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Electrochemical Evolution of Carbon Steel and Fe-9% Cr Steel Rebar in Simulated Concrete Pore Solution (SCPS) in the Presence of 3.5 wt% NaCl

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Abstract: Carbon steel rebar (ASTM A615) has been widely used in reinforced concrete (RC), but its susceptibility to chloride ions remains a critical issue. Low alloy chromium steel has been used to increase corrosion resistance and extend service life, such as in 9% Cr rebar (ASTM A1035-CS). In this work, we characterized two electrochemical systems over time: ASTM A615 and A1035-CS corrugated rebar immersed in SCPS in the presence of NaCl for 12 months. The interfacial processes evolution for the ASTM A1035-CS rebar for both general and local corrosion showed different active-passive responses from those of carbon steel. Because the 3.5% wt. NaCl exceeded the chloride threshold for passive breakdown of both materials, the ASTM A1035-CS showed a five-fold higher impedance and lower general corrosion rate. In localized conditions, the low alloy chrome content rebar showed less density localized attack than the ASTM A615 rebar. These results were attributed to the overall damage evolution involving the formation and stability of corrosion products over time. The local attack appeared to be a random spatial process due to changes in the local environment.

Keywords: reinforced concrete; rebar; long-term immersion; electrochemical



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1. Introduction

Carbon steel has been the preferred material for rebar in reinforced concrete (RC) structures to construct infrastructures in multiple environments. Increasingly harsh conditions, including chloride concentrations (from deicing chemicals), are introduced because of the exposure to environments with continuous weather cycling, thus affecting the structural capacity of RC structures, such as bridges [1]. A major cause of failure is deterioration, which is associated with the exposure of rebars to corrosive environments [2–5]. The ingress and accumulation of chlorides within the concrete matrix pose a critical threat to the integrity of the structures, owing to electrochemical reactivity. In addition, accumulated corrosion products can evoke a six times volume expansion that eventually initiates cracks across the concrete, thereby accelerating the ingress of chloride ions and material degradation [6]. The natural chemical composition of concrete material creates an alkaline environment, in which the rebar in concrete is protected by a passive film layer as a porous coating [5].

However, several factors, such as the poor corrosion resistance of rebar, cracks in concrete structures, and exposure to aggressive environments can cause this protection to fail, and lead to the onset of material degradation. Therefore, the study of rebar preservation and durability has provided several routes for corrosion control, and researchers have proposed various methods to improve the reliability and safety of RC structures in bridges. For example, studies have shown the benefits of applying mineral admixtures and cement replacement materials such as fly ash, silica fume, and blast furnace slag to improve corrosion resistance under saline environment [7–12]. Other studies have demonstrated improvements in concrete ductility with corrosion resistance additives such as polypropylene fibers [12,13]. Approaches have included protective coatings on rebars, such as fusion-bonded epoxy, ceramic coatings, and metallic coatings [14–16]. However, coatings

are susceptible to damage during preconstruction; therefore, their effectiveness may be limited. A viable concept may involve altering chemical composition of rebar materials to achieve better corrosion performance. Stainless steel, for example, has demonstrated their reliability when exposed to aggressive environment [17,18]. However, owing to its relatively high cost, the application of this material to bridges has not been feasible. Low Cr alloy steel has attracted attention because of its cost-effectiveness and previous studies have demonstrated improvements in corrosion resistance through decreasing the content of Cr [19–21]. Past studies have improved corrosion performance by using low alloying elements in rebar, such as chromium instead of carbon steel. Song et al. have reported a 40% decrease in the corrosion rate with only 0.86 wt% addition of Cr, thus suggesting strong relationship between Cr addition and corrosion reduction [21].

According to previous studies, the main benefits of low alloying steels include their relatively low cost, and better performance, thus substantially extending service life in a relatively aggressive environment [22–24]. Therefore, the concept of critical Cr content, i.e., the amount of Cr sufficient to form a Cr-based layer to effectively decrease corrosion, was proposed for low alloy steel [25–27]. This value has been suggested to be in the range of 3–4 wt% Cr. Wang et al. has demonstrated that low Cr steel with 2.42 wt% Cr has higher corrosion resistance than carbon steel after 200 days of exposure; the corresponding localized attack has also been found to show an improvement in corrosion resistance [24]. Mancio et al. have demonstrated that the critical component for improving the corrosion resistance of 9% Cr steel rebar is the formation of $\text{Cr}(\text{OH})_3$ in the passive film, thus reinforcing the contribution of Cr element [28]. Previous studies have focused primarily on general corrosion to evaluate the corrosion performance, whereas studies on localized attack are limited.

This work aimed at studying and comparing the overall and localized attack over 12 months via electrochemical methods. Two metallic rebar types (ASTM A615 and 1035-CS) were tested in SCPS with 3.5% wt NaCl. The 9% Cr steel rebar was selected in this study because its corresponding Cr content exceeded the critical Cr content, thus ensuring formation of a Cr-based protective layer. Through immersion tests with SCPS and continuous electrochemical monitoring, the interfacial reactions in real-time and in situ under steady-state conditions were characterized. The corresponding localized attack was observed by quantifying and characterizing the formation of local conditions and anomalies at different sites. Therefore, the influence of Cr content was quantified and characterized through observation of the depth magnitude and distribution during electrochemical testing. The purpose of this study was, therefore, to monitor the localized attack and overall surface evolution for both materials over time in long term exposure experiments.

2. Materials and Methods

The materials ASTM A615 (referred to as 615) and ASTM 1035-CS (referred to as 9% Cr) are good examples of the reinforced concrete rebar used for RC. They were immersed directly in SCPS with 3.5 wt% NaCl solutions under steady-state conditions for 12 months. Electrochemical and surface characterization methods were performed to analyze the overall and local behavior development over the testing period.

2.1. Materials

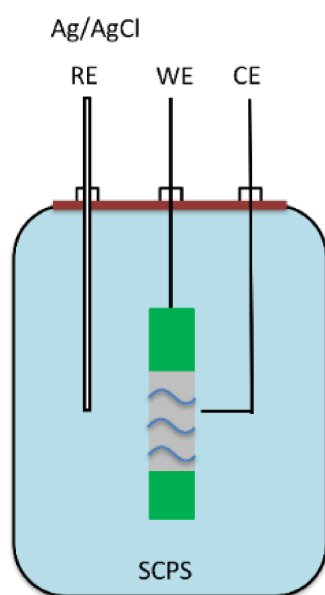
Two types of No. 5 rebar 6 inches in length with ~1.6 cm diameters were provided by the Commercial Metal Company (CMC). All rebar samples were first sandblasted to the SSPS-SP5/NACE No. 1 standard [29]. Then the samples were embedded in epoxy to expose a total area of approximately 25 cm². The chemical compositions of ASTM 615 and ASTM 1035 (9% Cr) steel rebars provided by CMC are presented in Table 1.

Table 1. Chemical compositions of ASTM 615 and ASTM1035 steel rebar (in wt%).

Rebar	C	Cr	Ni	Mo	Mn	P	S	Si	Cu	V	Sn	Al	N	Fe
ASTM A615	0.42	0.23	0.12	0.033	1.00	0.012	0.025	0.19	0.34	-	0.01	0.002	0.0045	Ba
ASTM1035-CS (9% Cr)	0.11	9.46	0.09	0.02	0.63	0.010	0.005	0.37	0.16	0.019	0.008	-	-	Ba

2.2. Experimental Setup

The typical three-cell electrochemical test is shown in Figure 1. A copper wire connected the tested steel sample as a working electrode; Ag/AgCl served as the reference electrode, and a platinum mesh as the counter electrode. Cyclic polarization from -0.1 V to 1.5 V to -0.1 V was performed to extrapolate the corresponding Tafel slope in a different set up to a potentiostat GAMRY 1000E instrument (Gamry Instruments, Warminster, PA, USA).

**Figure 1.** Configuration of a typical three-cell exposure test for rebar.

The samples were immersed in SCPS at room temperature with an initial pH of 12.9. The electrolyte contained 0.02 M NaOH, 0.08 M KOH, and saturated $\text{Ca}(\text{OH})_2$, and 3.5 wt% NaCl.

A total exposure time of 12 months was used to study the corrosion development of general corrosion and localized attack. Electrochemical tests, including linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS), were performed continuously.

2.3. Electrochemical Measurements

The electrochemical system included the following sequence of experiments: the rebar samples were immersed in SCPS, and the corresponding open circuit potential (OCP) was measured for 30 min to ensure that steady-state conditions had been reached, i.e., the fluctuation was within 10 mV for 10 min. Subsequently, the linear polarization resistance (LPR) test was performed from -0.015 V to 0.015 V vs. OCP with a scan rate of 0.167 mV/s. Then the sample was measured at OCP for 10 min and an EIS test was performed with a 10^{-2} Hz to 10^4 Hz frequency range with 10 mV amplitude. In a different setup, the cyclic polarization from -0.1 V to 1.5 V to -0.1 V was performed to extrapolate the corresponding Tafel slope. The slopes were generated on the basis of drawing tangential lines on the cathodic and anodic branches and performing linear fitting 50 mV above/below the corrosion potential with a linear regression coefficient greater than 0.98. All electrochemical tests were performed continuously up to 12 months of immersion.

The density used was 7.85 g/cm^3 [30]. The equivalent weight (EW) for 615 and 9% Cr rebar, calculated on the basis of the chemical compositions shown in Table 1, was 27.81 and 27.67, respectively.

2.4. Surface Characterization

After 2, 4, 8, and 12 months of immersion, the samples were retrieved and then scrubbed to remove all corrosion products, on the basis of ASTM standard G1-03 [31]. The samples were then cleaned with DI water and, ethanol, and air dried. The samples were then processed with a similar method to that in our previous work: they were observed under a microscope to assess the distribution of localized attack with the distance from a fixed reference point and, cut at that distance; the pits distributed in the cross section area were observed, as shown in Figure 2 [32]. An Olympus DXS 500 optical microscope (Olympus Corporation, Tokyo, Japan) was then used to identify the localized attack on the slides and the corresponding depth of the attack into the substrate.

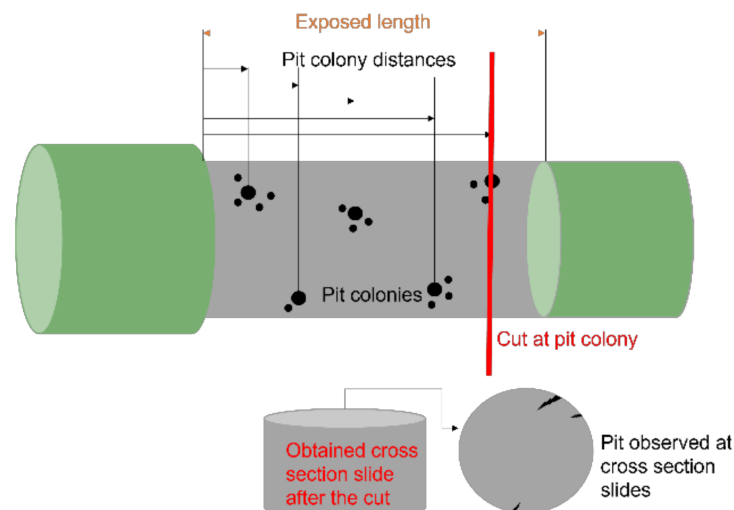


Figure 2. Schematic description of surface characterization [32].

3. Results and Discussion

SCPS provided an alkaline environment allowing the rebar to be in a passive state. Figure 3 shows the changes in pH values as a function of time. The solution started at a pH of approximately 12.9 in the initial stage. With time, under exposure to the room conditions, the pH values decreased significantly during 3 to 5 months, possibly because the formation of oxide at the metal/oxide interface and the dissolution of oxide at oxide/solution interface achieved steady state [33], or because of carbonatization [34]. The interaction between hydroxides in SCPS and carbon dioxide in the air formed precipitates such as calcium carbonate, thus depleting OH^- in SCPS and consequently decreasing the pH of the SCPS. A previous study has shown that the decreased pH promotes corrosion resistance by releasing more metal cations into the solution and increasing chromium in the film. In addition, carbonization enabled the solubility of iron species, thus resulting in the formation of the thicker protective film [23]. Therefore, it is expected to influence the bulk pH in the overall characterization process under long-term exposure.

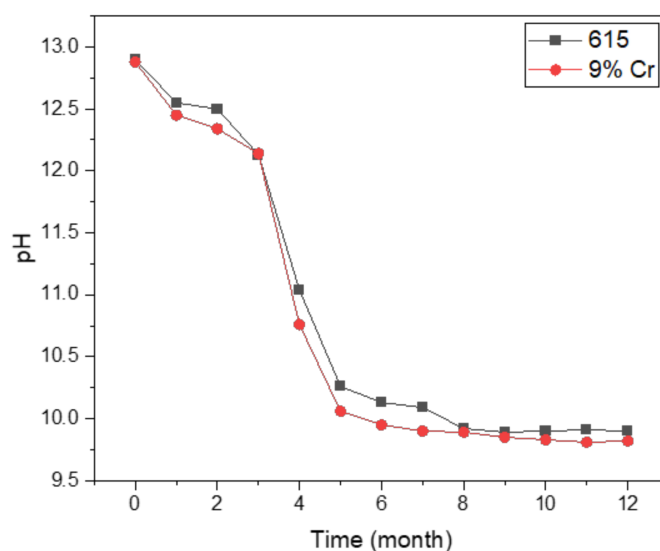


Figure 3. pH values of the solution during the immersion test.

3.1. OCP Analysis

The change in OCP values as a function of immersion time for both materials is shown in Figure 4. The potentials for each material exhibited relatively low fluctuations with a decreasing trend as immersion time increased. The low fluctuation could indicate that both materials were experiencing active dissolution. The decreasing trend could be due to the infiltration of chloride ions that cause the OCP to shift negatively [35]. For both materials, the OCP showed an increasing trend after 2 months of immersion, possibly because of the formation of porous rust layer. The Fe^{2+} ions might have contributed to the formation of the layer, which might have contained lepidocrocite ($\gamma\text{-FeOOH}$) on the top surface of the immersed material [36]. This layer provided some protection, corresponding to the observed increase in OCP. However, this protection was temporary and failed as the immersion time increased. The porous layer detached/dissolved, thus resulting in a loss of protection and a decrease in OCP after the increase. In a later stage of testing (after 8 months), the OCP values for 615 tended to be stable because the major corrosion products included non-protective lepidocrocite, whereas those for 9% Cr showed an increase and then stabilized at a higher OCP value, because the corrosion product included protective maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and Cr hydroxide, which provide better protection in addition to the lepidocrocite on the top surface [36]. Therefore, 9% Cr showed a higher OCP than 615 in general, in agreement with previous research indicating that the protective layer increases the OCP values, and therefore leads to better corrosion performance [37,38].

3.2. LPR Analysis

Figure 5 shows the cyclic polarization curves for ASTM 615 and ASTM 1035 steel immersed in SCPS with 3.5 wt% NaCl at a pH of approximately 12.9. Both materials exhibited similar behavior because no passive region was observed. Therefore, localized attack was expected under this aggressive environment. The findings corroborated that the chloride threshold was below the NaCl concentration used herein. Hurley et al. have studied the active-passive transition for carbon steel and 9% Cr rebar in different NaCl concentrations and found that passive region was no longer present [39]. The active region dominated when more than 0.5 M NaCl was present in the solution for both materials. At 0.6 M NaCl, the conditions exceeded the threshold for passive to active transition. As shown in Figure 5, sample 615 showed a decreased corrosion potential, indicating greater susceptibility to corrosion, whereas sample 9% Cr was less susceptible. In addition, 9% Cr demonstrated a decreased corrosion current density, based on the shift in anodic curve. The positive hysteresis also confirmed that both materials were subjected to localized corrosion. Additional polarization testing was performed to estimate the Tafel slopes,

and Equations (1) and (2) were used to estimate the corrosion rate. Previous studies have reported the value $B = 26$ mV for the active state and $B = 52$ mV for the passive state for steel in concrete conditions [40,41]. The corresponding Tafel slopes calculated for 615 based on potentiodynamic data were consistent with the previous findings. The Tafel slopes for 9% Cr steel and 615 are summarized in Table 2.

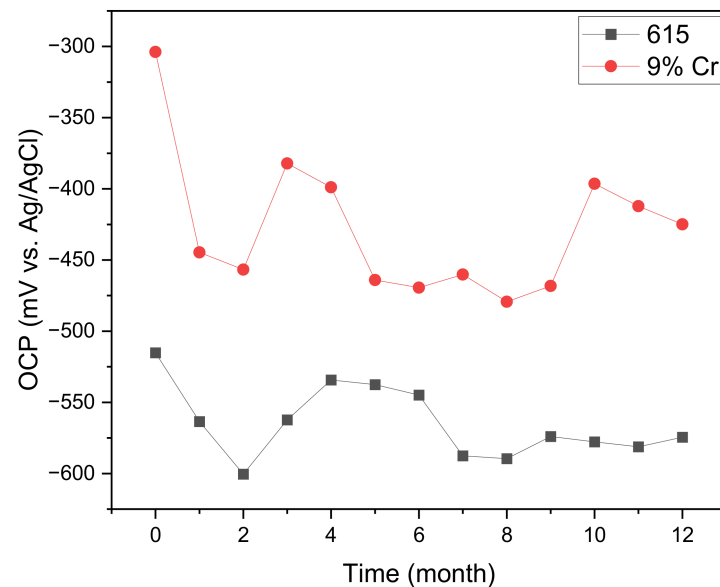


Figure 4. OCP values for ASTM 615 and ASTM 1035 as a function of time.

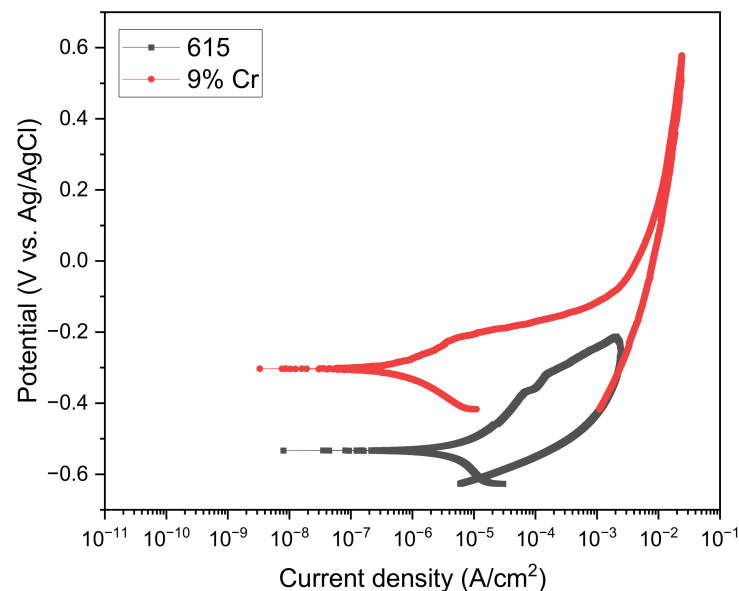


Figure 5. Cyclic polarization curves obtained for carbon steel 615 and low alloy steel 9% Cr.

Table 2. Tafel slopes for 615 and 9% Cr steel materials.

	ASTM 615 (V/dec)	ASTM 1035 (9% Cr) (V/dec)
b_a	0.12	0.12
b_c	−0.12	−0.115

According to Equations (1) and (2), the polarization resistance, R_p , can be obtained by extrapolating data based on LPR tests. The corresponding corrosion rates at different

immersion times were calculated and plotted in Figures 6 and 7. The 9% Cr steel was expected to have higher R_p values and, therefore a lower corrosion rate than 615. For 615, the resistance values started from approximately $5000 \Omega \cdot \text{cm}^2$ and eventually shifted to close to $1200 \Omega \cdot \text{cm}^2$. For 9% Cr, the resistance values started from approximately $30,000 \Omega \cdot \text{cm}^2$, a value approximately six-fold higher than that of 615. The resistance value increased to $5 \times 10^6 \Omega \cdot \text{cm}^2$ after 3 months of immersion and to $7 \times 10^6 \Omega \cdot \text{cm}^2$ after 4 months of immersion. The resistance then dropped continuously with time in the following four months; the pH magnitude reached the minimum magnitude. The R_p magnitude stabilized for the next eight months at approximately $5000 \Omega \cdot \text{cm}^2$, around five times the values of ASTM615.

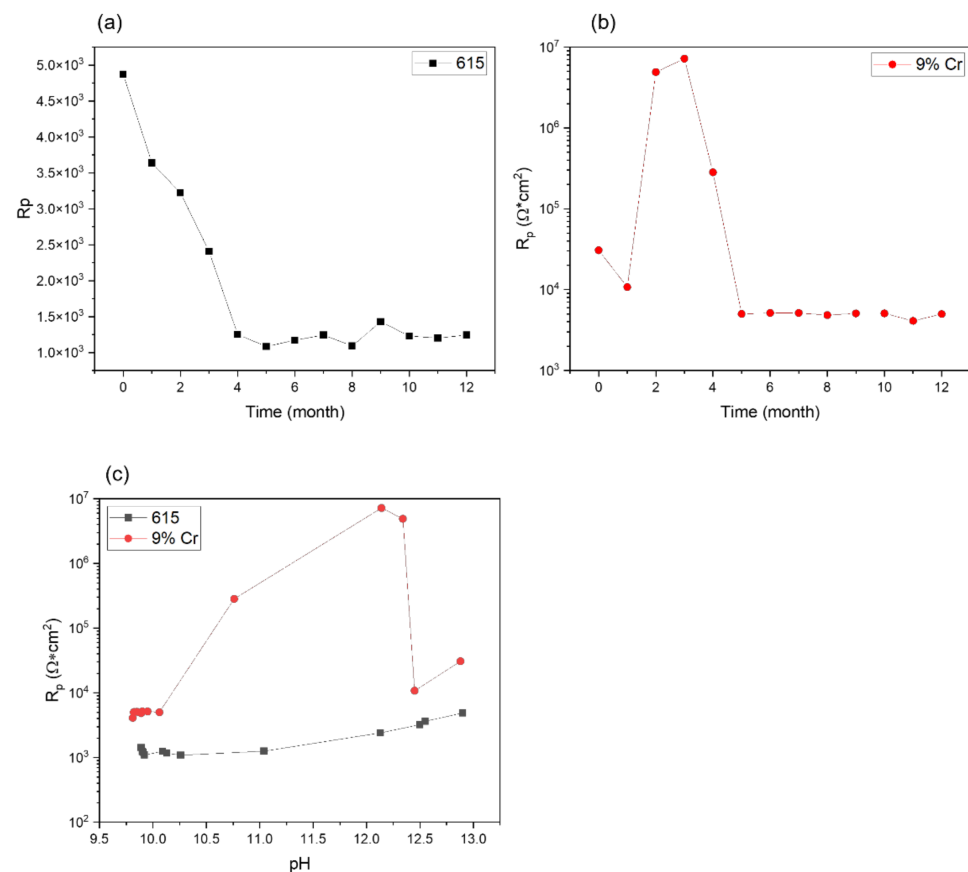


Figure 6. Summary of R_p for both 615 and 9% Cr rebars in SCPS with 3.5 wt% NaCl as a function of time: (a) R_p for 615; (b) R_p for 9% Cr steel (c) pH vs R_p for both 615 and 9% Cr.

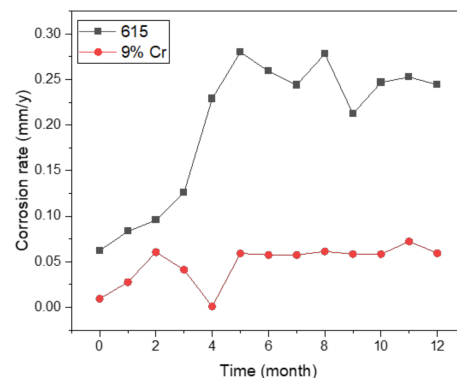


Figure 7. Summary of corrosion rate for both 615 and 9% Cr rebars in SCPS with 3.5 wt% NaCl as a function of time.

By combining the Tafel slope values from Table 2 and LPR test data, the corrosion current density was calculated according to the Tafel slope extrapolated by the following equation:

$$i_{\text{corr}} \left(\frac{\text{A}}{\text{cm}^2} \right) = \frac{b_a * b_c}{2.3 R_p * (b_a + b_c)} = \frac{B}{R_p} \quad (1)$$

where b_a is the anodic Tafel slope, b_c is the cathodic Tafel slope, and B is the proportionality constant calculated from the cathodic and anodic Tafel slopes.

Therefore, the corrosion rate can be converted with the following equation:

$$\text{CR} \left(\frac{\text{mm}}{\text{y}} \right) = 3276 \times \frac{i_{\text{corr}}}{M_{\text{eq}} * \rho} \quad (2)$$

where M_{eq} is the equivalent mass and ρ is the density of the material.

Figure 6 shows the polarization resistance as a function of time whereas Figure 7 shows the corresponding corrosion rate calculated with Equations (1) and (2). The damage evolution followed the different stages for the carbon steel described classically by Tutti, wherein the passive layer breakdown appears after the chloride threshold has been reached [42]. Chloride-induced depassivation of rebar in highly alkaline solutions is more likely to be caused by critical chemical conditions that lead to depassivation. The resistance decreased, as illustrated in the R_p magnitude in Figure 6. The decreased R_p values observed after 4 months of immersion could be due to the passive breakdown and the lower pH variation. An increase in R_p magnitude could be attributed to the formation and accumulation of corrosion products. The overall R_p magnitude was affected by the interfacial mechanisms along the surface; however, the LPR does not characterize local conditions over time. The trend for 9% Cr steel differed from that for carbon steel substrate, because the R_p increased during the first 3 months. This finding was attributed to the influence of alloying elements, such as chromium, that altered the surface condition of the material. Previous study has demonstrated that, for low Cr alloyed steel (6% Cr) in SCPS, compared with carbon steel, a more compact and protective layer was observed, which could provide temporary protection for the Cr alloyed steel [43]. Therefore, with 9% Cr addition, enhanced corrosion resistance was expected because of the formation of chrome and mixture of oxides at the surface. The polarization conditions showed no passive region, as demonstrated in Figure 4. However, the steady state conditions suggested that a protective layer formed in the initial stage of immersion, thus temporarily decreasing the corrosion rate. With the continuous exposure and changes in the electrolyte conditions, the protection decreased. The overall surface started to deteriorate gradually after 3 months of exposure and then reached a plateau after 5 months of immersion. The layer was attributed to the formation of Cr oxide/hydroxide and dense magnetite rust layer, as confirmed by a previous study [23,43]. However, this study has confirmed that such a layer was not sufficient to provide long-term protection, particularly after 5 months of immersion, because of the influences of both the continuous exposure and change in the solution pH. Therefore, after 5 months of immersion, the layer's effectiveness decreased, but remained sufficient to provide better protection than that in carbon steel on the basis of the R_p values with magnitudes higher than those for carbon steel.

The corrosion rate showed the same trend for both materials (Figure 7), thus indicating that the 9% Cr steel had higher corrosion resistance than ASTM615. Ai et al. have confirmed that the decreases in alkalinity might not necessarily negatively influence corrosion performance for 10% Cr rebar in the absence of chloride ions [23]. In their study, the passivity was maintained at high pH and failed when the pH went down to 10.5. Their findings are generally consistent with those in this study, in which the pH decreased below 10.5 after 4 months of immersion, and a significant decrease in R_p for 615 is observed (Figures 3 and 6). The R_p values eventually stabilized around $1000 \Omega \cdot \text{cm}^2$. For 9% Cr steel, the R_p values were also affected by the pH change. The additional alloying element, Cr, resulted in the markedly large R_p values observed from months 3 to 4. The values

subsequently decreased to approximately $5000 \Omega \cdot \text{cm}^2$ after pH decreased to 10.5. However, the resistance remained higher than that of 615, demonstrating the effectiveness of such Cr based protective films. Hence, this resulting a corrosion rate five-fold lower for 9% Cr steel than carbon steel during the 12 months of exposure.

3.3. EIS Analysis

EIS tests were performed during the immersion period to understand the electrochemical behavior of both 615 and 9% Cr steel, and the corresponding results are shown in Figure 8. The EIS results reflected the typical response of steel rebar immersed in SCPS in the presence of chloride: the arc radii decreased with immersion time increased, as previously described [38,44]. The capacitive form of corrosion behavior from both the semi-circle and phase angle decrease corresponded to the evolution of charge transfer over time. For 615, the arc magnitude showed a significant shift between 2 and 4 months of immersion, which might have resulted from the bulk pH conditions and the chloride content leading to carbonation of the solution. As indicated in Figure 3, the pH values decreased significantly between this period to approximately 10.5. A previous study has demonstrated that carbon steel scarcely passivates at a pH below 10.5, in agreement with the current result indicating that the material lost its passivity under such chemical conditions. A decrease in resistance was expected [23]. The 9% Cr steel showed less of an influence of pH on the resistance values than 615. The semicircle showed an increase in radii values with the protection from film formation, which was mitigated at lower pH; moreover, a low pH (approximately 10.5) would promote the effectiveness, as previously observed by Ai et al. [23]. The material then showed a decrease in the arc values, thus indicating that the formed film did not have the initial and short-term properties. The phase angle plot in Figure 8d shows a second time constant during the first 4 months of exposure. After 8 months, the second time constant disappeared, owing to a breakdown or change in active conditions of the previous layer formed under steady state conditions. The 8 months marked a shift due to the greatest change in pH conditions. The EIS results characterized the overall surface conditions under steady state and correlated with the LPR trend over time.

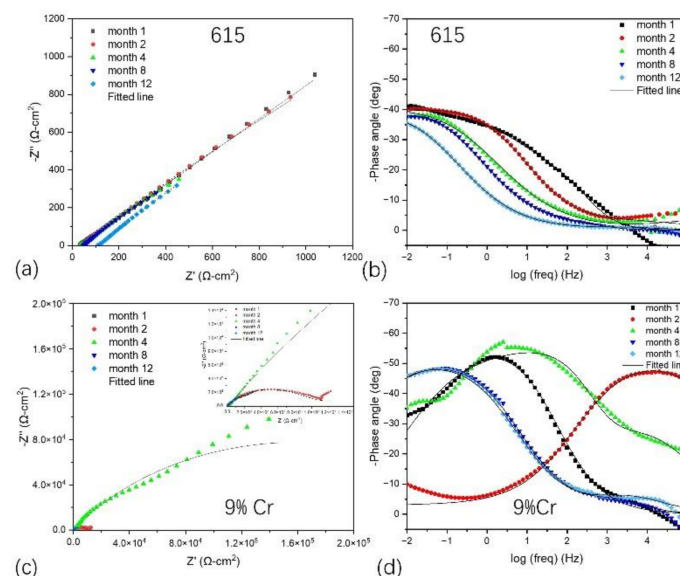


Figure 8. EIS results for both 615 and 9% Cr rebar in SCPS with 3.5 wt% NaCl as a function of time: (a) 615 Nyquist plot, (b) 615 Phase angle plot, (c) 9% Nyquist plot, (d) 9% Phase angle plot.

Qualitative analysis can be complemented by quantitative information associated with EIS results; therefore, the EIS data were fitted with an equivalent circuit (EC) shown in Figure 9; this latter has been used to characterize the steel surface involving the passive layer or the corrosion products and for the steel and SCPS double layer interface [23,45].

The equivalent circuit included a constant phase element CPE to represent the interface connected to other electrical elements. The circuit elements were the solution resistance R_s , the film resistance R_1 , the film capacitance Q_1 represented by a CPE, the charge transfer resistance R_2 , and the double layer capacitance Q_2 represented by a second CPE. The corresponding best fitting data with immersion times of 1, 2, 4, 8, and 12 months are shown in Table 3.

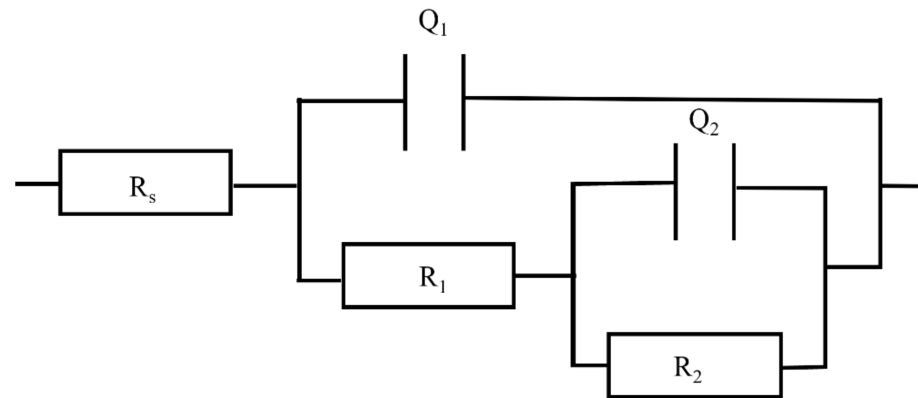


Figure 9. Equivalent circuit used for EIS fitting.

Table 3. Best fitting results.

	Time (Month)	R_s ($\Omega \cdot \text{cm}^2$)	Q_1 ($\mu\Omega^{-1}\text{cm}^{-2}$)	n_1	R_1 ($\Omega \cdot \text{cm}^2$)	Q_2 ($\mu\Omega^{-1}\text{cm}^{-2}$)	n_2	R_2 ($\Omega \cdot \text{cm}^2$)	χ^2
615	1	3.43×10^1	1.21×10^{-3}	1.00	8.10	6.73×10^{-2}	0.459	1.49×10^6	2.93×10^{-3}
	2	3.71×10^1	4.32×10^{-2}	0.388	15.5	3.45×10^{-2}	0.607	1.93×10^5	9.11×10^{-4}
	4	3.01×10^1	2.54×10^{-3}	0.445	13.6	1.69×10^{-1}	0.488	1.15×10^4	1.42×10^{-3}
	8	4.81×10^1	8.35×10^{-3}	0.879	3.46	2.26×10^{-1}	0.521	3.24×10^3	7.05×10^{-5}
	12	1.08×10^1	8.27×10^{-3}	0.614	7.16	2.09×10^{-1}	0.515	6.99×10^3	1.44×10^{-5}
9% Cr	1	3.27×10^1	1.55×10^{-2}	0.668	3.86×10^3	4.96×10^{-2}	0.578	6.23×10^4	1.06×10^{-3}
	2	4.34×10^1	4.42×10^{-5}	0.601	2.04×10^{-2}	2.13×10^{-3}	0.0356	3.39×10^5	1.53×10^{-3}
	4	7.26×10^1	3.55×10^{-4}	0.541	5.71×10^2	8.91×10^{-5}	0.754	3.27×10^5	3.03×10^{-3}
	8	3.17×10^1	1.69×10^{-3}	0.811	7.63	6.77×10^{-2}	0.590	1.07×10^4	8.75×10^{-4}
	12	2.71×10^1	4.63×10^{-3}	0.608	13.1	6.29×10^{-2}	0.592	1.01×10^4	4.16×10^{-4}

For the 615, both R_1 and R_2 values showed a general decreasing trend as the immersion time increased. It should be noted that at immersion time of 2 months, the initial magnitude was relatively high, and this charge transfer resistance could be attributed to the steady state conditions that existed at high alkaline initial pH of 12.9. The R_2 was influenced by the layer formed due to the accumulation of corrosion products. The layer may have provided a temporary barrier effect that caused a relatively high impedance magnitude and relative low corrosion rate, as shown in Figure 7. However, after 4 months of immersion, the R_2 magnitude decreased over time. This could be attributed to the pH and the presence of chloride ions influencing its protectiveness by activating the overall interface. The Q_2 magnitude characterized the double layer, the resulting magnitude is in the order of magnitude of $1 \times 10^{-2} \mu\Omega^{-1}\text{cm}^{-2}$ which considers a current leakage. In addition, the Q_1 magnitude characteristic of the layer formed considers higher magnitude compared to the classic 1×10^{-6} . The Q element is another indicator of the active state of the interface and the lower degree of protection that was observed over time [23].

It can also be observed that, for 9% Cr steel, the R_1 and R_2 values increased by one order of magnitude from immersion time 1 month to 2 months, respectively. The R_1 magnitude represents the layer resistance, and R_2 represents the charge transfer resistance. The magnitude Q_1 and Q_2 are the layer and double layer properties, respectively. The magnitudes on the order of 1×10^{-4} and $1 \times 10^{-5} \mu\Omega^{-1}\text{cm}^{-2}$ are smaller and characteristic

of the layer capacitance and a double layer [23]. The magnitudes characterize a more protective layer due to the low capacitance magnitudes. After 4 months of immersion, the resistance magnitude of R_2 was slightly higher. This behavior was attributed to the possible formation of a stable barrier layer that provided better protection in a less alkaline environment ($\text{pH} \sim 10.5$). The evolution of the parameters characterizing the later, such as R_1 and Q_1 shows the passive to active under steady state conditions. The pH and chloride effect influenced the R_1 and the Q_1 , which decreased and increased, respectively. The barrier quality due to the higher conductive media and potential physical breakdown of the barrier were monitored over time. The charge transfer resistance R_2 , and Q_2 for the double-layer for 9% Cr steel showed results consistent with the interfacial activity of the formed layer. The global activity was consistent with corrosion resistance and was also demonstrated by the LPR results in Figure 6b and the decrease in the corrosion rate in Figure 7.

3.4. Surface Analysis

To identify the corrosion degradation pattern, the surface morphology of steel rebar after immersion for 2, 4, 8, and 12 months were assessed. After the samples reached the indicated immersion times, they were retrieved, and the corrosion products were removed to expose the surface. Figure 10a–d for ASTM615 and Figure 10e–h for 9% Cr have revealed corrosion type, including general and localized corrosion of the tested rebar, on the basis of the changes in the surface during the immersion time.

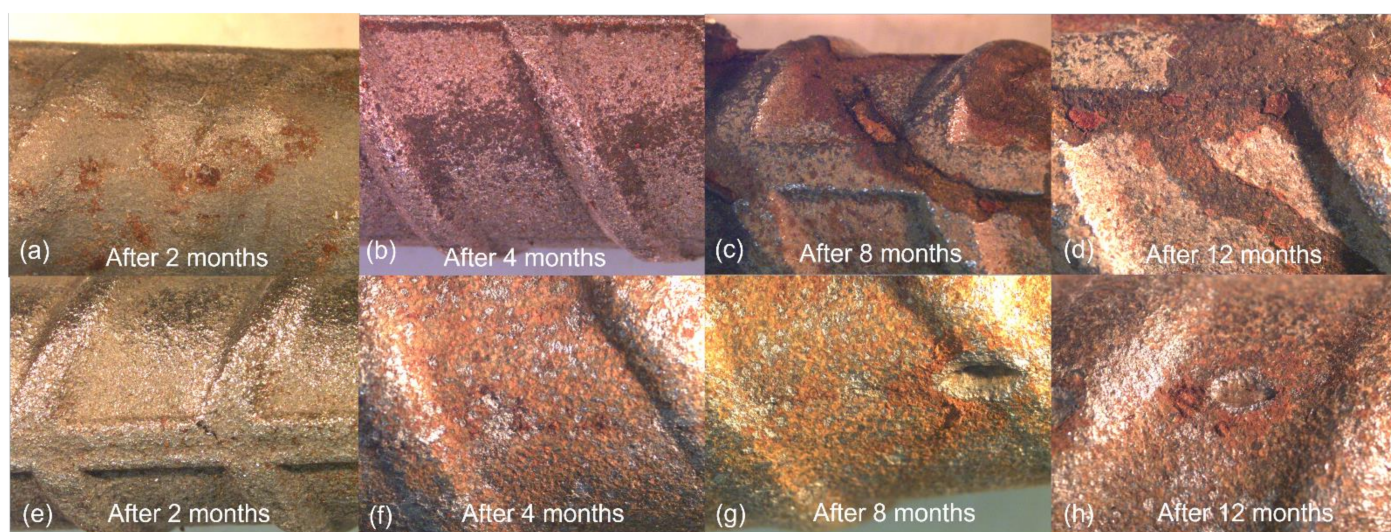


Figure 10. Surface morphology of rebars after 2, 4, 8, and 12 months of immersion: (a–d) 615; (e–h) 9% Cr steel.

As shown in Figure 10, the surfaces of both materials were uneven, and local corrosion attack is visible. From Figure 10a–d, ASTM615 experienced both uniform and local corrosion, because local corrosion colonies were observed, and the rib of the rebar showed severe decay. The damage across the rib of the rebar, as shown in Figure 10c,d, caused the rib to be broken and segregated. Given that the purpose of longitudinal ribs and transverse ribs (lugs) is to reinforce the cohesive properties between rebar and concrete, such damage might cause a loss of cohesiveness for rebar with concrete materials. In these samples, compared with new, untested 615 samples, the rib was penetrated, but less uniform corrosion was observed, in agreement with findings reported by Michel and Angst indicating that the geometry of the rebar influences the corrosion initiation site [46]. Corrosion tended to occur near or on ribs, because the OCP values around ribs were lower, thus indicating that those areas were susceptible to corrosion. In addition, pitting is more likely to be

caused by surface stress and metallic defects from the thermal mechanical processing for rib production.

In contrast to the carbon steel rebar, the 9% Cr showed different degradation conditions on its surface, which were less severe than those of 615. For 9% Cr samples, more uniform corrosion patterns were observed, and the ribs were flatter than those of 615. Particularly after 12 months of immersion, the rib shown in Figure 10d for 615 sample demonstrated a localized pattern with visible deep attack, whereas the rib shown in Figure 10h for the 9% Cr was scarcely visible, thus indicating that the layer that formed during the exposure time supported less localized attack. This finding is consistent with those in a the previous study by Dong et al., demonstrating the advantages of adding Cr element into reinforce corrosion resistance by improving corrosion uniformity [47]. In addition, the authors have also argued that the cohesiveness and the thickness of rust on steel substrate can be improved when uniform corrosion is dominated. Therefore, 9% Cr steel can benefit from the protective layer from Cr content, and a better rust layer from the substrate. Figure 7 shows the measured uniform corrosion rate, and Figure 11 demonstrated the local pit propagation rate and pit depth. Therefore, sample 615 showed approximately ten-fold higher values than those associated with the development of the localized attacks. For 9% Cr steel, the values were much lower, because they largely measured the uniform corrosion rate of the rebar. Therefore, the corrosion performance for 9% Cr is expected to be better, last longer, and have a lowered possibility of unexpected catastrophic failure caused by the localized attack.

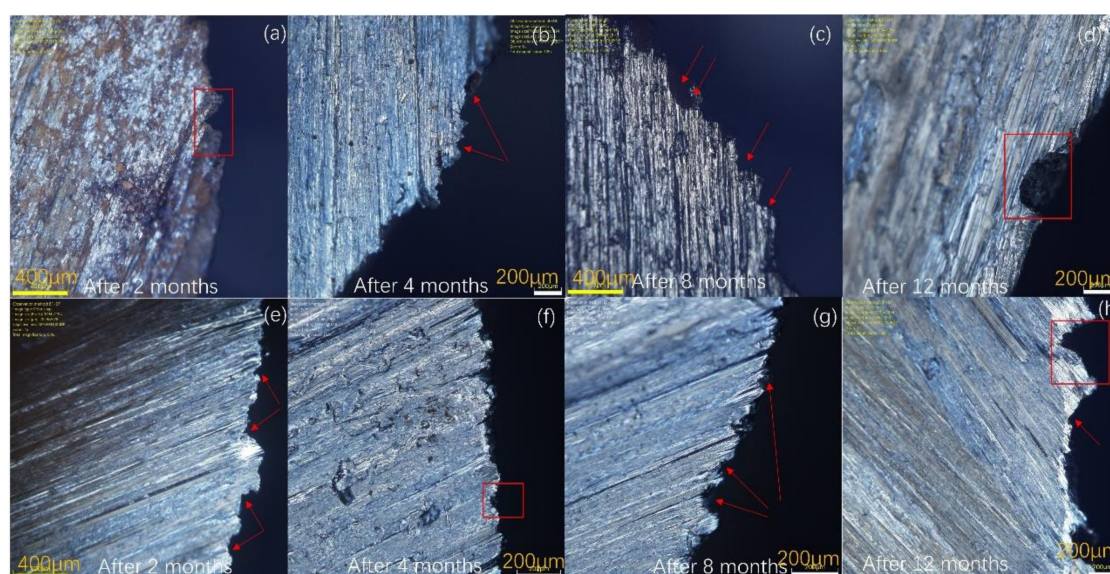


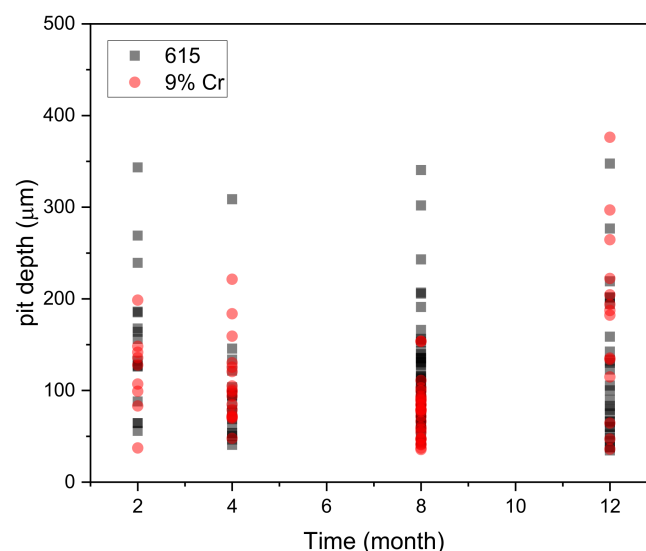
Figure 11. Cross-section pits in rebar after 2, 4, 8, and 12 months of immersion, observed under a microscope with arrows and boxes indicating localized attack: (a–d) 615; (e–h) 9% Cr steel.

To study the pit development over time, the samples were cut into slides after observation of surface morphology; typical cross section images over the course of immersion are presented in Figure 11a–d for 615 and Figure 11e–h for 9% Cr steel. The number of slides would depend on the number of pit colonies observed. The local attack depth was measured as shown in Figure 2, wherein the number of local attacks was counted per slide at the cross-section area. Figure 11 shows local attack, indicated by a red arrow and/or red box. The quantification of the local features included the depth measured with an optical microscope and documented; a summary of maximum, minimum, and average values is listed in Table 4.

Table 4. Summary of pit depth measurements on cross-sections of both ASTM615 and 9% Cr steel rebar.

	2 Months (μm)		4 Months (μm)		8 Months (μm)		12 Months (μm)	
	615	9%	615	9%	615	9%	615	9%
Max	343.314	198.553	308.715	221.37	340.565	153.898	347.563	376.286
Min	55.767	37.222	40.622	47.658	42.38	35.591	34.547	35.957
Avg	155.9298	119.7927	95.26067	107.8288	112.1155	76.73104	117.2754	175.6276

For better visualization, the pits depth distribution for up to 12 months is summarized in Figure 12. In early stages of immersion or after 1 month of exposure, for 9% Cr, the pitting or local events were smaller and more scattered than those in 615. Clusters of pit depth were observed with a range from 100 μm to 200 μm for both materials across the entire immersion time, because the pit depth density was higher in that range. However, after 8 months of immersion, the pit clusters were denser from 30 to 200 μm , thus indicating the development of new pits. After 12 months of immersion, more pits were observed around the 200 μm range, and several pits were as deep as 400 μm . Therefore, the development and growth of pit depth over time were observed as more pits grew to depths ranging between 100 μm and 200 μm over a 12-month immersion time. In addition, after 12 months of immersion, more pits were found for 615, because the black color was more intense in Figure 11. As shown in Table 4, the maximum pit depth of 615 in early stages had the highest magnitude. The pit corrosion penetration rate (length per unit time) was higher than that of uniform corrosion. After 2 months of immersion, the penetration rate for uniform corrosion increased and eventually led a decreased average pit depth. For 9% Cr, the maximum pit depth showed an increasing trend, but the average pit depth remained relatively stable until 8 months, and a clear increase was observed at 12 months. The average value might have been substantially influenced by an outlier value, such as the maximum pit depth of 9% Cr after 12 months of immersion. This value was approximately 100 μm higher than the second largest value. Notably, the existence of this outlier might have been due to the local area where data were collected. In general, the results were consistent with previous findings indicating that the development of localized attack is mitigated by the addition of Cr, owing to the formation of Cr oxide/hydroxide [36]. In addition, the effectiveness of Mo and Ni in inhibiting pitting is well known. However, a previous study has not detected an Ni peak with XPS because of its low content (0.53 wt%) [43]. Given the chemical composition from Table 1, the pitting mitigating effects provided by Ni and Mo in this study were likely to have been limited.

**Figure 12.** Pit depth distribution as a function of time.

4. Conclusions

In this study, the corrosion behavior of 615 and 9% Cr rebar were characterized to study the long-term effects of Cr on overall and localized attack in immersion tests in SCPS with 3.5 wt% NaCl for 12 months. The following conclusions have been identified:

1. The formation of corrosion products provided a temporary protective layer, but the layer eventually failed for 615. However, Cr promoted the formation of a protective layer exhibiting better corrosion resistance.
2. The additional Cr content increased the material's corrosion resistance, with an approximately five times lower corrosion rate after 12 months of immersion, on the basis of electrochemical testing.
3. ASTM A1035-CS (9% Cr) rebar showed better performance in overall corrosion resistance than ASTM A615.
4. Most pit depth values for both materials are concentrated in the range of 100–200 μm .
5. ASTM A1035-CS (9% Cr) rebar in general was less affected by localized attack than ASTM A615, because it showed a smaller average pit depth distribution and magnitude.

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