts, with volumes reaching three to six times more than that of the original steel. The expanded steel increases the internal stresses around the reinforcement, leading to the formation of cracks or spalling. Consequently, the corroded reinforcing steel reduces the structural performance, leading to a catastrophic collapse. Many countries including South Korea, USA, Canada, Australia, India, European countries, Japan, etc., specify limiting values in the codes to avoid steel corrosion of steel

in concrete, but the limiting values suggested in the codes cannot fully cover prevention of RC corrosion. Therefore, evaluation and prevention of RC corrosion are crucial for ensuring safety. Many studies have examined the modelling and mechanisms of steel corrosion through the effects of chloride attack and carbonation [4]. However, the studies examining corrosion detection in RC structures have had significant limitations owing to differences in the corrosion behaviour between laboratory experiments and actual structures, nonhomogeneous concrete materials, and local conditions which can influence the results.

Various corrosion detection methods have been developed and applied in this field, including non-electrical and electrical methods. Non-electrical methods typically include the following: (1) the half-cell potential (HP) method, in which the potential of steel is measured with respect to a standard electrode, such as a copper–copper sulphate electrode (CSE), a saturated calomel electrode (SCE), or a silver–silver electrode [5]; (2) the galvanic current method, in which the currents are measured between anodes for steel in corrosive environments and the cathode for a noble metal, such as stainless steel, graphite, or titanium [6]. Electrical methods artificially apply an electrical current or potential to steel to measure its polarisation resistance which can be used to quantify steel corrosion. Polarisation resistance can be obtained using direct current (DC) methods, such as the linear polarisation resistance technique (LPR), the Tafel extrapolation technique, the galvanostatic pulse (GP) technique, and the potentiostatic technique; however, among the alternating current (AC) methods, electrochemical impedance spectroscopy (EIS) typically uses AC in the frequency domain.

EIS provides a better understanding of the corrosion process and a more accurate corrosion rate; however, this technique has a high potential sensitivity to the response under various conditions. A previous study demonstrated that a complete description of an electrochemical system can be made for impedance using an equivalent circuit [7]. However, determining the equivalent circuit for steel embedded in concrete remains challenging because the responses regarding the number of phenomena related to the corrosion process are ambiguous [8]. In addition, controlling the steel embedded in concrete after casting is also challenging. Thus, the corrosion process of steel in concrete appears as black box data. Therefore, proposing various circuits to describe the corrosion process may be impractical. Improving the interpretation of impedance data for steel corrosion would be more beneficial.

This study aimed to analyse the impedance of the steel response for concrete samples subjected to chloride-induced corrosive environments. To overcome the difficulty in controlling the variables for steel casts in concrete, the GP technique was employed as a complementary method to verify the EIS results.

2. Reviews for Corrosion Detection Techniques

2.1. Half-Cell Potential

HP measurement is essential in corrosion science because the electrical potential of steel needs to be identified to apply the polarisation technique and directly determine whether the steel is corroded. Thus, this technique is suitable for practical applications. However, the measured corrosion potential is also sensitive to various factors, including concrete resistivity and binder type. For example, the corrosion potential of steel in concrete saturated by chloride [9] or in concrete using replacements [10] (e.g., ground granulated blast furnace slag (GGBS)), occasionally indicates less than -350 mV vs. CSE, corresponding to a high corrosion possibility ($>90\%$) even though steel maintains a passive state. Therefore, corrosion potential measurement is qualitative rather than quantitative. The corrosion state of steel can be expressed with a probability, as shown in Table 1 [11]; however, detecting corrosion according to the gradient of the corrosion potential in the field is preferable [5]. These reasons make HP measurement the preferred auxiliary method for corrosion measurement.

Table 1. Possibility of corrosion risk with corrosion potential according to ASTM C876.

Open Circuit Potential (mV vs. CSE)	Corrosion Condition
<−500	Severe corrosion
<−350	High (<90% risk of corrosion)
−350 to −200	Intermediate corrosion risk
>−200	Low (10% risk of corrosion)

2.2. Galvanostatic Pulse Technique

The GP technique is a polarisation transient technique that uses the time domain with a potentiostat in the galvanostatic mode. This technique involves applying a small constant current ranging from 10–100 μA to the working electrode. The potential perturbation of the working electrode with respect to the corrosion potential (vs. the reference electrode) is recorded over a short duration (<10 s) [12]. A previous study suggested that a small perturbation of less than 100 $\mu\text{C}/\text{cm}^2$ should be applied to preserve the system between concrete and steel and eliminate the diffusion process [13]. For data analysis, a numerical procedure based on an electrical circuit, such as the Randle circuit, is typically employed. Owing to the non-exponential relaxation in the parameters, a capacitor in the Randle circuit is replaced with a constant phase element (CPE) representative of a non-ideal capacitor [14], or the time-domain equation for a Randle circuit is modified with the Kohlrausch–Williams–Watt (KWW) function [15], as shown in Equation (1). The potential perturbation during electrode charging can be expressed as follows:

$$V_t(t) = I_{app}R_{ohmic} - I_{app}R_p \left[1 - \exp\left(\frac{-t}{\tau}\right)^\beta \right], \quad (1)$$

where $V_t(t)$ is the potential of steel with measuring time t , I_{app} is the applied current, R_p is the polarisation resistance, R_{ohmic} is the ohmic resistance, τ is the time constant ($= R_p C_{dl}$), C_{dl} is the double-layer capacitance, and β is the exponent.

Two different methods have been proposed for the fitting procedure: linearisation and exponential curves [16]. The ohmic resistance is estimated with a sudden change in the corrosion potential when a constant current is applied (at $t \approx 0$ s). Figure 1 shows an example of the measured data and fitting for the active and passive states of the steel. This technique is beneficial to engineers owing to its rapid response and the direct elimination of ohmic resistance. In addition, because the time-domain response is transformed into the frequency domain using Laplace transformation [17,18], the results based on the GP technique are complementary to that of the EIS technique. Commercial products, such as GalvaPulse, have also been developed as portable equipment for practical use. However, common limitations in corrosion measurements remain, such as the estimation of the polarised area [19]. This technique requires controlling the potential perturbation because steel is polarised by current rather than voltage [20].

2.3. Electrochemical Impedance Spectroscopy

Unlike traditional electrochemical measurements which only provide faradaic and non-faradaic components, EIS could provide all electrical characteristics of the interface over a wide range of frequencies. Thus, faradic responses can be extracted from non-faradic signals regarding all interface information when using EIS-based techniques.

Impedance is the complex resistance created by a resistor, capacitor, and inductor when current flows through a circuit. A small voltage, generally 5–15 mV peak-to-peak, is applied to the electrode, and then the current response is recorded [7]. The reasons for using a small voltage are as follows: (1) the linear relationship between the potential and current in the electrode–electrolyte interface system; (2) the minimisation of system

disruption in the concrete. High resolution is necessary to measure the current in a concrete sample. Therefore, an increase in the sensitivity of the measurement is unavoidable.

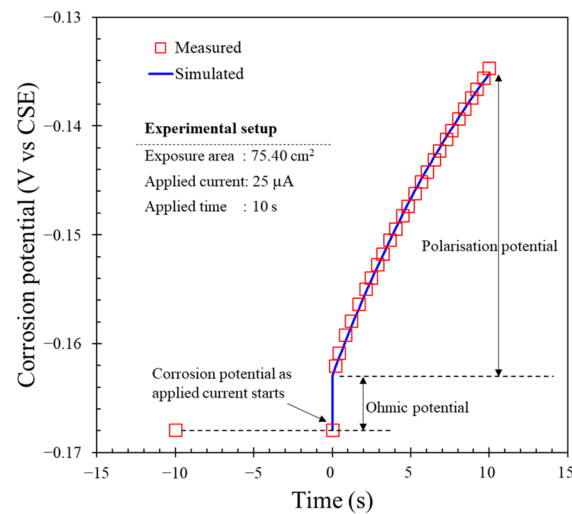


Figure 1. Data fitting for GP technique.

John et al. [21] were the first to use EIS to study the corrosion of steel in concrete. Although the equipment used has been improved technically, the interpretation of the impedance data remains relatively challenging. AC can be used for corrosion measurement to reduce system disturbance. However, it has limitations in evaluating the corrosion of steel in concrete, including the time-consuming use of lower frequencies, the presence of concrete, and the ambiguous responses. In addition, measurement sensitivity limits the practical application of these methods.

3. Experiments

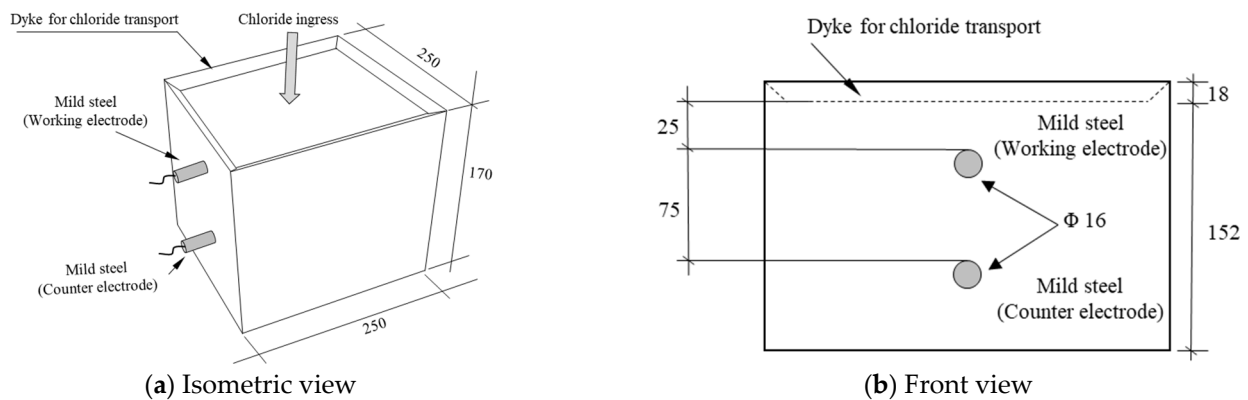
3.1. Experimental Setup

Table 2 lists details of the materials and mix design used in this study. Ordinary Portland cement (OPC) CEM I 52.5N to BS EN 197-1:2000 was used [22]. The water-to-cement ratio (w/c) was set to 0.4 and 0.6. Three replicates of the concrete samples were fabricated. The sample dimensions were 250 mm $\times$ 250 mm $\times$ 170 mm with a dyke against a 250 mm $\times$ 250 mm face to facilitate the wet–dry cyclic regime. Two mild steel bars with a diameter of 16 mm and length of 300 mm were placed into each concrete sample while being electrically isolated. A copper wire was attached to one end of each mild steel bar, and heat-shrinkable tubes were wrapped around both ends of the bar to create a specific area of exposure. All steel bars were degreased with acetone before casting. The installed steel bars were used as the working and counter electrodes for each sample. For the working electrodes, the steel was covered with heat-shrinkable tubes to determine the exposure area—this area covered 75.40 cm². To achieve uniform current distribution on the working electrode, steel counter electrodes were selected at a 10 cm depth and covered with heat-shrink insulation with a 75.40 cm² surface area. For concrete strength, the average values are shown with one standard deviation in Table 2. Figure 2 shows a schematic of the sample. After casting, the samples were wrapped in a polythene film and cured in a mould for 7 days. All faces of the samples, except for the dyke, were double coated with epoxy resin and then wrapped with a polythene film. The wrapped samples were cured in a curing chamber (20 ± 2) °C.

Table 2. Mix design and physical properties.

Type of Cement	W/C *	Cement Content (kg/m ³)	Aggregate (kg/m ³)	Sand (kg/m ³)	Compressive Strength (MPa)	
					F ₂₈	F ₁₈₀
CEM I 52.5N	0.4	460	1012	650	65.32 (7.62) **	84.23 (2.20) **
	0.6	300	1100	707	38.34 (1.19) **	46.99 (1.35) **

* W/C water to cement ratio, ** values in brackets are one standard deviation for average values in compressive strength.

**Figure 2.** Schematics of concrete slab samples.

To accelerate the corrosion process, a wet–dry cyclic regime was employed using a sodium chloride solution (chloride content = 19.5 g/L). Before initiating the cyclic regime, the sample surface was soaked in distilled water for an additional 7 days, followed by exposure to a wet–dry cyclic regime. This allowed the sample to become saturated and prevented any potential absorption effects induced by the drying process. The chloride solution was eliminated from the concrete surface during the drying period. The surface was subsequently exposed to laboratory conditions, with a temperature of $(20 \pm 1)^\circ\text{C}$ and relative humidity of $(55 \pm 5)\%$. By contrast, a chloride solution was contained on the concrete surface using a dyke during the wetting period. The drying period in the cyclic regime gradually intensified, with 2 days of drying and 5 days of wetting during the first month, 5 days of drying and 2 days of wetting during the second month, and 8 days of drying and 6 days of wetting during the remaining periods. The corrosion tests were performed for up to 382 days and the tests are discussed below in detail.

3.2. Testing for Corrosion Measurement

Corrosion tests were performed to investigate steel corrosion using HP measurements, the GP technique, and EIS. The HP was measured after each wet–dry cycle. A wet synthetic sponge, squeezed to remove excess water, was placed on the concrete surface for approximately 10 min to facilitate electrical conduction between the reference electrode and the steel within the concrete. After approximately 190 days of concrete ageing, the polarisation resistance was measured using the GP technique after each wet cycle was completed. EIS measurements were obtained at specific times (186, 270, and 382 days), indicated in the legend within the figures or tables.

A conventional electrode configuration (i.e., a three-electrode setup) was used, including two mild steels placed in concrete as the working and counter electrodes, and a CSE corresponding to the reference electrode. To measure the corrosion potential against the reference electrode, a high-impedance multimeter was used ($>10\text{ M}\Omega$ of acceptable impedance).

A potentiostat/galvanostat (Solartron Analytical 1287 Electrochemical Interface) was used in the galvanostat mode for the GP technique. A current of $25 \mu\text{A}$ was applied for 10 s to the working electrode, equating to $3.32 \mu\text{C}/\text{cm}^2$, to prevent any disturbance in the system between the concrete and steel and to avoid the diffusion process [13]. The potential bias from the corrosion potential was recorded at a rate of 5 points/s. Before the measurements, the corrosion potential was measured for a minimum of 1 min to verify potential alterations within 10 mV/min.

EIS measurements were obtained using a frequency response analyser (Solartron 1260A Impedance/Gain-phase Analyser) and a potentiostat (Solartron Analytical 1287 Electrochemical Interface). A sinusoidal wave (root mean square value of 10 mV at the open-circuit potential) was applied within a frequency range of 5–100 kHz based on a logarithmic sweep at 10 frequency points per decade. The open-circuit potential was maintained below 10 mV/min. Corrosion threshold potential and current were -350 mV vs. CSE and $2 \text{ mA}/\text{m}^2$ [23].

4. Results and Discussion

4.1. Corrosion Potential with Time

The HP monitoring results were obtained from 42 days of concrete curing, at which point the chloride solution was exposed to the concrete, for approximately 385 days, as shown in Figure 3. After immersion in a chloride solution, a sharp decrease in the potential was observed for all samples, resulting from an increase in the electrical conductivity of the concrete owing to the contamination of the chloride solution [6]. In the passive state, the potentials fluctuated with the concrete conditions caused by the wet–dry regimes before reaching a critical corrosion potential of -350 mV vs. CSE . The fluctuation was more severe for the 0.4OPC concrete than for the 0.6OPC concrete. It appeared that having more restrained pore structures in the concrete affected the corrosion potential determination. The results indicated that concrete and steel conditions affect the corrosion potential of the steel, as in a previous study [24]. In addition, the corrosion potentials of the steels in the 0.4OPC concrete grow after 240 days, which may indicate an improved corrosion resistance, such as growth of the passive layer [25]; however, this cannot be determined based only on the trend of corrosion potential.

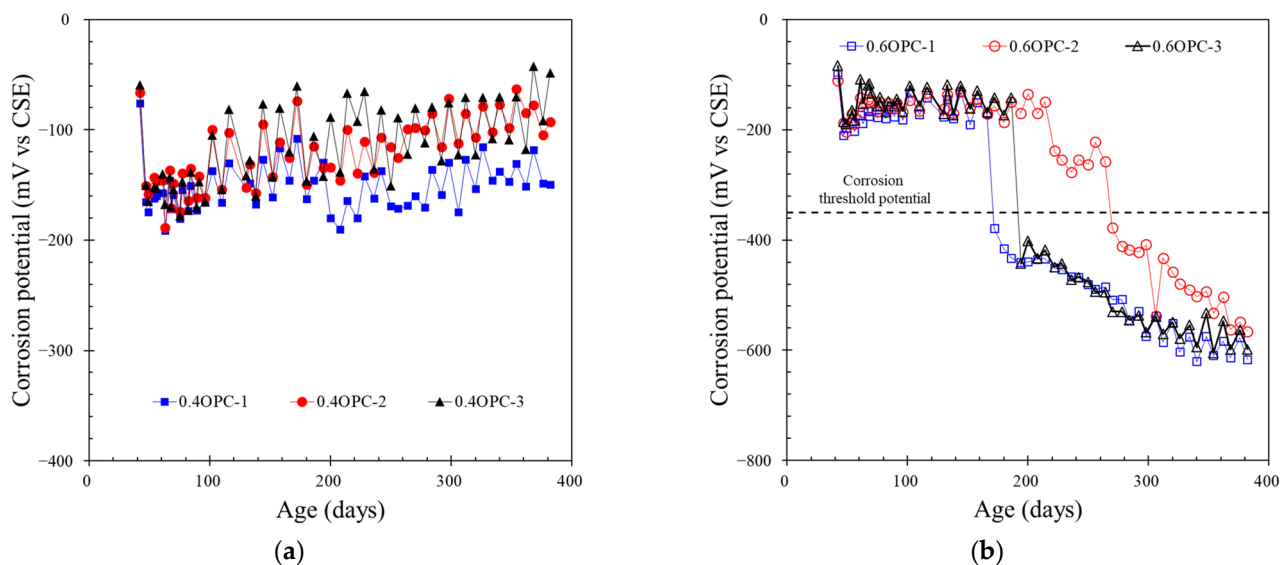


Figure 3. Corrosion potential of (a) W/C = 0.4 and (b) W/C = 0.6OPC concrete with time.

When the critical corrosion potential for corrosion initiation was set to -350 mV vs. CSE , only the onsets of corrosion for the 0.6OPC concrete were detected during the experiments. Corrosion initiation typically occurs when the corrosion potential decreases.

The fluctuations for the 0.6OPC concrete in Figure 3b were reduced after the onset of corrosion. Furthermore, the following cases regarding the corrosion behaviour or depassivation process were observed, as shown in a previous study [25]: (1) a sharp decrease in corrosion potential; (2) a slow decrease in corrosion potential with the corrosion potential maintained between -250 mV to -350 mV. The time to onset of corrosion with steel was 171–269 days of concrete age, even though the steel is present in the same concrete. This implies that local effects, such as steel conditions and concrete, significantly influence the depassivation process in addition to environmental conditions, including chloride content, oxygen availability, and moisture content.

After the corrosion initiation, the corrosion potentials decreased continuously with exposure time. Considering that the chloride effect is negligible after the onset of corrosion [26], the continuous decrease in corrosion over time, that is, the ongoing corrosion process, is attributed to the consistent supply of oxygen and moisture for the wet–dry phase. However, a continuous drop in the corrosion potential does not necessarily indicate a propagation phase in corrosion, which is an ongoing corrosion process, because the HP technique is considered a qualitative method. Therefore, quantifying the corrosion rate through HP monitoring is difficult.

4.2. Electrical Parameters in Galvanostatic Pulse Technique

Steel bars in concrete subjected to chloride-induced corrosive environments were monitored using the GP technique. The fitting was performed using Equation (1) using the Levenberg–Marquardt algorithm coded in Matlab® (R2022a). Figure 4 shows the ohmic resistance with respect to time. The measured values are depicted as an average value with a one standard deviation error bar, which sometimes appears to be absent owing to the relatively large markers. The ohmic resistance for both samples continuously increased within the measurement duration; from 177.6Ω to 303.2Ω for 0.4OPC and from 108.5Ω to 131.0Ω for 0.6OPC. The results showed that hydration in the cement matrix had proceeded to a great extent for both concretes. The hydration process of concrete with a lower w/c was expected to be terminated owing to less free water for the process in the concrete; however, this was not observed. This appeared to be caused by the rapid loss of free water in the 0.6OPC concrete during the drying phase and additional pore refinements by chloride binding in the 0.4OPC concrete. Overall, the ohmic resistance of the 0.4OPC concrete was 87.8% higher than that of the 0.6OPC concrete, and no corrosion of steel in the 0.4OPC concrete was detected. Therefore, a higher ohmic resistance indicated a higher corrosion resistance owing to less connectivity of the pore structure, resulting in the lower permeability of aggressive agents, such as chloride.

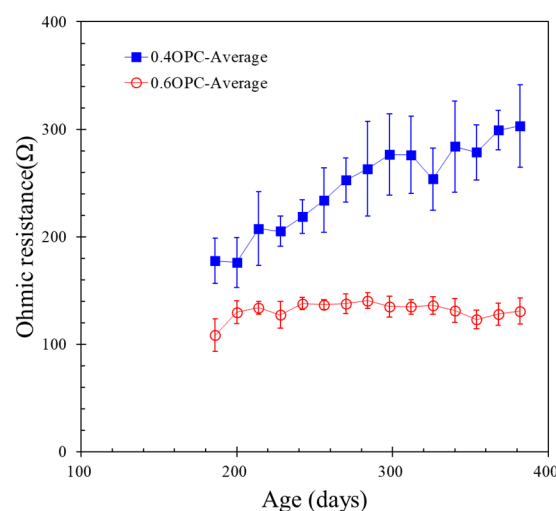


Figure 4. Ohmic resistance with time using GP technique.

Figures 5 and 6 show the capacitance and polarisation resistance of steel which account for its characteristics, and the plots are depicted for each steel rather than the average value. For the capacitance, the values in the low-w/c concrete, ranging from 10 mF to 15 mF, were generally lower than those in the high-w/c concrete, with values up to 130 mF. The expected causes are explained as below. (1) More uniform types of passive film are formed on steel embedded in the low-w/c concrete [27,28], or a layer of $\gamma\text{-Fe}_2\text{O}_3$, comprising the outer products in the passive film and having a lower dielectric constant, thickens through the transformation of magnetite, which is the main inner product in the passive film [29,30]. Thus, a uniformly distributed passive film on the steel may provide a higher corrosion resistance, such as that in a well-coated steel. However, a higher capacitance indicates a higher roughness on the steel, such as that in a poorly coated steel. (2) Chlorides reached the steel depth during the measurement. Thus, higher values resulted in depassivation caused by chloride, resulting from an increase in the steel roughness. The tendency for an increase in the capacitance of the corroded steel was consistent with that found in previous studies [31,32].

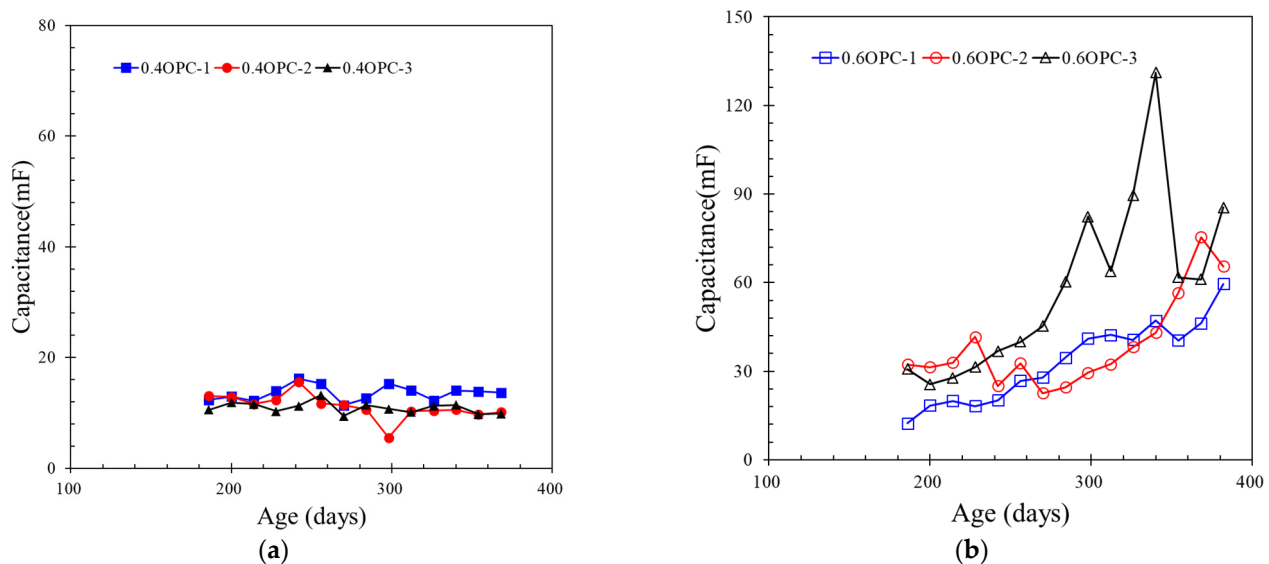


Figure 5. Capacitance of (a) W/C = 0.4 and (b) W/C = 0.6 OPC concretes with time.

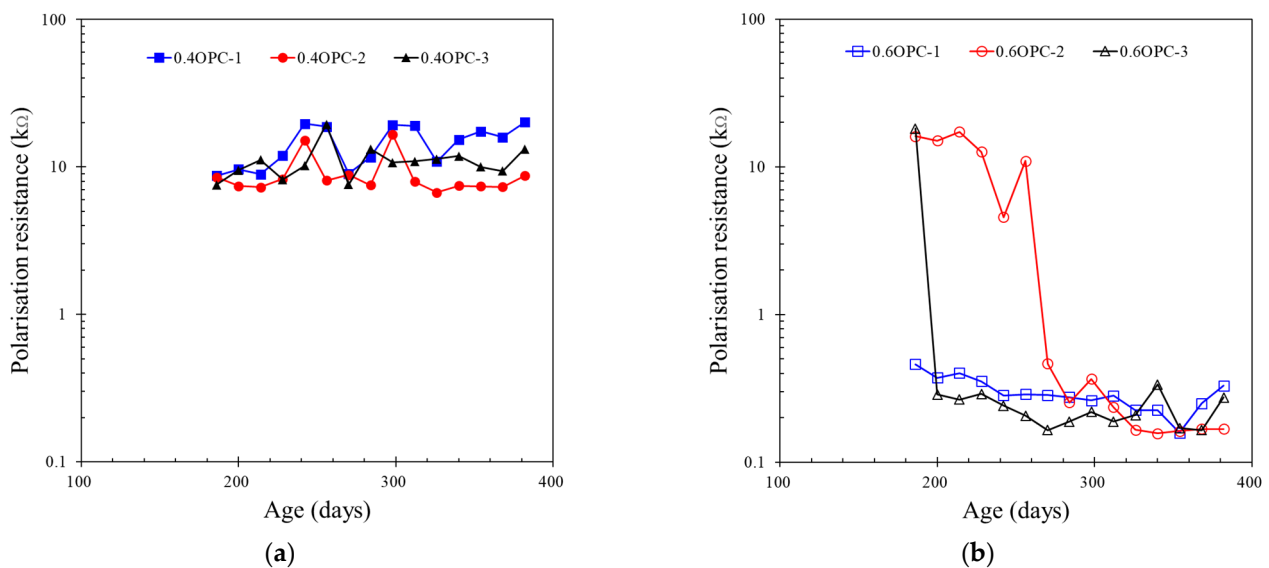


Figure 6. Polarisation resistance of (a) W/C = 0.4 and (b) W/C = 0.6 OPC concretes with time.

Figure 6 shows that polarisation resistances were significantly high, with values up to 20 k Ω for all samples, irrespective of exposure time for the passive state. After depassivation, the polarisation resistance of steel decreased significantly. In addition, corrosion propagation was maintained owing to the continuous decrease in the polarisation resistance. Before the aggressive agents reached the appropriate steel depth, electrochemical conditions in the steel were stable owing to the presence of a protective layer on the steel surface, such as a passive film comprising γ -Fe₂O₃ with low conductivity. The corrosion rate with only oxygen and moisture under high-alkalinity conditions was extremely slow without a catalyst, such as chlorides; thus, it was negligible in this phase. Consequently, the values of both parameters changed significantly after the transition phase; that is, the depassivation process. After depassivation, the steel roughness increased, and ionic movement became more active because the passive film on the steel surface was destroyed, increasing the capacitance and reducing the polarisation resistance [13].

When the polarisation resistance decreased significantly, the capacitance also decreased and then increased. This phenomenon was not observed for the 0.6OPC-1, for which considerable corrosion was found to proceed. Provided that the capacitance indicates the steel conditions, such as the presence of a passive film and corrosion products, depassivation can be explained. The capacitance trend indicated the destruction of the passive film and the formation of corrosion products. The passive film comprising Fe₃O₄, which is a main product with a 20 dielectric constant, was destroyed and transformed by γ -FeOOH, with a dielectric constant of 2.6 [30]. Finally, α -FeOOH was formed as a corrosion product, which is more porous and has a higher dielectric constant of 11 [30]. The steady increase in capacitance accounted for the change in the corrosion product phase. Both the capacitance and polarisation resistance of the steel in the 0.6OPC-1 were lower than those in the 0.6OPC samples at 186 days. The results indicate that magnetite was significantly transformed into γ -FeOOH, which is relatively more corrosive.

The time constant, the required time to charge a capacitor by approximately 63% of the difference from an initial value or to discharge a capacitor by approximately 36.8% [32], is an indicator of the electrochemical condition of steel embedded in concrete. If the electrical circuit comprises a resistor parallel to a capacitor, the time constant is equal to the product of the resistance and capacitance, which is independent of geometrical factors. Thus, the steel condition can be described using a time constant. The time constant is given with respect to the corrosion potential for all the samples, as shown in Figure 7. The figure shows that the time constant in the active state, corresponding to less than 20 s, was lower than that in the passive state, corresponding to more than 70 s, consistent with previously reported data [33]. This indicates that less adherent/porous corrosion products on the steel surface readily charge/discharge electrons during the polarisation process, leading to a rapid response in the time constant. The long time constant in the passive state can explain the difficulty in achieving a steady state when using the DC polarisation technique owing to the low capacitance and diffusion process. In addition, the values were independent of time, as shown in Figure 7. Hence, the time constant is useful for determining the steel condition; however, it is suggested as a qualitative rather than a quantitative indicator.

4.3. Responses for Elements in Equivalent Electrical Circuit

The electrical impedance of RC is roughly divided into two parts: the steel and the concrete responses. In addition, each part can be separated into subdivisions, such as interface, presence of passive film, sponge effect, and pitting corrosion process; however, response interpretation is not straightforward. The corrosion of steel induced by chloride in concrete is described by a series of processes, including chloride transport, depassivation, and corrosion propagation; thus, different impedance responses for steel and concrete are shown at each stage. Based on these differences, the practicability of electrically equivalent circuits was suggested. Unlike concrete, the steel embedded in concrete cannot be easily controlled under experimental conditions. Therefore, the impedance response of

the steel was analysed through monitoring rather than through one-off experiments with controlled variables.

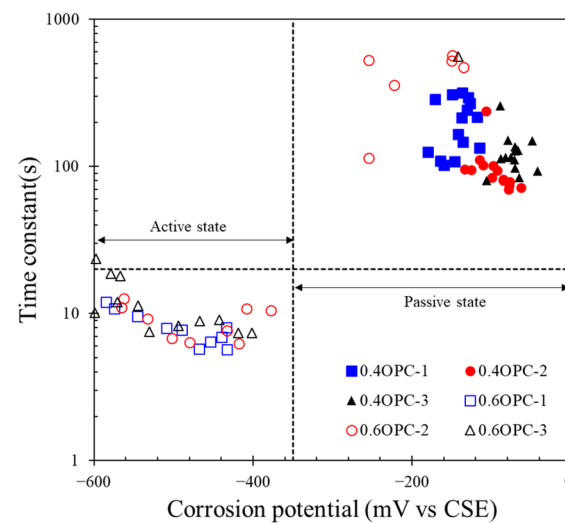


Figure 7. Time constant of steel with respect to corrosion potential.

To minimise errors caused by unexpected variables [34], such as the conditions of the sponge, location of the counter electrode, and contact pressure, EIS data were analysed for the samples using an internal counter electrode (i.e., steel embedded in the concrete sample). Figure 8 shows examples of the impedance measurements for the active and passive states. Two parts (i.e., the steel and the concrete responses) in both figures were confirmed. For the concrete response, the cusps represent the ohmic resistance. However, a difference in the steel response between the active and passive states was observed. The impedance shapes of the passive and active states differed. For the active state, semi-circular shapes were formed in the steel response (i.e., from a 1 kHz frequency), whereas the steel response for the passive state was almost a straight line.

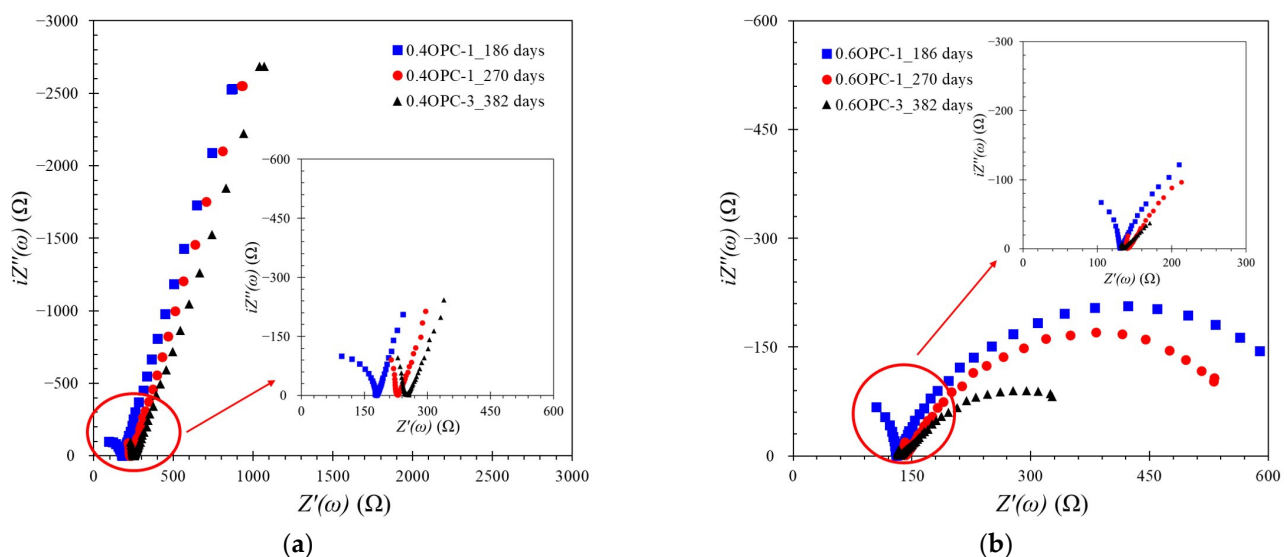


Figure 8. Examples of electrochemical impedance spectrum of steel in (a) passive state and (b) active state.

To clarify the steel response, the reference frequency was set to 1 kHz to roughly divide it into two parts (i.e., the concrete and the steel responses) because the impedance at this frequency was closer to the real axis. This frequency was also suggested as a low-frequency

limit for estimating the concrete resistance [35]. Figure 9 shows the impedance spectra, which were redrawn with the origin of impedance at 1 kHz to describe the impedance response of steel with respect to time, based on the data in Figure 8. The results confirmed that the impedance response was time dependent. Thus, the slopes for the passive state and radii of the semicircles for the active state decreased with exposure time. The reduced slope indicates the depassivation process induced by the chloride at the steel depth, while the straight line appears to be a part of a large semicircle. The expected semicircle was formed after depassivation. Two hypotheses were formulated from the results: (1) the depassivation process is relatively slow compared with the corrosion propagation; thus, the change in slope is marginal; (2) the impedance response in steel contains at least two phases, corresponding to the response of the steel itself and that of the corrosion products. Performing an impedance spectroscopy analysis using an electrical equivalent circuit is crucial. Considering a series of simplified Randle circuits, the former corresponds to one Randle circuit for the steel response in the circuit. For the latter, the electrical equivalent circuit is formed with a minimum of two series of simplified Randle circuits for the steel response. Determining the more accurate circuit based solely on the data is difficult owing to this invisible phenomenon.

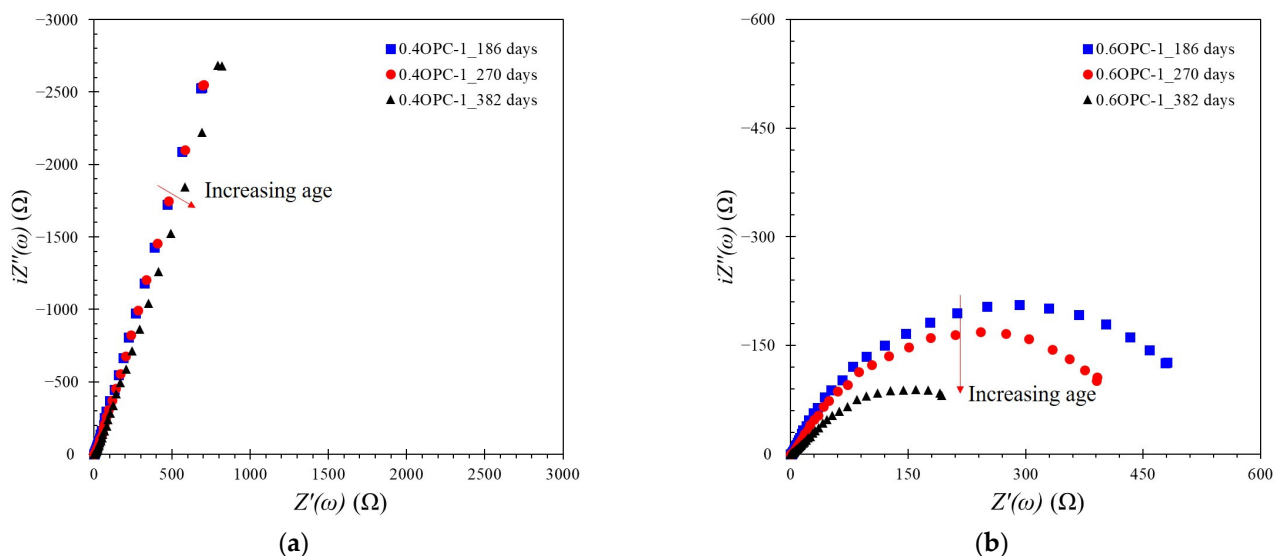


Figure 9. Examples of electrochemical impedance spectrum of steel in (a) passive state and (b) active state when setting up origin at 1 kHz.

This study fitted the data with a circuit. The results confirmed that the latter had better fit values. Notably, the fitting accuracy always improved when additional circuits were added. In addition, the value of the element varied with the arrangement of elements in an equivalent electrical circuit. Thus, the proposed equivalent electrical circuit was not unique. The following procedure was performed to determine the circuit for analysis. After forming several Randle circuits and performing fitting, the dispensable circuits, that is, those containing high errors, were successively eliminated. Subsequently, the obtained values were compared with those obtained using the GP technique. Thereafter, the optimised circuit was determined, as shown in Figure 10, comprising four modified Randle circuits in series. The capacitor was replaced with a CPE to improve the fit.

As shown in Figure 10a, in the electrical equivalent circuit, the first two R-CPE loops considered the concrete response involving the bulk concrete resistance and interfacial effect, while the other loops corresponded to the steel response accounting for the corrosion product/passive film and the steel itself. The concrete response and interfacial effect were a high-frequency semi-arc and an intermediate frequency range normally up to, ca. 1 kHz, as discussed in the previous section. The steel response is described with a low-frequency semi-arc ranging from 5 mHz.

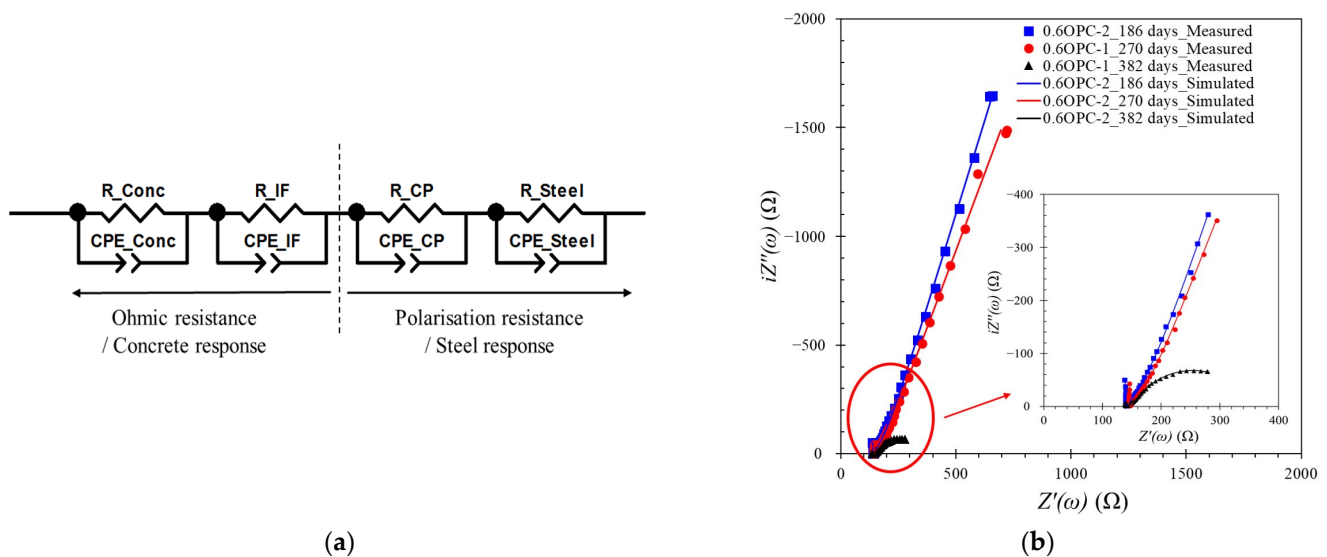


Figure 10. (a) Proposed electrical equivalent circuit and (b) fitting examples from passive state to active state.

The impedance data for the steel response appeared as a straight line in the passive state, as shown in Figures 8 and 9. Although two R-CPE loops for the steel response were suggested in this study, dividing them into subparts with a specific frequency can be challenging. This is because of a limitation in the fitting procedure when using impedance spectroscopy. The resistance of the passive film/corrosion products fluctuated significantly owing to the fitting. In addition, the charge transfer resistance of a passive film cannot be measured, as found in a previous study [36], because of the high resistance within this equivalent electrical circuit or the omission of diffusion impedance, as discussed below. Furthermore, whether CPE is an artefact [37] remains debatable; nonetheless, CPE is evidently a flexible parameter for improving curve fitting to the measured impedance spectra [38]. This CPE characteristic is valuable for describing the time dependence of each element in the electrical equivalent circuit. Moreover, for steel embedded in concrete, measurements are significantly limited even in good conditions owing to unexpected variables; thus, CPE enables the observation of the steel response with time.

4.4. Electrical Response for Time-Dependency

The analysis of the GP and EIS techniques is based on an electrical circuit, and these results are comparable. Recently, values represented in the time domain using the GP technique have been transformed into values in the frequency domain [17]. The required parameters for calculating the corrosion rate of steel in concrete are the ohmic and polarisation resistances. The corrosion rate is generally underestimated when the uncompensated polarisation resistance is used to calculate the corrosion rate. Accurate estimation of the ohmic and polarisation resistances is beneficial to engineers. Extracting the values corresponding to the parameters from the EIS measurements is challenging because the electrical equivalent circuit in EIS is more complicated than that in the GP technique.

In this study, a simple circuit arrangement (four parallel R-CPE combinations) was employed, roughly comprising the steel response and ohmic drop, to extract the parameters for comparison. In the circuit, the first two R-CPE combinations were considered as ohmic drops, and the other RC combinations were considered as steel responses. The values of the circuit elements corresponding to each part were added and compared with the values obtained from fitting in the GP method. In addition, the corrosion rate and time to the onset of corrosion were determined.

In this study, the ohmic drop accounted for the interfacial effect and bulk concrete resistance. The interfacial effect, which indicated that a layer was formed between the

concrete and electrode, was unavoidable owing to the electrode configuration in the polarisation technique. Confirming whether the ohmic resistance was pure concrete resistance was necessary; however, the capacitance was excluded in the comparison because the ohmic resistance in the GP technique was considered only with a resistor. Figure 11 shows the ohmic resistances of the samples. The exposure area (75.40 cm^2) was considered for calculating the corrosion rate for the EIS measurement and for data for the GP technique. The ohmic resistances of both samples were similar, irrespective of the electrochemical measurements. This discrepancy was approximately 10%. These results confirmed that the ohmic resistances could differ depending on the electrical measurements, leading to errors in estimating the corrosion rate.

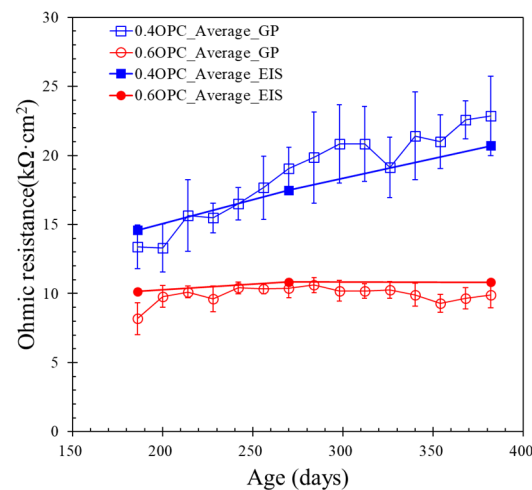


Figure 11. Comparison of ohmic resistances depending on electrical measurements.

In addition to the ohmic resistance, the resistance of steel based on EIS, that is, the polarisation resistance, is compared with that in the GP technique in Figure 12. The comparison was performed only for the 0.6OPC concrete because the resistances corresponding to the charge transfer resistance in the circuit were not measurable by fitting in the passive state. The polarisation resistance initially decreased with time. In the passive state or at the early stage of corrosion, the EIS measurements were more than 10 times higher than those from the GP technique, and the gap between both values decreased significantly as the corrosion progressed.

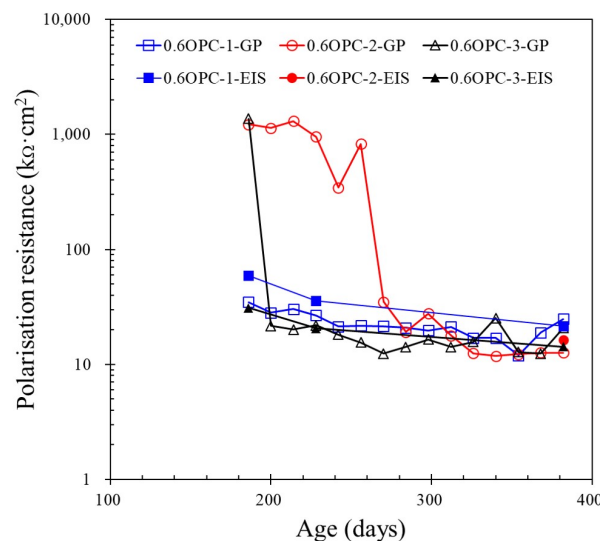


Figure 12. Comparison of polarisation resistances depending on electrical measurements.

Considering that the diffusion process in the GP technique was avoided with a short application time, and unmeasurable resistance in the passive state for EIS was observed, the impedance by the diffusion process appeared to be restricted within the low-frequency range. However, a low-frequency tail representing the diffusion process was not confirmed or may have overlapped. This impedance was not always observed in previous studies [39,40]. Therefore, employing a Warburg impedance in the electrical equivalent circuit is difficult because an additional fitting error is involved when an uncertain value is employed.

From the electrochemical measurement, corrosion initiation was determined with empirical values, such as -350 mV vs. CSE for HP measurement and $1\text{--}2$ mA/m² for the polarisation resistance technique [23]. The time to the onset of corrosion for the 0.6OPC concrete was estimated using the corrosion potential and corrosion rate. Figure 13 shows an example of this phenomenon. Ohm's law was used to calculate the corrosion rate as follows:

$$I = \frac{B}{R_p}, \quad (2)$$

where I is the corrosion rate (mA/m²), B is the Stern–Geary constant, generally 26 mV in the active state (mV), and R_p is the polarisation resistance ($\Omega \cdot \text{m}^2$).

For simple calculations, B was set to 26 mV under both steel conditions. As shown in Figure 13, a slight discrepancy in the estimation of the corrosion initiation was observed. The results confirmed that the critical corrosion potential (-350 mV vs. CSE) for the 0.6OPC concrete is valid for detecting the corrosion of steel, and the GP technique is practical. However, owing to the limited results, the corrosion initiation time from the electrical equivalent circuit differed; however, the gap in the corrosion initiation time can be reduced by increasing the measurement time. In this study, the utilisation of the corrosion rate as a reference demonstrates a scientific corrosion detection approach; thus, a higher sensitivity for corrosion detection is expected. Therefore, from an engineering perspective, establishing a practical reference for detecting the corrosion of steel in concrete using electrochemical techniques is necessary.

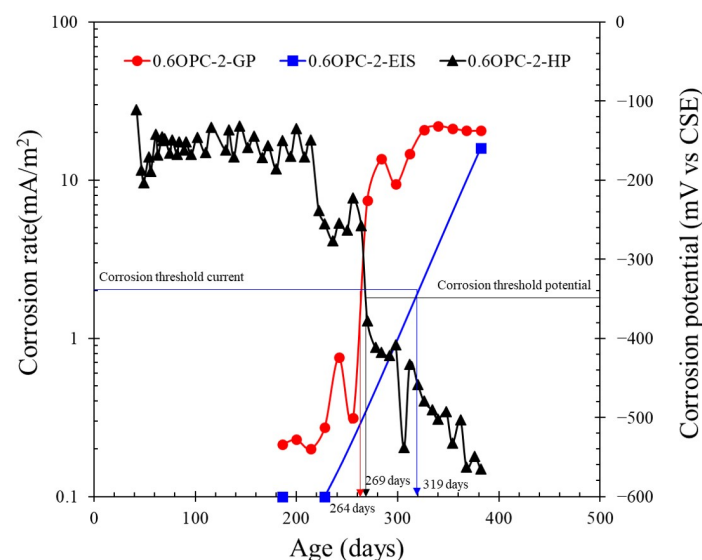


Figure 13. Example for estimation of time to corrosion initiation depending on electrochemical measurement.

5. Conclusions

This study evaluated the chloride-induced corrosion of steel in concrete as part of a performance-based method for evaluating the durability of concrete structures. Laboratory-based experiments were performed using electrochemical techniques with concrete samples

simulated in a marine structure. Consequently, the data from both techniques used in this study were proven to be comparable for estimating corrosion when possible error sources from the experimental conditions were excluded. In addition, the results confirmed that a simplified electrical equivalent circuit, rather than a complex one, is suitable for analysing the impedance data for EIS measurements. The following conclusions were drawn from the results of this study:

(1) The corrosion potential from the HP measurements and the time constant from the GP technique are valuable corrosion indicators owing to their rapid response and simple measurement; however, they are only qualitative and thus, additional experiments or analyses are necessary for quantifying the corrosion rate.

(2) The impedance response was confirmed to be more stable when using an internal counter electrode than when using an external counter electrode owing to the reduction in the experimental variables. Analysing the impedance data that are consistently sensitive to various variables is beneficial. Carbon steel, which is less resistant to corrosion, was used as the counter electrode, and its utility was confirmed.

(3) The results obtained from the EIS measurements were analysed with a simple equivalent electrical circuit, and the ohmic and polarisation resistances from the EIS were compared with those from the GP technique. The difference in the calculated time for each technique was observed to estimate the time to the onset of corrosion. Moreover, the results confirmed the feasibility of the analysis methods.

As previously discussed, EIS is an elaborate and sensitive technique for describing the corrosion process, whereas the GP technique is practical; therefore, this study demonstrated that the understanding of the corrosion process and the accuracy of the corrosion rate can be improved by enhancing the compatibility of both techniques. However, these techniques have the following limitations for elaborate applications: (1) quantification of the polarised area [41]; (2) quantification of impedance related to the diffusion process [42]; (3) sensitivity of measurements, such as the geometry factor [43]. Further studies are necessary under the aforementioned conditions.

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