

Article

Quantitative Characterization of Passivation Process of Steel Reinforcement in Concrete towards Durability against Anticorrosion Based on Electrochemical Methods

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Abstract: The passivation behavior of steel reinforcements in concrete is significantly influenced by the environment, concrete pore solution, and the passive film formed on the steel surface. The present study used electrochemical methods to successfully characterize the passivation process of steel reinforcements in concrete. The passivation behavior of commonly used HRB400 steel reinforcement material in concrete was studied using various electrochemical parameters quantitatively. As the soaking test time increased, the OCP gradually increased and stabilized after 5 days, indicating that the steel electrode transitioned from an active state to a passive state in the simulated liquid environment of concrete. The steel reinforcement developed a protective passive film that reduced its tendency to corrode. According to EIS, after soaking for one day, the steel electrode showed significant early passivation, indicated by an increase in its arc diameter. The WE arc gradually increased in the first 5 days of immersion, suggesting dynamic passive film formation and development. Beyond 5 days, the passive film stabilized with minimal further changes in its impedance spectrum, indicating carbon steel electrode passivation. The working electrode's impedance increased significantly on the fifth day, and gradually increased slightly after 10 days, indicating comprehensive coverage by the oxide film. Attributed to the growth and development of the oxide film, the electrode resistance reached a relatively stable state after the fifth day. The shift in corrosion potential offers an indication of the level of passivation of the steel reinforcements. The decrease in the anode Tafel slope and increase in the corrosion potential indicate the formation and stabilization of an oxide film on the steel surface, which is beneficial for its long-term durability in concrete structures. By analyzing the OCP, EIS, and dynamic potential polarization curve method data, it is possible to gain insights into the passivation behavior of steel reinforcements in concrete structures. This study aims to provide a basis for optimizing the corrosion protection of steel reinforcements in concrete structures. The significance of this study lies in a deep understanding of the passivation behavior of steel bars in concrete, providing a theoretical basis for improving the durability and lifespan of steel bars in concrete structures.



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1. Introduction

Concrete has long been a stalwart of construction, renowned and widely used as a reliable and durable building material [1–3]. For decades, it has been a crucial component in a wide array of civil engineering projects, including bridges, roads, skyscrapers, and dams [4,5]. The strength and stability that it provides for these structures are unparalleled. Steel reinforcement, an integral part of concrete's composition, significantly adds to its overall strength and durability [6,7]. The presence of steel reinforcement converts concrete into a versatile and highly resistant material capable of withstanding heavy loads and

extreme environmental conditions [8,9]. However, in a corrosive environment, a steel reinforcement within concrete is highly susceptible to corrosion. The corrosion of a steel reinforcement can lead to structural failure, weakening the overall integrity of the concrete. As time passes, this corrosion can spread, causing the concrete to crack and crumble [10–12]. To prevent such structural decay, it is crucial to quantitatively characterize the passivation process of steel reinforcement in concrete.

The passivation process refers to the formation of a protective layer on the surface of steel, which primarily consists of an oxide film [13]. This film not only prevents direct contact between the steel and the corrosive environment but also acts as a diffusion barrier, further retarding the corrosion process [14]. Electrochemical methods have become a popular tool for studying the passivation process of steel in concrete. These methods are easy to implement and provide quantitative data that can be used to assess the condition of steel reinforcements within concrete [15–18]. Techniques such as potentiodynamic polarization scans, electrochemical impedance spectroscopy (EIS), and linear polarization resistance (LPR) have been widely used to study the passivation process [19–21]. Each method has its own advantages and limitations, but together, they provide a comprehensive understanding of the process. Potentiodynamic polarization scans allow for the determination of the corrosion potential and corrosion rate by scanning the potential of a steel reinforcement in a controlled manner. This method provides a dynamic picture of the corrosion behavior of steel in concrete, enabling engineers to identify areas that may be susceptible to corrosion. EIS is an impedance-based technique that measures the capacitance and impedance of the oxide film on a steel reinforcement. It offers insights into the structure and integrity of the passivation layer, allowing engineers to assess its effectiveness in protecting the steel from corrosion. LPR is a semi-empirical method that quantitatively characterizes the passive film on steel by measuring the charge-transfer resistance at the steel/electrolyte interface. It provides a direct assessment of the condition of the passive film on the steel reinforcement, enabling engineers to identify any defects or areas of corrosion. The electrochemical methods used are destructive in nature, and this needs to be known, especially when used to characterize the corrosion behavior of a material in a given environment.

The passivation of steel bars is an electrochemical behavior, so electrochemical testing techniques can be used to detect and analyze the passivation state and behavior of steel bars. Jin et al. examined the passivation and depassivation properties of Cr–Mo corrosion resistance (CR) steel in a simulated concrete pore solution, finding that the corrosion resistance steel completes passivation faster than ordinary carbon (LC) steel and has higher corrosion resistance [22]. The passive film is mainly composed of metal oxides or hydroxides. The growth of the passive film was divided into four steps, and the theoretical thickness of the CR steel was thinner than that of the LC steel. Li et al. examined the impact of the rust layer on the passivation and corrosion of Q235b carbon steel in a simulated concrete pore solution, revealing that pre-rusted steel can reach a passive state under high pH conditions without chloride ions but forms a poorer passive film compared to finely polished steel. The removal of the outer rust layer enhances the pitting corrosion potential. Rust layer reactions with hydrogen ions inhibit pitting initiation, while consuming corrosive agents retards pit area expansion [23]. Yao et al. evaluated 304 types of stainless steel's natural passivation ability and chloride-induced corrosion behavior in alkaline concrete pore solutions containing red mud and fly ash. The synergistic effect of these solid wastes formed a passive film with high corrosion resistance to chloride attack. Chloride-induced corrosion mechanisms were proposed, offering insights into designing high-durable and low-carbon concrete in marine environments [24]. Ji et al. characterized the passive film, critical chloride threshold, and depassivation mechanism of HPB335 carbon steel in various solutions using a Mott–Schottky analysis, the open-circuit potential, the linear polarization resistance, and a point defect model (PDM). The results showed that the passive film quality and aggressive ion threshold were mainly influenced by pH, with a strong correlation between the resistance and chloride threshold. PDM effectively predicted carbon steel passivation and depassivation in highly alkaline solutions [25]. Cai

et al. found that the passive film of B500 stirrups had a higher concentration of Fe^{2+} oxides at its first 2 nm depth, resulting in a better protective property than Fe^{3+} oxides and a higher chloride threshold value, making it more suitable for severe service environments than S275 stirrups [26]. Zhu et al. found that the primary passive film on 2507 super duplex stainless steel (SDSS) has superior corrosion resistance compared to the secondary passive film. This difference is due to the primary film having fewer defects, which results in a lower passive current density and higher polarization resistance [27]. Zheng et al. revealed that the addition of supplementary cementitious materials affected the Ca^{2+} concentration and pH value of concrete pore solutions, influencing the passivation of galvanized steel bars. The passive film in the saturated $\text{Ca}(\text{OH})_2$ solution showed the best protective properties, while no reaction occurred in solutions with lower Ca^{2+} concentrations at a pH of 12.5 [28]. Shi et al., who used EIS to study its passivation behavior in a simulated concrete pore solution (SCPS), found that the pitting corrosion resistance of passivated 00Cr10MoV steel is significantly higher than that of passivated 20MnSiV steel due to the formation of a protective passive film and dense Cr-bearing corrosion products [29]. Xu et al. found that the corrosion characteristics of HRB400 and HPB235 steel were exceedingly similar; the chloride threshold for HRB400 steel is smaller than that for HPB235 steel [30]. By providing a detailed analysis of these electrochemical methods and their application in characterizing the passivation process of steel reinforcement in concrete, the results could guide researchers and practitioners in selecting the appropriate techniques for their specific research or engineering applications. Furthermore, it highlights the need for further research in this field.

For HRB400 reinforcing steel (i.e., the main reinforcing steel in China), the present study built an electrochemical method-based multi-parameter system to characterize the passivation process of steel reinforcement in concrete, which aims to provide a basis for optimizing the corrosion protection of steel reinforcements in concrete structures. The passivation behavior of the commonly used HRB400 steel reinforcement material in concrete was studied quantitatively using various electrochemical parameters. This study will enable us to develop more effective strategies for preventing or mitigating corrosion-related issues in concrete structures, ensuring their long-term performance and durability.

2. Materials and Methods

2.1. Experimental Materials and Preparation

In this study, the commonly used grade HRB400 steel was utilized as the material for fabricating the working electrodes, the preparation process of which is shown in Figure 1a. A chemical composition analysis on the HRB400 steel sample was also performed, indicating 0.24% C, 0.77% Si, 1.57% Mn, 0.036% P, and 0.041% S by weight. The chemical composition of this batch of HRB400 steel complies with the composition control requirements of GB/T 1499.2-2018 for HRB400 steel [31]. The steel reinforcements were first polished to a smooth finish using a grinder and then cut into 1 cm-long sections, with one end serving as the working surface and the other end connected to a copper wire via welding. The welded steel reinforcements were then encapsulated using a layer of polytetrafluoroethylene (PTFE) to prevent any possible contact between the electrolyte and the copper wire. Prior to use, the working electrodes required sanding to prepare their surfaces. The working surfaces of the electrodes were gradually polished using sandpaper of grades 1000#, 1200#, 1500#, and 2000# until the surfaces were clean, uniform, and scratch-free. These surfaces were then cleaned using ultrasonic cleaning to remove any residual particles or contamination. The oxide layer on the polished working electrode surface was completely removed, leaving a mirror-like finish. To prevent moisture and other atmospheric components from rusting the bright working electrodes, they should be stored in a dryer for future use.

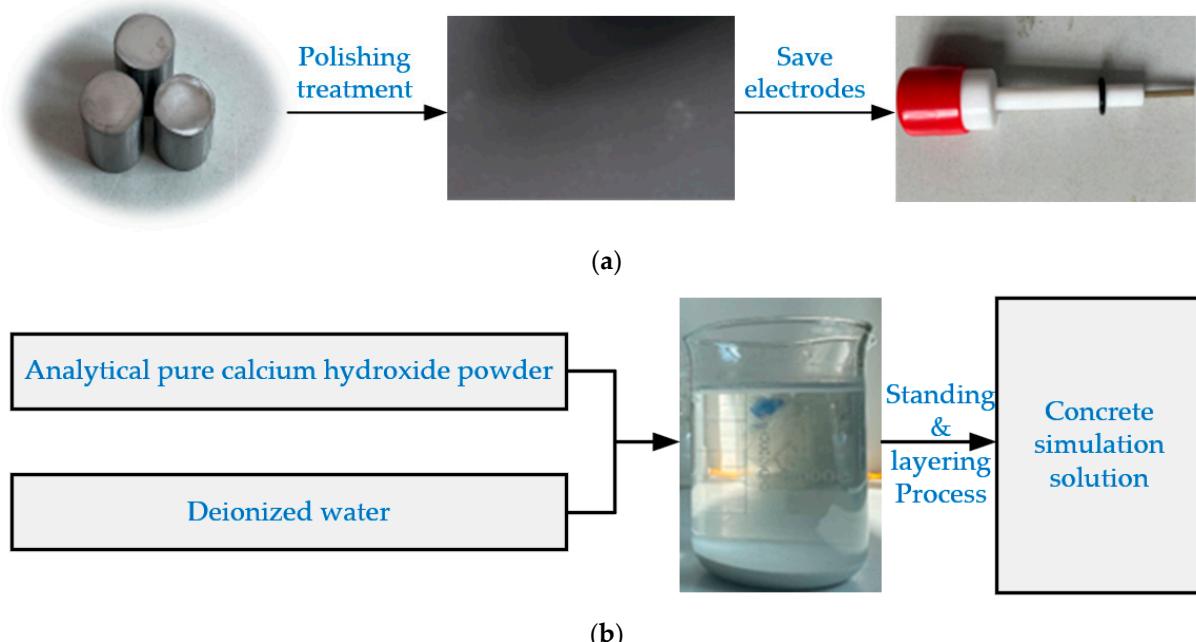


Figure 1. The experimental materials and preparation process: (a) HRB400 working electrode; (b) concrete simulation solution.

To enhance the practical engineering significance of studying the passivation characteristics for steel reinforcements in concrete, this study used $\text{Ca}(\text{OH})_2$ solution and deionized water to prepare an electrolyte in which the working electrode of the steel reinforcement was immersed to simulate the environment in which the steel reinforcement is located in concrete in actual engineering applications. The pH value of the prepared electrolyte was around 12.5, which is similar to that of a concrete solution. After standing for 24 h to ensure that the solution was stable, the mixture was filtered using quantitative filter paper to obtain the electrolyte, which was then sealed with clingfilm for future use. The concrete simulation solution was prepared by following the process in Figure 1b. The electrolyte solution prepared in this study can simulate the environment of steel reinforcements in concrete in actual engineering applications, providing a more accurate prediction of the passivation of steel reinforcement in concrete.

2.2. Experimental Procedures

This study utilizes electrochemical testing technology to investigate the passivation of steel reinforcements in concrete with a three-electrode system, consisting of a working electrode (WE), a reference electrode (RE), and a counter electrode (CE). This experiment selected the CS350H electrochemical workstation produced by Wuhan CORRTEST Co., Ltd. (Wuhan, China) for electrochemical testing. The experimental setup included a potentiostat/galvanostat, a three-electrode system, a stirrer, and a temperature controller. In this experiment, the WE was the HRB400 steel reinforcement, which was polished and cleaned before testing. The RE was the saturated calomel electrode (SCE), which was used to measure the potential of the working electrode accurately and stably. The CE was the platinum electrode, which was used to form a conductive circuit with the working electrode.

The experimental process involved several steps. First, the steel reinforcement was polished and cleaned, then placed in the electrolyte. The reference electrode and counter electrode were also immersed in the electrolyte. Second, the potentiostat/galvanostat was connected to the three-electrode system, and the temperature controller was set to the desired temperature. Third, the experiment began with a certain potential applied to the working electrode, and the current density was recorded at regular intervals. Fourth, the

open-circuit potential (OCP), electrochemical impedance spectrum (EIS), and dynamic potential polarization curve (DPPC) methods were used to test the passivation process of the steel reinforcements. Finally, after a certain period of time, the experiment was terminated, and the steel reinforcement was removed from the electrolyte for further analysis. Figure 2 illustrates the electrochemical testing system and methods. It should be noted that the electrochemical testing system needed to be maintained with an alkaline solution during the long-term tests, in which the solution was refreshed periodically and covered with plastic wrap to protect it from interactions with the atmosphere such as carbonation and evaporation.

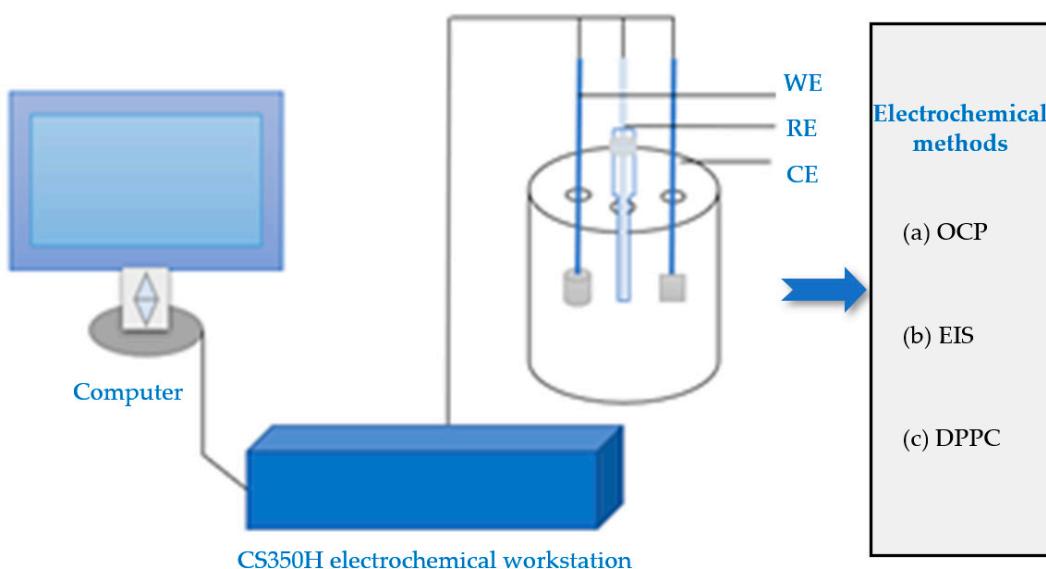


Figure 2. The electrochemical testing system and methods.

The open-circuit potential (OCP) method involves measuring the potential of the working electrode in open-circuit conditions over time. For the OCP test, the test system should monitor the OCP for at least 30 min to ensure that the OCP remains at a relatively stable value, which is similar to the previous study [32]. Electrochemical impedance spectroscopy (EIS) is an important electrochemical method for studying electrode reaction kinetics, with a larger measurement frequency range. Following the previous study [33], in this study, based on the fact that a 10 mV sine wave signal and a 0.335 V potential difference were applied, the EIS test was carried out in a frequency range of 10^{-2} Hz to 10^5 Hz and fitted by ZView software 3.0a version using the least-squares method. Then, the parameters of each equivalent component in the equivalent circuit diagram can be obtained. In addition, similar to the previous study [34], the potentiodynamic polarization method was conducted at a potential scan rate of 0.167 mV/s in a range of 0.25 V. The Tafel dynamic potential polarization curve method involves using the dynamic potential scanning approach to scan the Tafel region of the working electrode and obtain the Tafel polarization curve of that electrode.

3. Results and Discussion

3.1. Characterization of Steel Reinforcement Passivation Based on Open-Circuit Potential

The passivation process of steel reinforcements in concrete is a crucial aspect of corrosion protection as it aims to reduce the exposure of the steel to corrosive agents, such as water and oxygen, and enhance the longevity of the structure. This electrochemical process involves the movement of ions in the electrolyte surrounding the steel reinforcements in the same direction, effectively making the entire structure behave as an electrical conductor. Electrochemical testing is a commonly used method to quantitatively measure the corrosion status of steel reinforcements, primarily by assessing the current intensity on the surface

of these steels. The OCP test is one of the key electrochemical tests for a more qualitative assessment of the corrosion behavior and corrosion protection of steel in a given environment because the potential value is influenced not only by the anodic process (passivation) but also by the cathodic depolarization reaction. In this study, OCP measurements were taken on the working electrode, which was a HRB400 steel reinforcement, in a simulated concrete solution. The results of this test are presented in Figure 3.

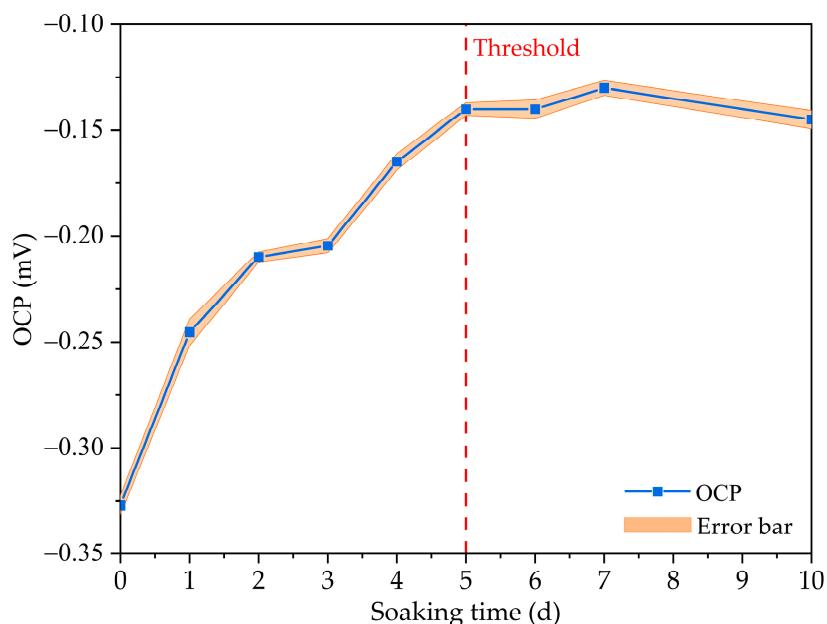


Figure 3. The variation law of the OCP during the passivation process of steel reinforcements in concrete.

Figure 3 clearly shows that the OCP variation of the steel electrode in the concrete simulation solution is noteworthy. As the soaking test time increases, the OCP gradually increases and stabilizes after 5 days. This trend indicates that the steel electrode transitions from an active state to a passive state in the simulated liquid environment of concrete. At 0 days, the OCP of the steel electrode is -310 mV. From the fifth day onwards, the amplitude of the OCP stabilizes at -140 mV and tends to remain constant. The OCP observation with time suggests that the steel reinforcement develops a protective passive film that reduces its tendency to corrode. This passive film is believed to be primarily composed of corrosion products such as iron oxides and/or surface deposits (such as CaCO_3 or calcium oxide CaFe_2O_4 , etc.). The gradual stabilization of the OCP after 5 days indicates that a relatively stable and protective passive film was formed on the steel surface, reducing its exposure to corrosive agents. Furthermore, it can also be inferred from Figure 3 that there is a correlation between the soaking time and the potential increment of adjacent days. As time progresses, the potential increment of adjacent days gradually decreases, indicating that the steel electrode transitions from an active state to a passive state in the simulated liquid environment of concrete. This observation supports the notion that a protective passive film forms on the steel surface with increasing time. Taken together, these results provide valuable insights into the passivation process of steel reinforcements in concrete. Specifically, they suggest that after an initial passivation period (0–5 days), the steel reinforcement enters a passive state where a protective film forms on its surface, significantly reducing its tendency to corrode. These findings have important implications for optimizing corrosion protection strategies for steel reinforcements in concrete structures. For example, coating protection methods can be used, such as applying anticorrosion coatings, to enhance the protective effect of the oxide film to a certain extent.

3.2. Characterization of Steel Reinforcement Passivation Based on Electrochemical Impedance Spectrum

Electrochemical impedance spectroscopy (EIS) is a powerful testing technique that has been widely used to evaluate the passivation behavior of steel in concrete. This method allows for the determination of the impedance spectrum of steel electrodes after soaking in concrete simulation solution for different times. By analyzing the changes in impedance, it is possible to assess the corrosion resistance and passive film stability of steel in concrete. Figure 4 presents the working electrode impedance spectra (Nyquist plots) after soaking for 0–10 days in the concrete simulation solution. Each spectrum represents the impedance response of the steel electrode at a given soaking time. The circular arc shape observed in the Nyquist plots indicates that the impedance response is dominated by a single time constant, which corresponds to the charge transfer process at the electrode/solution interface. The diameter of the arc represents the polarization resistance of the working electrode, which is a measure of its corrosion resistance. As the soaking time of the concrete simulation solution increases, the polarization resistance of the working electrode increases, indicating a more stable passive film. This observation suggests that the steel electrode becomes increasingly resistant to corrosion as it ages in the simulated concrete pore solution.

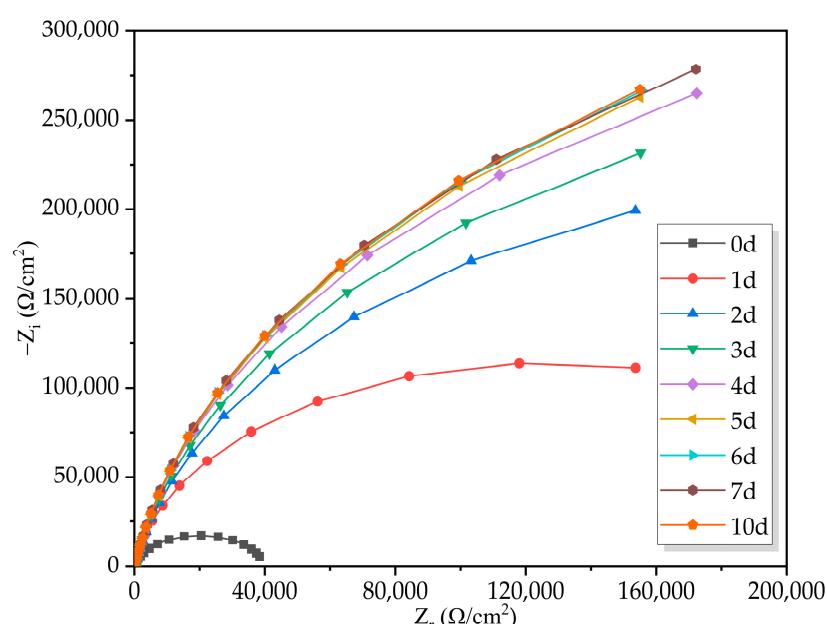


Figure 4. The EIS curve during the passivation process of steel reinforcements in concrete.

After soaking in the concrete simulation solution for 1 day, a significant increase in the diameter of the arc is observed. This change indicates that the steel electrode has already undergone significant passivation in the early stages of soaking. The impedance spectrum capacitance arc of the working electrode gradually increases and shows significant changes in the first 5 days of soaking. This observation suggests that the formation and development of the passive film on the steel surface are dynamic processes that occur within this time frame. However, when soaked for more than 5 days, the capacitance arc diameter of the working electrode remains large, and no significant changes occur. This indicates that the carbon steel electrode undergoes passivation in the simulated concrete pore solution for 5 days. Beyond this time point, the passive film stabilizes, and further changes in the impedance spectrum are minimal. These findings have important implications for assessing the corrosion resistance and passive film stability of steel in concrete. For example, the alkalinity of concrete can be maintained by using cement with a higher alkalinity or by adding a certain proportion of alkaline additives to form a passivation film that protects the surface of steel bars. The use of EIS as a testing technique provides a convenient and

effective means to evaluate the passivation behavior of steel reinforcements in concrete structures. By analyzing the changes in impedance spectra, engineers can gain insights into the corrosion resistance of steel and ensure its long-term performance in concrete structures.

To quantitatively analyze the results of EIS experiments and further investigate the passivation behavior of HRB400 carbon steel in simulated pore fluids of concrete, experts and scholars have proposed the use of an equivalent circuit method. By selecting appropriate equivalent circuit models, electrochemical kinetic processes and reaction mechanisms can be better characterized and quantified. During the passivation process, a capacitive circuit is formed on the surface of the steel electrode, as shown in Figure 5. An equivalent circuit with a single time constant can be used to fit all the EIS data. In this circuit, R_s represents the solution resistance, R_f and the constant phase angle element (CPE_f) are the passive film resistance and constant phase element of the passive film, respectively, R_{ct} is the charge transfer resistance through the passive film, and the constant phase angle element (CPE_{dl}) can be used to reveal the deviation of the ideal passivation film capacitor caused by surface roughness, in which the double-layer capacitance parameters on the working electrode surface are Q_{dl} and n_{dl} . The use of ZView software allows for the fitting of experimental data curves and the extraction of the fitting values for each circuit component in the equivalent circuit model of the test system. This approach provides a more accurate and reliable means of analyzing EIS data and understanding the electrochemical behavior of carbon steel in simulated pore fluids of concrete. With the help of an equivalent circuit analysis, scholars and experts can gain insights into the passivation behavior of carbon steel and take appropriate measures to enhance its corrosion resistance and durability in concrete structures.

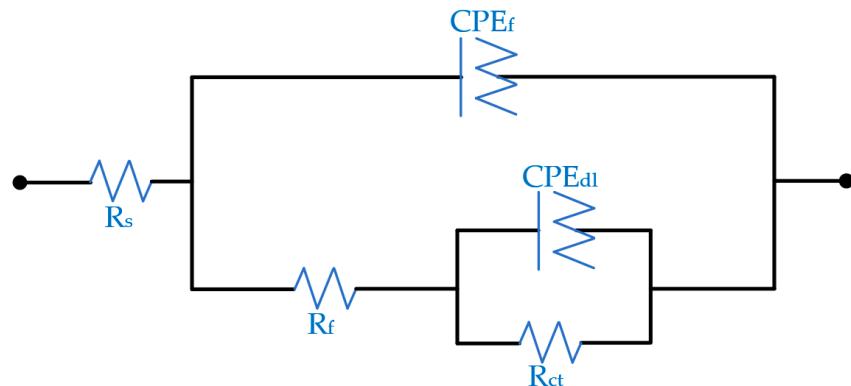


Figure 5. The electrochemical equivalent circuit diagram.

As the steel electrode undergoes a soaking test in the concrete environmental solution, a dense oxide film gradually forms on the surface of the electrode. This oxide film plays a crucial role in protecting the steel from corrosion and is considered a passivation layer. From the perspective of the entire electrochemical system, the Helmholtz double layer, which is located between the passivation film and the electrolyte, is in contact with the surface of the oxide film. It is noteworthy that the thickness of this oxide film is significantly greater than that of the Helmholtz double layer (typically, the carbon steel oxide film thickness is about 1 nm, while the Helmholtz double layer thickness is about 0.1 nm [35]). This difference in thickness implies that during impedance spectroscopy testing, the potential signal is predominantly determined by the properties of the oxide film. In other words, the oxide film resistance (R_f) contributes to almost all of the overall polarization resistance (R_p). This observation is further supported by the experimental data obtained from the EIS testing during the passivation stage of carbon steel in the simulated pore fluids of concrete, which are summarized in Table 1. Table 1 presents a comprehensive analysis of the EIS test results, providing insights into the electrical and kinetic properties of the oxide film formed on the carbon steel during its passivation process in the simulated pore fluid environment.

By quantitatively analyzing these data, researchers can gain valuable information on the passivation behavior of carbon steel and take appropriate measures to enhance its corrosion resistance and durability in concrete structures.

Table 1. The electrochemical parameters of steel reinforcement passivation tested by EIS.

Passivation Time (d)	R_s ($\Omega \cdot \text{cm}^2$)	CPE _f		R_f ($\text{k}\Omega \cdot \text{cm}^2$)	CPE _{dl}		R_{ct} ($\text{k}\Omega \cdot \text{cm}^2$)	R_p ($\text{k}\Omega \cdot \text{cm}^2$)
		Q_f ($\mu\text{F} \cdot \text{s}^n$)	n_f		Q_{dl} ($\mu\text{F} \cdot \text{s}^n$)	n_{dl}		
0	43.32	4.81×10^{-11}	0.909	39.967	5.76×10^{-11}	0.935	0.095	40.105
1	51.08	4.06×10^{-11}	0.932	217.96	3.57×10^{-11}	0.873	38.317	256.328
2	56.10	3.90×10^{-11}	0.915	378.00	3.40×10^{-11}	0.830	230.290	608.346
3	62.47	3.71×10^{-11}	0.919	468.82	3.10×10^{-11}	0.816	407.000	875.882
4	143.90	3.34×10^{-11}	0.923	546.02	2.86×10^{-11}	0.829	431.150	977.314
5	76.37	3.55×10^{-11}	0.921	600.37	3.15×10^{-11}	0.846	475.360	1075.806
6	76.24	3.57×10^{-11}	0.917	604.85	2.97×10^{-11}	0.882	449.170	1054.096
7	175.4	3.29×10^{-11}	0.924	599.12	2.83×10^{-11}	0.837	465.310	1064.605
10	82.81	3.52×10^{-11}	0.921	619.07	3.13×10^{-11}	0.847	505.560	1124.713

Based on the data presented in Table 1, it is evident that as the soaking test progresses, the working electrode experiences a significant increase in impedance, from approximately $40 \text{ k}\Omega \cdot \text{cm}^2$ on the first day to approximately $1000 \text{ k}\Omega \cdot \text{cm}^2$ on the fifth day. This increase is a direct result of the formation of a protective oxide film on the steel electrode surface, which serves to hinder the corrosion process. When the soaking period extends to the tenth day, the electrode resistance remains above $1000 \text{ k}\Omega \cdot \text{cm}^2$ and gradually increases slightly, indicating that the oxide film has achieved comprehensive coverage on the steel surface. This gradual increase in electrode resistance is attributed to the growth and development of the oxide film, which becomes thicker and more uniform over time. The observation that the electrode resistance reaches a relatively stable state after the fifth day highlights the significance of the protective oxide film in safeguarding the steel electrode from corrosion. The film's ability to establish a high-impedance barrier effectively curtails further corrosion reactions. It is noted that the 7-day R_s value is about 2–3 times the 3-day R_s value, which may be attributed to the difference in electrode spacing. Figure 6 presents the variation pattern of the electrode resistance with time during the passivation process. Notably, this pattern is consistent with the variation pattern of the open-circuit potential. After an initial increase in impedance, a relatively stable state is reached after the fifth day. This observation further validates the assertion that the protective oxide film on the steel electrode surface achieves a stable state that provides effective corrosion protection. Overall, these results suggest that as the soaking test progresses, the steel electrode's passivation process—marked by the formation and growth of an oxide film—contributes significantly to an increase in the electrode impedance and resistance. By extension, this passivation process provides a reliable protective layer that guards against corrosion, promoting the long-term stability and durability of steel components in concrete structures.

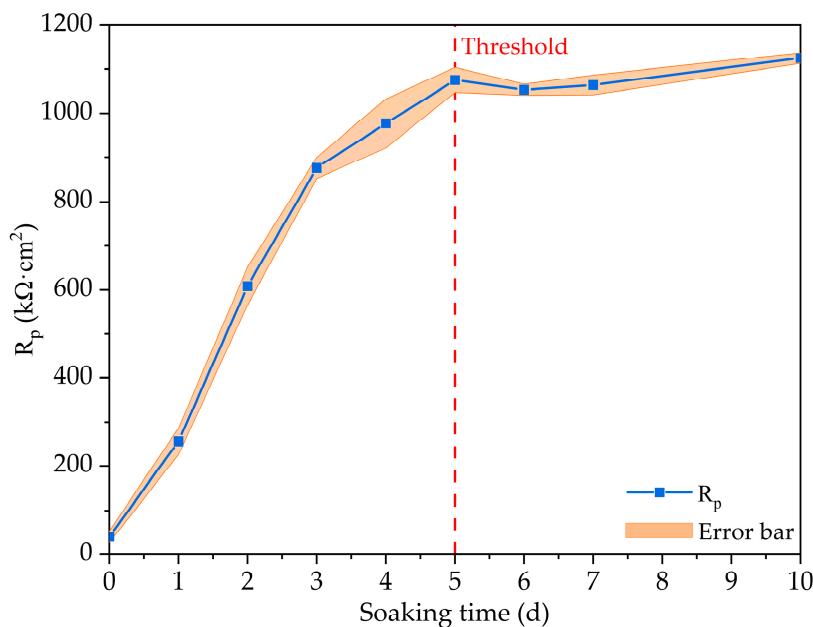


Figure 6. The variation law of polarization resistance during the passivation process of steel reinforcements in concrete.

3.3. Characterization of Steel Reinforcement Passivation Based on Dynamic Potential Polarization Curve

The analysis of the polarization curves allows for an examination of the relationship between the electrode potential and the current density within a material system, providing crucial information about the corrosion behavior of the material. The polarization potentiodynamic method in this case was used to show what the behavior of the material is in the anodic region. Through kinetic parameters, what is the resistance of the material and whether there is a region of passivity under certain conditions can be understood. Thus, electrochemical polarization curve tests were conducted on the simulated solution of concrete in the soaking test to analyze the passivation process of steel reinforcements. By utilizing the electrochemical dynamic potential polarization method, a polarization curve of the steel electrode versus soaking time was obtained, as shown in Figure 7. Observing Figure 7, it is evident that the shift in the corrosion potential, E_{corr} , offers an indication of the level of passivation of the steel reinforcements. As the corrosion potential progressively moves in the positive direction, it indicates that the passivation film on the surface of the steel reinforcement electrode is forming and maintaining stability. Research by relevant scholars has shown that, compared to saturated calomel electrodes, the critical corrosion potential of steel electrodes is approximately -0.275 V [36]. This research also showed that when the corrosion potential falls below this threshold, steel exhibits significant corrosion activity, with a corrosion probability exceeding 90%. Furthermore, the self-corrosion current density, i_{corr} , can be used to evaluate the passivation rate of steel reinforcements. When the corrosion current density is low, it indicates that the passivation film of steel reinforcements tends to stabilize. The critical corrosion current density of steel reinforcements in concrete is approximately $0.2 \mu A/cm^2$, corresponding to the critical corrosion potential. These findings suggest that electrochemical polarization curve testing can effectively assess the passivation status and corrosion risk of steel reinforcements in concrete structures. By monitoring these key parameters, engineers and researchers can gain insights into the behavior of steel reinforcements in concrete and take appropriate measures to mitigate corrosion-related issues.

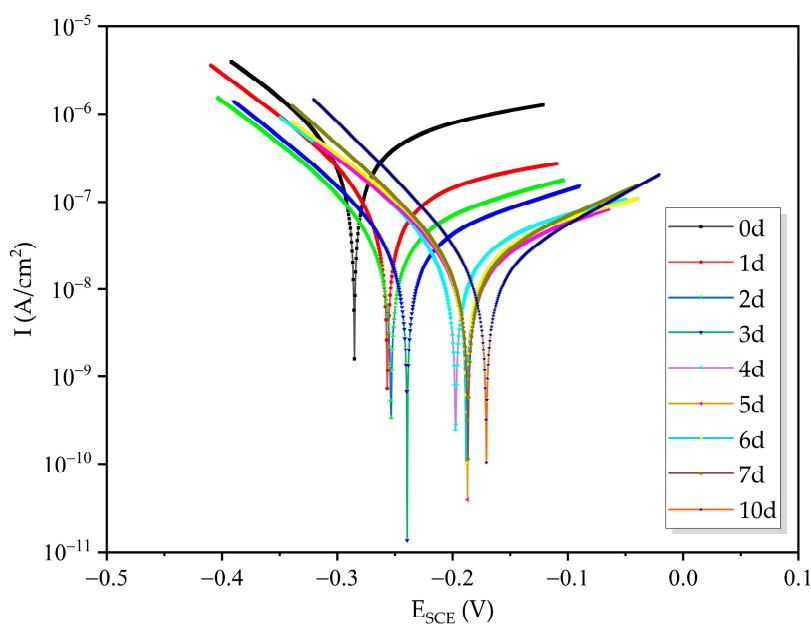


Figure 7. The dynamic potential polarization curve during the passivation process of steel reinforcements in concrete.

In Figure 7, the corrosion potential (E_{corr}) of the steel electrode is significantly higher than -0.275 V, which suggests that the steel electrode gradually forms an oxide film and remains stable in the simulated concrete environment. To provide a more detailed quantitative analysis of the passivation situation on the surface of the steel reinforcements, the Tafel polarization curve parameters of the working electrode were fitted using the extrapolation method. These parameters include the anode Tafel slope (b_1), the cathode Tafel slope (b_2), the Stern–Grey coefficient (B value), the working electrode self-corrosion current density (i_{corr}), and the corrosion potential (E_{corr}), which are presented in Table 2. The anode Tafel slope (b_1) parameter reflects the anodic reaction rate on the steel surface, while the cathode Tafel slope (b_2) parameter characterizes the cathodic reaction rate. The self-corrosion current density (i_{corr}) parameter reflects the degree of corrosion activity on the steel surface, with lower values indicating lower corrosion activity. Finally, the corrosion potential (E_{corr}) parameter represents the thermodynamic tendency towards corrosion, with a more positive value indicating a lower corrosion tendency. By analyzing these parameters, it is possible to quantitatively evaluate the passivation status and corrosion risk of steel reinforcements in concrete structures. This information can guide engineers and researchers in developing appropriate strategies to mitigate corrosion-related issues and ensure the long-term durability of concrete structures.

Table 2. The Tafel curve parameters of steel reinforcement passivation.

Passivation Time (d)	b_1 (mV/Decade)	b_2 (mV/Decade)	B (mV/Decade)	i_{corr} (μ A/cm ²)	E_{corr} (V)
0	512.86	128.59	44.64	0.6292	-0.2853
1	562.29	111.16	40.30	0.1513	-0.2566
2	316.25	105.66	34.39	0.0596	-0.2535
3	267.34	98.49	31.25	0.0420	-0.2394
4	326.57	109.95	35.72	0.0382	-0.1974
5	249.58	107.09	32.54	0.0276	0.1872
6	289.43	108.56	34.28	0.0338	-0.1883
7	181.52	88.40	25.81	0.0237	-0.1867
10	144.63	78.69	22.13	0.0185	-0.1708

Table 2 shows that as the soaking test time increases, the anode Tafel slope (b_1) significantly decreases. This indicates that the oxide film on the carbon steel working electrode gradually forms and tends to stabilize, which is consistent with the results in the previous study [34]. The corrosion potential (E_{corr}) increases and is much higher than -0.275 V, indicating that the passivation film on the surface of the steel reinforcement electrode is forming and maintaining stability. When the passivation film stabilizes, the anode reaction activity of the steel working electrode significantly decreases. According to study [25], when a uniform and dense oxide film is formed on the surface of carbon steel, the corrosion current density on its surface will stabilize at $0.1 \mu\text{A}/\text{cm}^2$. Figure 8 shows the variation trend of the self-corrosion current density (i_{corr}) obtained by fitting a Tafel curve during the passivation process. As shown in the figure, the self-corrosion current undergoes a sudden change from $0.6292 \mu\text{A}/\text{cm}^2$ in the first three days of the soaking test to $0.1 \mu\text{A}/\text{cm}^2$. This suggests that after 3 days of the soaking test, the dynamic parameters of the oxide film are basically stable, but they become even more stable after 5 days. These results provide important insights into the passivation process of carbon steel in a simulated concrete environment. The decrease in the anode Tafel slope and increase in the corrosion potential observed with the increasing soaking time indicate the formation and stabilization of an oxide film on the steel surface. This suggests that the steel reinforcement electrode becomes increasingly passive as time passes. The stabilization of the oxide film is accompanied by a significant decrease in the anode reaction activity of the steel working electrode, which is beneficial for its long-term durability in concrete structures. This information can guide engineers and researchers in developing appropriate strategies to mitigate corrosion-related issues and ensure the long-term durability of concrete structures. For example, cathodic protection technology can be used to make steel bars become the cathode of a battery through external currents, thereby suppressing the occurrence of corrosion reactions.

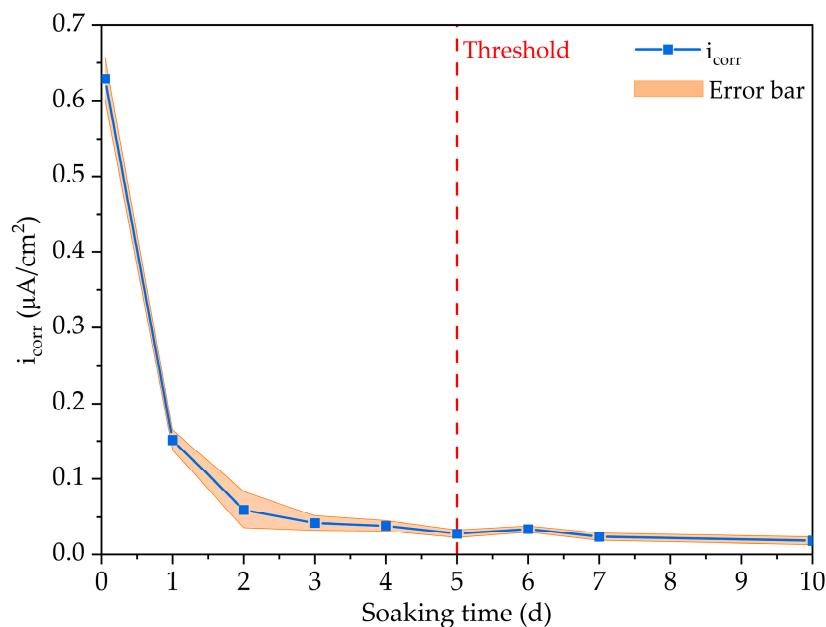


Figure 8. The variation law of the corrosion current density during the passivation process of steel reinforcements in concrete.

4. Conclusions

The present study successfully characterized the passivation process of steel reinforcements in concrete using electrochemical methods. The results indicate that the passivation behavior of steel reinforcements in concrete is significantly influenced by the environment on the steel surface and the soaking time.

- (1) As the soaking test time increased, the OCP gradually increased and stabilized after 5 days, indicating that the steel electrode transitioned from an active state to a passive state in the simulated liquid environment of concrete. The steel reinforcement developed a protective passive film that reduced its tendency to corrode.
- (2) After soaking for one day, the steel electrode showed significant early passivation, indicated by an increase in arc diameter. The EIS arc of the WE gradually increased in the first 5 days of soaking, suggesting dynamic passive film formation and development. Beyond 5 days, the passive film stabilized with minimal further changes in its impedance spectrum, indicating carbon steel electrode passivation.
- (3) The working electrode's impedance increased significantly on the fifth day and gradually increased slightly after 10 days, indicating comprehensive coverage by the oxide film. Attributed to the growth and development of the oxide film, the electrode resistance reached a relatively stable state after the fifth day.
- (4) The shift in corrosion potential offers an indication of the level of passivation of steel reinforcements. The decrease in the anode Tafel slope and increase in the corrosion potential indicate the formation and stabilization of an oxide film on the steel surface, which is beneficial for its long-term durability in concrete structures.

In conclusion, the present study provided a comprehensive understanding of the passivation process of steel reinforcements in concrete. By analyzing the OCP, EIS, and dynamic potential polarization curve method data, it is possible to gain insights into the passivation behavior of steel reinforcements in concrete structures, which provides a basis for optimizing the corrosion protection of steel reinforcements in concrete structures. However, further research under dangerous conditions, including different pH values as well as the influence of ions that break the passive state, is needed to optimize the passivation process. The composition of the corrosion products as a result of their interaction with the environment should be analyzed, and corrosion-resistant materials suitable for concrete should be developed accordingly, which would enhance its long-term stability under various environmental conditions.

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