

Influence of Cement Superplasticizer on Steel Corrosion in 3.5 % NaCl Solution

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The corrosion of reinforcement steel present under different conditions namely bare steel (S_I), steel in cement mortar (S_{II}), and steel in cement mortar containing polycarboxylate superplasticizer (S_{III}) was investigated in 3.5 % sodium chloride solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The polarization results showed that the corrosion rate of steel in a mortar containing superplasticizer is much less than that of steel in mortar only or that of uncovered steel surface, i.e. the corrosion rate follows the order $S_{III} < S_{II} < S_I$. Also, the results of EIS spectra revealed that the charge transfer resistance of steel samples decreases in the order $S_{III} > S_{II} > S_I$ conforming potentiodynamic polarization results. The corrosion rate increases and consequently the charge transfer resistance decreases with increasing the immersion time for all steel specimens in sodium chloride solution. This means that the presence of cement mortar around the steel bar decreases the contact of NaCl solution with metal which occurs through the pores in the cement mortar and hence the corrosion rate of steel decreases. In the presence of the superplasticizer within the cement mortar its porosity decreases and consequently decreases the passing of NaCl solution to steel surface results in decreasing in its corrosion rate. Increasing of the superplasticizer concentration in cement mortar results in more decrease in the rate of steel corrosion in NaCl solution. Examining the steel surface through scanning electron microscopy (SEM) indicated that this surface (S_I) exhibits much damage more than that of steel in a mortar containing superplasticizer (S_{III}) when both exposed to the corrosive sodium chloride solution.

Keywords: Potentiodynamic polarization; polycarboxylate superplasticizer; cement mortar; sodium chloride; EIS; SEM.

1. INTRODUCTION

Superplasticizers are used broadly to disperse the cement particles and to increase the fluidity of concrete in the production machine ensuing in better strength and higher durability of the hardened

products. Superplasticizers which belong to the copolymers of polycarboxylate superplasticizers have been demanding recently. The adsorption of polycarboxylate superplasticizers on the particles of cement, through the carboxylate groups, disperses those particles due to the steric repulsive generated via the lengthy ether group chains [1, 2]. Also, polycarboxylate superplasticizer acts as a water-reducing agent in cement mortar preparation that's take into account one of the solutions of the corrosion problem of reinforcement steel. Some of the methods used to decrease steel corrosion in concrete are cathodic protection [3], organic, inorganic, or metallic coatings, and using inhibitor as an additive during the mixing of fresh concrete [4, 5] or for surface application on the hardened concrete[6-8].

The present work aims to use the potentiodynamic polarization and EIS techniques to analyze the occurrence of steel corrosion out and in cement mortar at various immersion times in 3.5 % sodium chloride solution. In addition to this, the effect of superplasticizer mixed with cement mortar on steel corrosion in sodium chloride was studied. Also, the surface micrograph of the corroded steel was examined via SEM.

2. EXPERIMENTAL

2.1. Mortar specimens

Mortar specimens cylindrical in shape of 8 cm in height and 4cm in diameter were prepared. The ordinary Portland cement was used for fabrication of mortar with cement/sand (c/s) ratio of 1/3 and water/cement (w/c) ratio of 1/2, and then the polycarboxylate superplasticizer (PC) was added. Also, the mortar without PC was prepared with the same conditions. Reinforcement steel with a chemical composition (wt.%) of 3.5 C, 2.3 Si, 0.01 S, 0.3 Mn, 0.06 Cu, 0.04 Mg, 0.01 P, 0.05 Cr and balance Fe. Steel rod with a diameter of 1.1cm and length of 10cm was embedded centrally in mortar specimen. A wire of copper was soldered to one end of the steel rod for electrical contact, and both ends were covered with Araldite epoxy resin, leaving 2cm in length and area equal to 6.9 cm² of the rode in contact with the mortar.

2.2 Testing samples and solution

Steel sample was prepared in different three states: first bare steel (S_I), second steel in a mortar (S_{II}), and third steel in mortar contains 1% superplasticizer by weight of cement (S_{III}). The superplasticizer used here is polycarboxylates superplasticizer (PC) namely Sika viscoCrete-3425. Also, samples of steel in a mortar with different percentages of PC were prepared. Sodium chloride solution of concentration 3.5 % was prepared using Analar grade reagents (BDH) and triple distilled water.

2.3. Electrochemical measurements

EIS and potentiodynamic polarization measurements were conducted using the electrochemical workstation IM6 Zahner potentiostat (Germany) [9, 10] joined to Thales software for electrochemical data analyses. The experimental impedance spectra were best fitted by using the equivalent circuits of

the “SIM” program which built-in the IM6 package.

Measurements of EIS were performed at open circuit potential using an excitation ac signal of 10 mV peak to peak in the frequency range from 0.01 Hz to 10^5 Hz. Potentiodynamic scans were traced at a scan rate of 1mV/s within the range from -1.2 to -0.1 V vs. SCE. The experimental measurements were carried out using a three electrode electrolytic cell. A large platinum sheet was used as a counter electrode facing the mortar for impedance measurements. A coil of platinum metal was used for potentiodynamic polarization experiments. A saturated calomel electrode was used as a reference electrode during potential recording.

2.4. Characterization of surface morphology

After breaking up the cement mortar around the steel rod, the morphology of the steel surface was observed via SEM (Quanta 250 FEG, FEI company, Netherlands).

3. RESULTS AND DISCUSSION

3.1. Polarization behaviour

3.1.1. For different steel samples

The three steel samples were embedded in 3.5 % sodium chloride solution for 28 days at 298 K before starting the potentiodynamic polarization measurements. The polarization curves for the steel samples S_I , S_{II} , and S_{III} are given in Figure 1 and are characterized by similar cathodic and anodic Tafel behavior. The corrosion parameters were listed in Table 1 and had been analyzed to obtain the following important corrosion parameters: corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate in MPY, slope of the cathodic branch (β_c) and slope of the anodic branch (β_a).

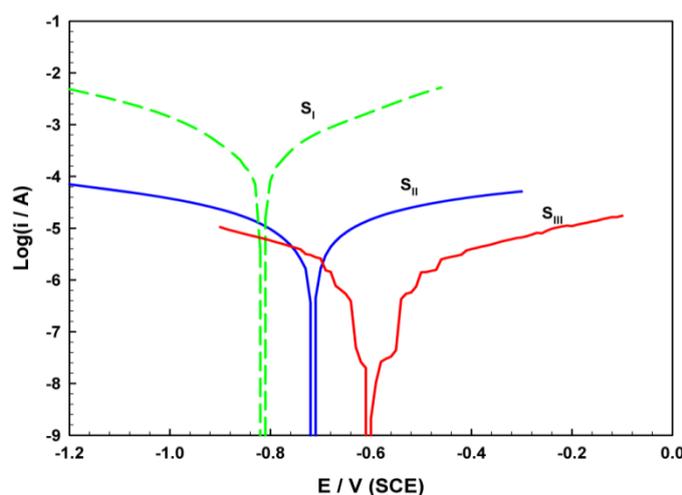


Figure 1. Potentiodynamic polarization curves of the steel samples S_I , S_{II} and S_{III} after 28 days of immersion in 3.5 % NaCl solution.

From Table 1 it is clear that S_I has more negative E_{corr} (-817 mV) at the same time S_{II} has less

negative E_{corr} (-715 mV) while S_{III} has the least negative E_{corr} (-595 mV), i.e. the corrosion potential gets less negative in the following order $S_{\text{I}} > S_{\text{II}} > S_{\text{III}}$. Also, the corrosion current density, I_{corr} , as well as the corrosion rate, decrease in the same order ($S_{\text{I}} > S_{\text{II}} > S_{\text{III}}$). This means that the presence of cement mortar around the steel bar decreases the contact of NaCl solution with metal which occurs through the pores in the cement mortar and hence decreases the rate of corrosion of steel. The presence of PC superplasticizer within the cement mortar lowers its porosity and therefore decreases the penetration of NaCl solution to steel surface which results in a lowering in its corrosion rate.

Table 1. Potentiodynamic polarization parameters for the three steel samples S_{I} , S_{II} and S_{III} after 28 days in 3.5 % NaCl solution.

Sample	E_{corr} mV	I_{corr} $\mu\text{A cm}^{-2}$	β_{c} mV dec^{-1}	β_{a} mV dec^{-1}	Corrosion rate mpy
S_{I}	-818	102.95	74	73	44.32
S_{II}	-715	49.310	99	83	21.23
S_{III}	-595	22.930	32	39	9.870

3.1.2. For steel in a mortar containing different PC percentages

The effect of the addition of different percentages of the PC superplasticizer namely 0.2, 0.6, and 1 % by weight of cement to cement mortar on the steel corrosion in 3.5 % sodium chloride solution was studied.

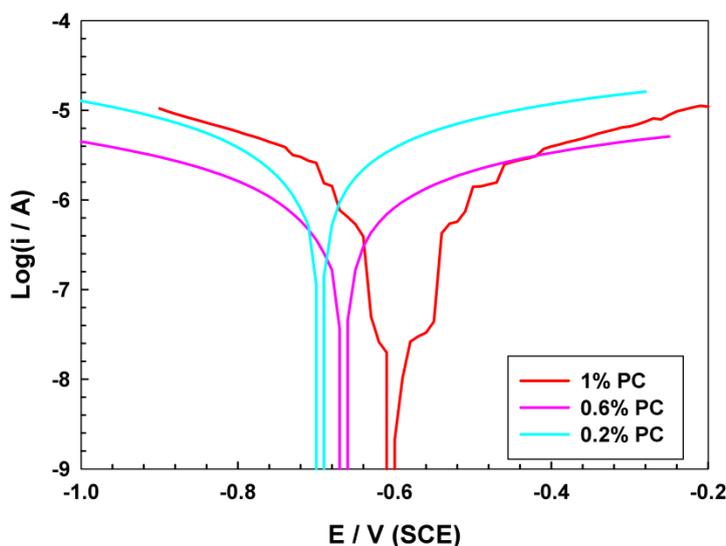


Figure 2. Potentiodynamic polarization curves for steel within mortar containing different concentrations of PC after 28 days in 3.5 % NaCl solution.

The polarization curves of steel within mortars containing PC with different concentrations after 28 days in the test solution are represented in Figure 2. The electrochemical corrosion parameters were listed in Table 2. From this Table, it is clear that the corrosion rate of steel within mortar in

sodium chloride solution decreases with the increase of superplasticizer concentration in mortar due to decreasing of its porosity which controls in NaCl solution passing into steel and consequently its corrosion decreases.

Table 2. Potentiodynamic polarization parameters for steel within mortar containing different concentrations of SP after 28 days in 3.5 % NaCl solution.

Wt. % PC	E_{corr} mV	I_{corr} $\mu A\ cm^{-2}$	β_c mV dec ⁻¹	β_a mV dec ⁻¹	Corrosion rate mpy
0.2	-683	33.50	40	49	14.42
0.6	-642	25.83	30	36	11.12
1.0	-595	22.93	32	39	9.87

3.2. EIS studies

3.2.1. For differentsteelsamples

Electrochemical impedance experiments of the samples S_I, S_{II}, and S_{III} were carried out in naturally aerated 3.5 % NaCl solution at different immersion time. The experiments of EIS were recorded at the open circuit potential of the samples in the test solution.

The Nyquist plots for steel (S_I) in the NaCl salt at different immersion times are recorded in Figure 3. The acquired Nyquist plot in most cases doesn't show perfect semicircle due to the frequency dispersion because of roughness and inhomogeneity of the test surface. From the results of Nyquist plots in Figure 3 it is clear that the capacitive semicircle size decrease with increasing the time of immersion in the test solution. This occurs as a result of decreasing the corrosion resistance of the steel surface as time passes due to corrosion in the salt solution.

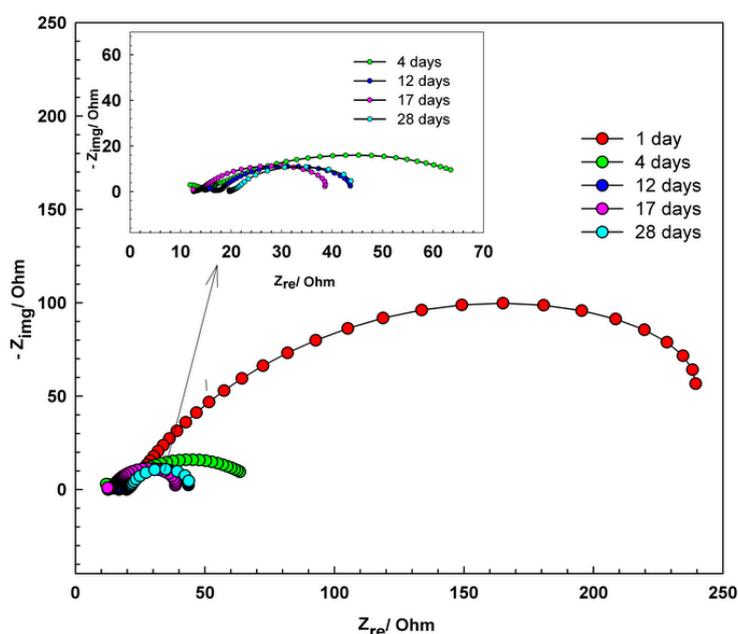


Figure 3. Nyquist plots for steel (S_I) in 3.5 % NaCl solution at different immersion times.

Figure 4a and b shows the EIS spectra as Bode plots for steel (S_1) at various time of immersion in sodium chloride solution. Figure 4a shows the Bode plots wherein $\log Z$ vs. $\log f$ reveal that the impedance value decreases with increasing the immersion time. Previously, it was observed that the entire impedance of steel decreases with increasing of the aging time in humidity circumstance indicating an increase of corrosion [11]. Also, Figure 4b shows the Bode plots wherein phase angle (Θ) versus $\log f$ imply that the phase angle maximum Θ_{max} decreases with an immersion time of steel in the chloride solution because of its corrosion [12].

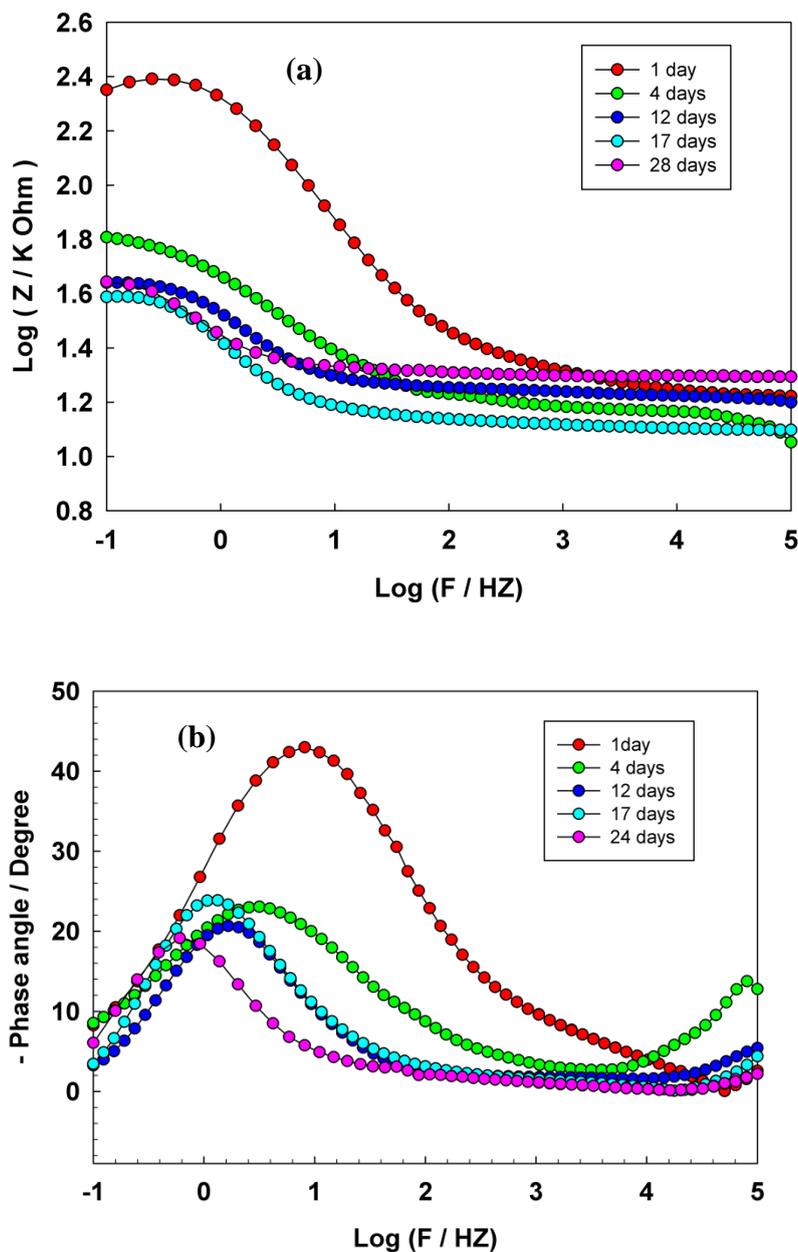


Figure 4. Bode plots for steel (S_1) in 3.5 % NaCl solution at different immersion times (a) $\log Z$ vs. $\log f$; (b) phase angle vs. $\log f$.

The simple Randle equivalent circuit (EC) representing the surface properties of steel sample (S_I) in sodium chloride solution consists of a parallel combination of the charge transfer resistance, R_{ct} , that related to the corrosion process, and the double layer capacitance, C_{dl} , with constant phase angle element (CPE) behavior in series the solution resistance, R_s , see Figure 5. The same EC was used before for analyzing the impedance behavior of steel [11].

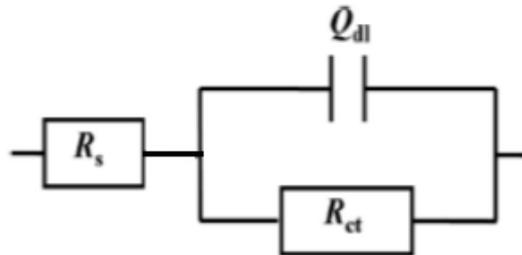


Figure 5. Equivalent electrical circuit model used to fit the EIS experimental results for steel (S_I) in 3.5 % NaCl solution at different immersion times.

The constant phase element (CPE) is used instead of the pure capacitance to consider the non-uniform distribution of current as a result of roughness and surface defects [13]. The impedance of a phase element is defined as [14]:

$$Z_{CPE} = \frac{1}{Y(j\omega)^n}$$

where j is the imaginary number ($j^2 = -1$); ω is the angular frequency ($\omega = 2\pi f \text{ rad s}^{-1}$); Y is the real constant of the CPE which can represent capacitance at $n = 1$, and n is a factor varies between 1.0 for a perfectly smooth surface and 0.5 for a porous surface [15].

The fitted EIS parameters for steel (S_I) in NaCl solution were listed in Table 3. It is clear from this Table that the R_{ct} decreases and simultaneously C_{dl} increases as the immersion time of steel in the test solution increases. These variations can be attributed to the increase of the active surface area of steel caused by the corrosion.

Table 3. Characteristic parameters for fitting the experimental EIS results for steel (S_I) in 3.5 % NaCl solution at different immersion times.

Time day	R_s ohm	R_{ct} ohm	C_{dl} μF	α
1	19.69	49.08	1.02	0.77
4	1.058	25.58	2.47	0.68
12	1.356	19.75	5.31	0.57
17	1.632	18.43	5.97	0.75
24	2.755	5.600	6.21	0.70

The EIS experiments for steel within mortar (S_{II}) in 3.5 % NaCl solution were measured at various times and the results are represented as Nyquist and Bode plots in Figures 6 and 7 respectively.

Figure 6 shows a small partial capacitive semicircle at a high frequency that is because of the dielectric properties of mortar and a large capacitive semicircle at a low frequency that is attributed to the surface reaction on steel. The depressed semicircle in Figure 6 reflects a non-ideal behavior of C_{dl} at the steel/mortar interface and is replaced by Q_{dl} (CPE). The diameter of the low frequency semicircle which equals the resistance R_{ct} of steel decreases with the increasing the immersion time of sample S_{II} in the test solution indicating corrosion acceleration of steel inside cement mortar. Also, from Figure 7a and b, it is clear that both the impedance value (Figure 7 a) and the phase angle (Figure 7 b) decrease as immersion time passes confirming steel corrosion (S_{II}).

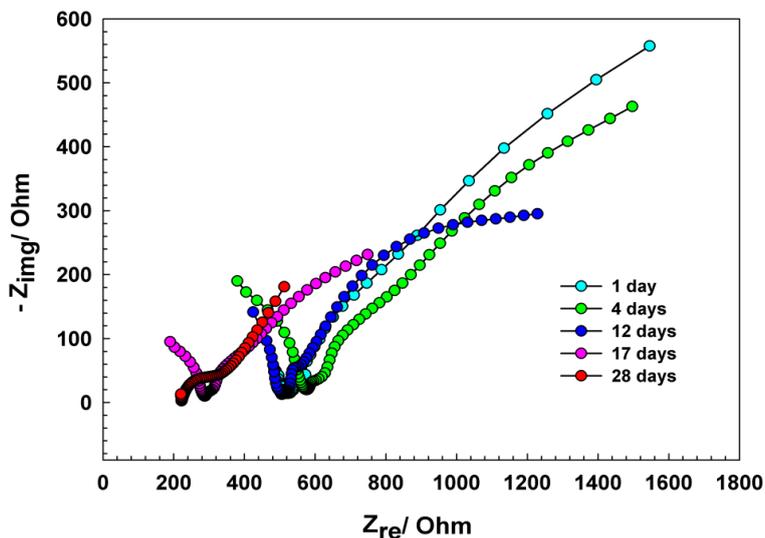


Figure 6. Nyquist plots for steel within mortar (S_{II}) in 3.5 % NaCl solution at different immersion times.

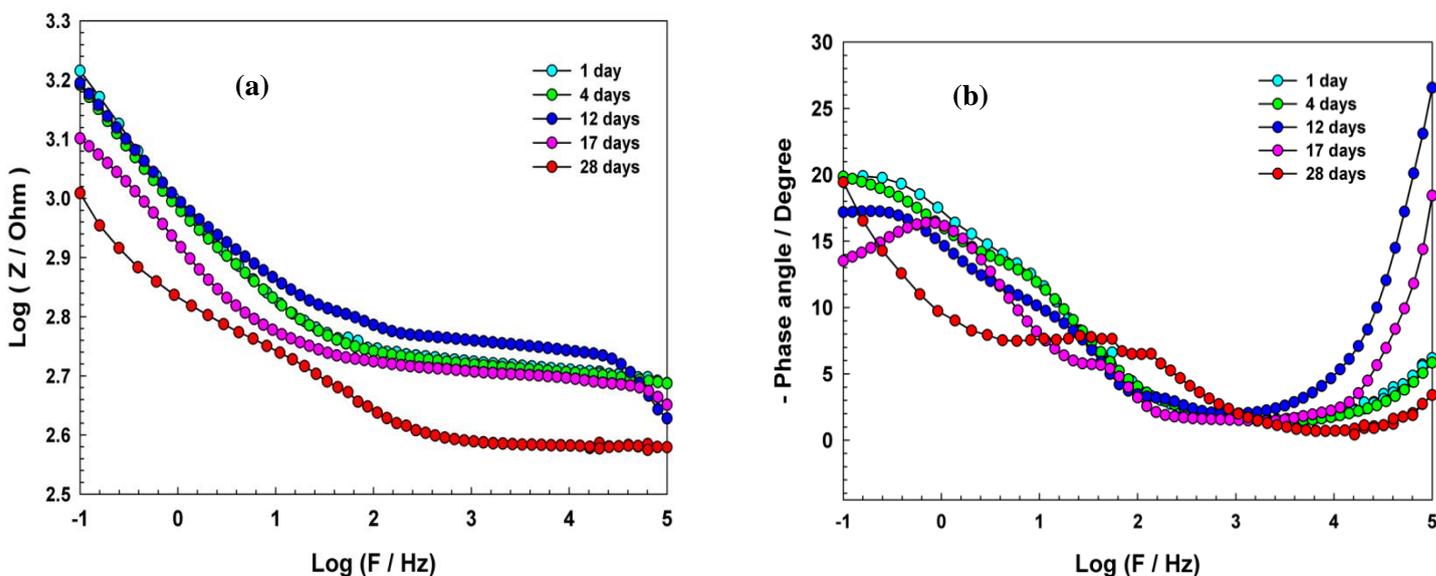


Figure 7. Bode plots for steel within mortar (S_{II}) in 3.5 % NaCl solution at different immersion times (A) log Z vs. log f; (B) phase angle vs. log f.

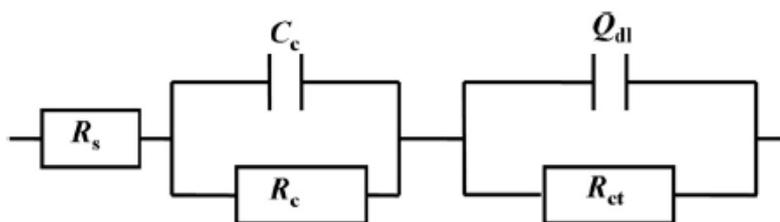


Figure 8. Equivalent electrical circuit model used to fit the EIS experimental results for steel within mortar (S_{II}) in 3.5 % NaCl solution at different immersion times.

Figure 8 shows the EC with two time constants used for fitting the EIS experimental results for steel within mortar (S_{II}) immersed in NaCl solution for various times. In this circuit, R_s is the electrolyte solution resistance, the pair C_c - R_c (first time constant) represents the high frequency response from a mortar matrix and the pair Q_{dl} - R_{ct} (second constant time) is equivalent to the reaction occurring at the steel surface. A similar two-time constants equivalent circuit was suggested for fitting the impedance results of reinforcing steel in mortar exposed to 3.5 % NaCl solution [16]. The parameters values of the electrical equivalent circuit for steel within mortar in NaCl solution are given in Table 4. The obtained results in Table 4 reveal that the value of the charge transfer resistance of steel, R_{ct} , decreases, while that of the capacitance, C_{dl} , increases with the time of immersion of the sample S_{II} in the chloride solution because of increasing steel corrosion within the mortar.

Table 4. Characteristic parameters for fitting the experimental EIS results for steel in mortar (S_{II}) in 3.5 % NaCl solution at different immersion times.

Time day	R_s Ω	R_c Ω	C_c μF	α_1	R_{ct} Ω	C_{dl} nF	α_2
1	236.7	821.4	386.8	0.95	564	2.356	0.85
4	268.3	708.1	396.4	0.92	542	2.448	0.81
12	148.3	660.9	406.1	0.96	501	2.817	0.86
17	236.4	553.3	427.6	0.89	429	3.053	0.79
28	123.0	553.9	467.3	0.94	486	5.698	0.97

The EIS experiments for steel in cement mortar containing 1% PC superplasticizer (S_{III}) exposed to 3.5 % NaCl solution were performed and the results are represented in Figures 9 and 10. Figure 9 shows small and large capacitive semicircles at high and low frequencies, respectively, as in the case of sample S_{II} . Also, the depressed semicircle in Figure 9 is due to a non-ideal behavior of C_{dl} at the interface of steel/mortar and is replaced by Q_{dl} . The low frequency semicircle diameter which equals the resistance R_{ct} of steel decreases with the increasing the immersion time of sample S_{III} in NaCl due to corrosion of steel within mortar containing 1 % PC. In Figure 10, the impedance value (Figure 10 a) and the phase angle (Figure 10 b) decrease as immersion time passes confirming the corrosion of steel of sample S_{III} .

The two time-constants EC in Figure 8 was used for fitting the EIS spectra for steel within mortar containing 1 % PC(S_{III}) in 3.5 % NaCl solution and the results were listed in Table 5. It clear that the value of R_{ct}, decreases while that of C_{dl} increases with the increasing the immersion time of sample S_{III} in NaCl solution suggesting the acceleration of steel corrosion in a mortar containing 1 % PC.

Table 5. Characteristic parameters for fitting the experimental EIS results for steel in mortar containing 1 % of PC (S_{III}) in 3.5 % NaCl solution at different immersion times.

Time day	R _s Ω	R _c κΩ	α ₁	C _c μF	R _{ct} Ω	C _{dl} nF	α ₂
1	796.6	16.21	0.86	68.80	1061	68.80	0.76
4	793.3	15.34	0.84	123.4	1024	123.4	0.56
12	767.4	14.12	0.78	324.6	987.0	324.6	0.57
17	627.8	12.58	0.88	361.2	651.0	342.1	0.65
28	618.9	11.81	0.89	355.4	534.0	351.4	0.63

The EIS results in Tables 3-5 reveal that the charge transfer resistances of steel in case of the three tested samples S_I (bare steel), S_{II} (steel in a mortar) and S_{III} (steel in a mortar containing 1% PC) decrease with increasing the immersion time in 3.5 % NaCl solution. The value of the charge transfer resistance, R_{ct}, for the investigated samples follows the order: S_I< S_{II}< S_{III}. This means that the presence of the mortar alone or with the PC superplasticizer around the steel inhibits its corrosion in the test solution.

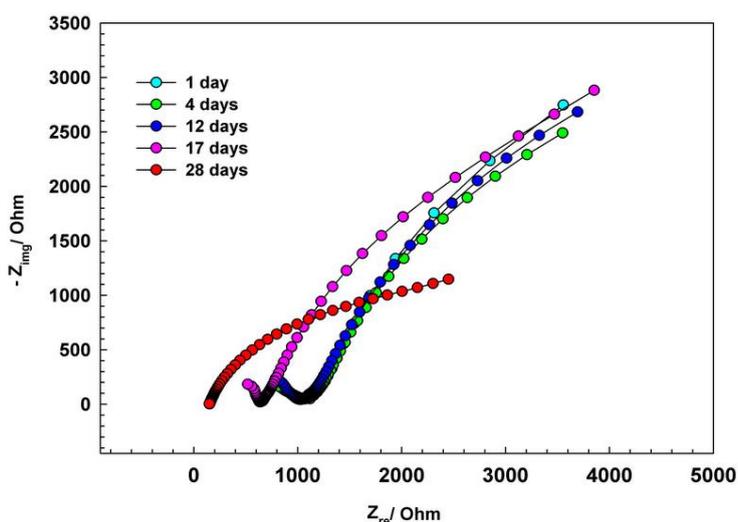


Figure 9. Nyquist plots for steel within mortar containing 1 % of PC (S_{III}) in 3.5 % NaCl solution at different immersion times.

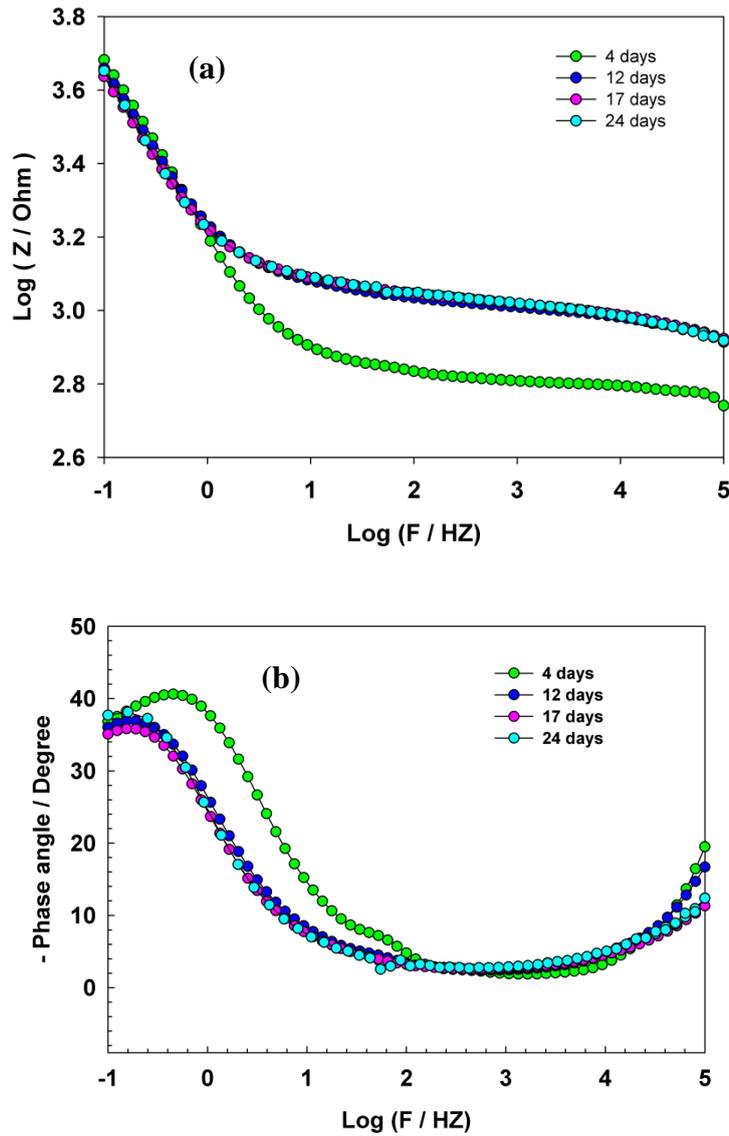


Figure 10. Bode plots for steel within mortar containing 1% PC (S_{III}) in 3.5 % NaCl solution at different immersion times (a) log Z vs. log f; (b) phase angle vs. log f.

3.2.2. For steel in a mortar containing different SP concentrations

The effect of the addition of the polycarboxylate superplasticizers (Sika vescocrete-3425) to cement mortar on the corrosion of steel in 3.5 % NaCl solution was studied by using different concentrations of the PC namely, 0.2, 0.6 and 1 % SP by weight of cement.

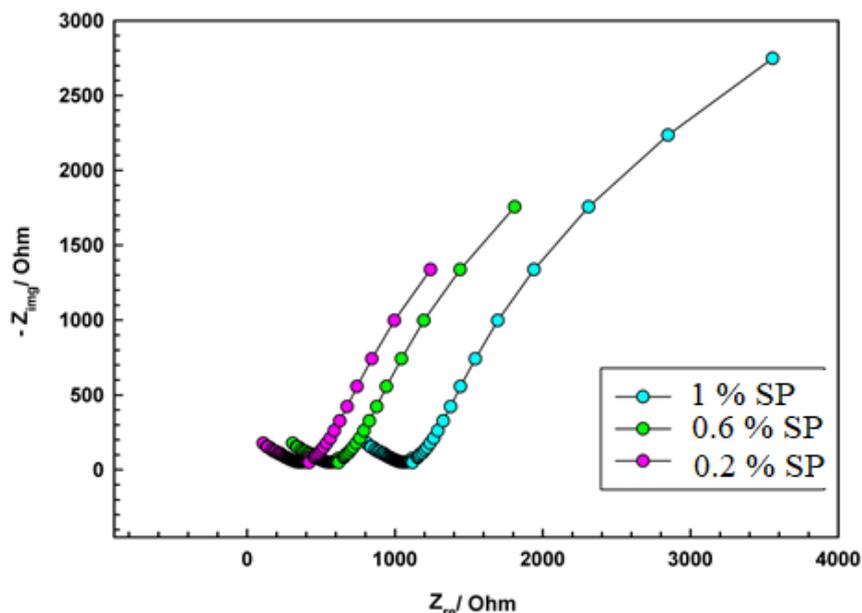


Figure 11. Nyquist plots for steel within mortar containing different concentrations of PC exposed to 3.5 % NaCl solution for one day.

The EIS experiments of steel in a mortar containing different PC concentrations and dipped in sodium chloride solution for one day are shown as Nyquist plots in Figure 11. The EIS results were fitted using the EC in Figure 8 and listed in Table 6. From this Table, it is obvious that the charge transfer resistance, R_{ct} , of steel within mortar in sodium chloride solution increases and consequently C_{dl} decreases with the increasing of superplasticizer concentration in mortar due to decreasing of its porosity which controls in NaCl solution passing through pores into steel and consequently its corrosion decreases.

Previously, it was found that with increasing the superplasticizer percentage in cement mortar and concrete their porosity decreases [17-20]. Also, superplasticizers reduce and refine the porosity of mortar leading to enhancement of its resistance against chloride penetration [21]. The adsorption of superplasticizers on cement particles, through their carboxylate corporations, disperses those particles due to the steric repulsive generated via the lengthy ether group chains [1, 2]. The cement particles disperse more stably in the presence of superplasticizer molecules which adsorbed on these particles and fill the interstitial voids between cement and sand grains and consequently decreases the porous inside the mortar and concrete.

Table 6. Characteristic parameters for fitting the experimental EIS results for steel within mortar containing different concentrations of PC exposed to 3.5 % NaCl solution for one day.

Wt. % PC	R_s Ω	R_c $\kappa\Omega$	α_1	C_c μF	R_{ct} Ω	C_{dl} nF	α_2
0.2	679.6	5.40	0.81	294.4	354.0	421.5	0.66
0.6	762.4	7.88	0.75	213.2	516.0	277.1	0.52
1.0	796.6	16.21	0.86	68.83	1061	68.80	0.76

3.3. Surface morphology analysis

SEM was used to investigate the surface morphology of the bare steel (S_I) and steel within cement mortar containing 1% PC superplasticizer (S_{III}), both had been immersed for 28 days in 3.5 % NaCl solution at 298 K. The surface of steel inside the mortar was examined after the mortar has been broken.

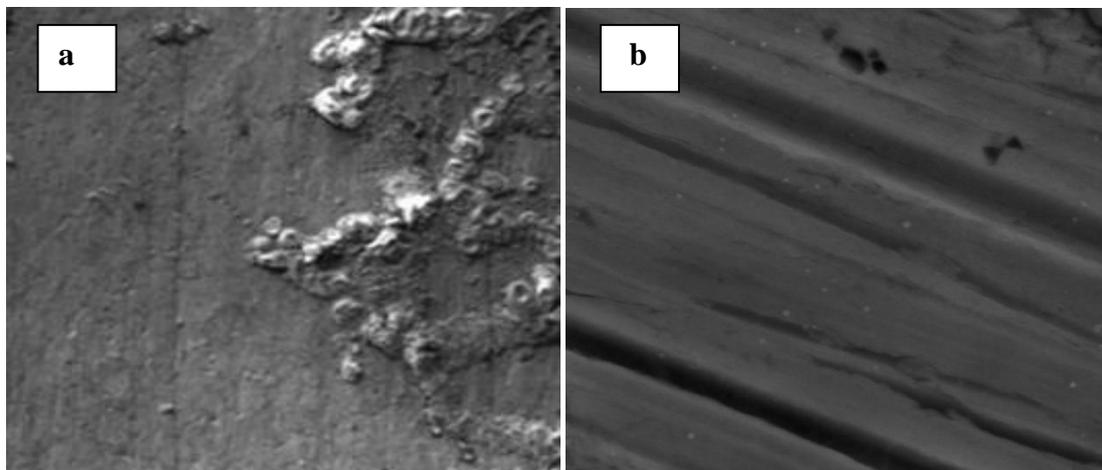


Figure 12. Scanning electron micrographs of (a) steel specimen (S_I) and (b) steel sample S_{III} after 28 days immersion in 3% NaCl solution.

The SEM photographs of the steel samples, S_I and, S_{III} , are shown in Figure 12a and b. Figure 12a reveals that the steel surface of sample S_I is strongly damaged while that of sample S_{III} which is covered by cement mortar containing 1 % PC (S_{III}) well-known shows less pits formation as proven in Figure 12b. This is attributed to the fact that steel in the sample S_{III} is less exposed to NaCl solution than bar steel of sample S_I . Therefore, the results of SEM are in a reasonable agreement with those of polarization and impedance.

4. CONCLUSIONS

The results of the potentiodynamic polarization of the tested samples namely bare steel (S_I), steel in cement mortar (S_{II}) and steel in cement mortar containing 1 % superplasticizer (S_{III}) in 3.5 % sodium chloride solution indicated that the rate of corrosion decreases in the order $S_I > S_{II} > S_{III}$. The results of the EIS spectra of the steel samples revealed that R_{ct} decreases with the increasing of the immersion times in NaCl solution following the order $S_{III} > S_{II} > S_I$. This means that the corrosion rate of steel in mortar decreases due to the much less amount of NaCl reaches the steel surface through mortar pores and this corrosion rate decreases more while steel within mortar containing 1 % PC which incorporates much fewer pores than the mortar itself and consequently the quantity of salt solution reach steel surface decreases. Also, the charge transfer resistance of steel within mortar in

sodium chloride solution increases, and consequently C_{dl} decreases with the increase of superplasticizer concentration in mortar due to decreasing of its porosity which controls in NaCl solution passing through pores into steel and consequently its corrosion decreases.

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