Int. J. Electrochem. Sci., 15 **(2020)** 11643 – 11652, doi; 1020964/2020.12.16

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Electrochemical Corrosion Behavior of Carbon Steel Reinforcement in Concrete Containing Limestone and Mesoporous Silica Nanoparticles under Acidic Environment

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Received: 5 August 2020 / *Accepted:* 17 September 2020 / *Published:* 31 October 2020

In this study, corrosion behavior of carbon steel rebar embedded in concrete structures containing Limestone and mesoporous silica nanoparticles (MSNs) as partial replacement materials of Portland cement (PC) in 5% sulfuric acid solution were investigated. Polarization analysis, electrochemical impedance spectroscopy (EIS) measurement, water absorption test and mass loss evaluation were utilized to investigate the corrosion resistance of carbon steel rebars. The concrete sample containing both limestone and MSNs admixtures (10M10L) indicated a lower value of mass loss for carbon steel rebar than the other samples which caused superior corrosion behavior of steel reinforced concrete. The 10M10L concrete sample shows a considerable reduction in water absorption. The passive current density in the 10M10L sample was lower compared to the other samples, indicating the enhanced corrosion resistance of carbon steel reinforced concrete containing both MSNs and limestone admixtures. The EIS result reveals that the 10M10L sample indicates a significant improvement in polarization resistance value showing a higher corrosion resistance compared to the other samples.

Keywords: Electrochemical corrosion; Carbon steel rebar; Limestone; Mesoporous silica Nanoparticles; Sulfuric acid solution; Admixture effect

1. INTRODUCTION

Concrete is the second most extensively used material by humans and one of the most main materials for construction and other infrastructure around the world. Nowadays, Reinforced concrete has been used in main structures such as bridges, tunnels, marine construction and ports [1]. However, the durability of steel rebars is mostly compromised by corrosion procedures [2]. Admixtures are attractive as they are relatively inexpensive [3, 4]. The concrete structure quality can be enhanced by the addition of various mineral additives such as Silica Fume, metakaolin, fly Ash , Rice Husk Ash and Palm Oil Fuel Ash [5-7]. By adding these admixtures, the problems of concrete structures are minimized and have positive environmental effects in relation to its disposal. The admixtures form a denser concrete, enhance electrical resistance, limit ion flow, and decrease its permeability and reduce corrosion current. Several researchers have indicated that supplementary cementitious materials decrease porosity and penetration of chloride ions [8, 9]. Incorporating supplementary cementitious materials into a concrete mixture decreases its penetrating properties and reduces capillary pores of concrete structure [10]. Consequently, achieving a surface of steel reinforcement in chloride-contaminated water becomes more difficult.

Nowadays, sulfuric acid (H_2SO_4) has been revealed to be a harsh chemical for steel reinforced concrete structure. H_2SO_4 is used in various fields, such as the food industry and organic material. Furthermore, concrete is related to H_2SO_4 in the manufacturing procedure [11, 12].

It has been well-known that the performance mechanism of limestone as a concrete admixture can be associated to chemical [9], nucleation [8] and filling [10] effects. Using limestone as an additive material can develop the mechanical and durability properties of concrete structures [13].

Many studies have been done to develop reinforced concrete by silica fume, which has led to the enhancement of its chemical resistance and mechanical properties [14-16]. Moreover, silica admixture is an important approach that may be adopted to reduce mechanical, physical and chemical restrictions of steel reinforced concrete and improve their applications [17].

However, limestone and silica nanoparticles have been confirmed able to improve electrical resistivity and decrease the permeability and specific surface area, the simultaneous effect of both on corrosion resistance of stainless steel reinforced concrete has not been previously reported. Thus, this research focused on the simultaneous effect of both admixtures on the mechanical and electrochemical corrosion resistance of steel reinforced concrete.

2. MATERIALS AND METHOD

In this work, the different components of mesoporous silica nanoparticles (MSNs) and limestone admixtures in Portland cement (PC) were used. Properties of the limestone and PC are shown in Table 1. MSNs were purchased from Sigma-Aldrich with an average diameter of 150 nm and a pore size of 5 nm.

Table 1. Chemical compositions of PC and limestone

	PC (wt%)	**Limestone (wt%)**
SiO_2	20.35	0.22
Al_2O_3	4.74	-
Fe_2O_3	3.32	0.15
CaO	63.25	55.16
MgO	3.04	1.13
K_2O	0.62	0.02
Na_2O	0.30	-
SO_3	2.95	0.09
LOI	0.89	43.23

The proportions of mixes for every specimen are shown in Table 2. The mixtures were poured into the cylinder molds with 10 cm diameter and 25 cm height, and then stored for one day at room temperature with a relative humidity of 90%.

Table 2. The mix proportions of concrete samples

Sample no.	PC (wt%)	MSNs (wt%)	Limestone (wt%)
PC	100	0	0
20M	80	20	0
20L	80	0	20
10M10L	80	10	10

Table 3. The chemical composition of carbon steel reinforcement (wt%)

Carbon	Si	Mn	P	Ni	S	Cr	Fe
0.17	0.26	0.45	0.0047	0.10	0.017	0.15	Residual

In order to study the effect of MSNs and limestone admixtures on corrosion behavior of stainless steel reinforced concrete, electrochemical tests were performed on steel rebar. The chemical composition of carbon steel reinforcement is shown in Table 3.

A homemade electrochemical cell was applied to consider the EIS analysis of the specimens. Steel reinforced concrete, a standard copper/copper sulfate (CSE) and graphite were applied as a working, a reference and counter electrodes, respectively.

All reinforced concrete specimens were exposed to 5 wt% sulfuric acid (H_2SO_4) electrolyte solution. The evaluation of the obtained results were done using specialized software. The EIS measurements were done in the frequency range from 100 kHz to 0.1 mHz with ±10 mV AC perturbation. The polarization characterizations were performed at a scanning rate of 1 mV/s. The initial weight of the carbon steel rebar was obtained using Metler before testing for determining gravimetric weight loss. Water absorption was measured according to ASTM C642. Scanning electron microscope was used to study the morphologies of the specimens.

3. RESULTS AND DISCUSSION

Figure 1 shows polarization curves of carbon steel reinforced concrete in different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months. As indicated in Fig. 1, the anodic polarization curves are studied by passive regions at all carbon steel rebars, indicating that the passive films have obviously formed on the steel surface when the steel rebars were exposed to the acidic environment [18]. Moreover, an important shift was observed in corrosion potential toward a positive direction which exhibits that the anodic metal dissolution was efficiently retarded by varying the content of admixtures in concrete structures.

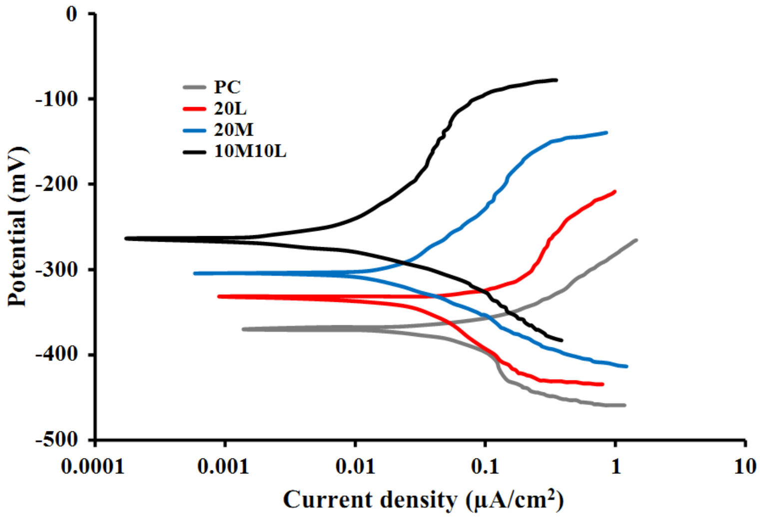

Figure 1. The polarization of carbon steel rebars in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months

Table 4. Corrosion parameters obtained from polarization curves in Fig. 1.

Admixtures	Corrosion current density (μA/cm^2)	Corrosion potential (V)	β_c (mVdec^{-1})	$-\beta_a$ (mVdec^{-1})
PC	0.221	-362	48	28
20L	0.084	-328	51	32
20M	0.067	-302	53	36
10M10L	0.028	-271	47	41

The passive zone at the 10M10L sample was much broader than the other samples. Furthermore, the passive current density in the 10M10L sample was lower compared to the other samples, indicating the enhanced corrosion resistance of carbon steel reinforced concrete containing both MSNs and limestone admixtures. It can be attributed to the MSNs that reacted with free calcium hydroxide during the process of cement hydration and formed further calcium silicate hydrate, which enhanced the mechanical features and durability in the concrete structures [23]. Corrosion parameters obtained from polarization curves in Fig. 1 are shown in table 4.

The corrosion level can be separated in four levels introduced by the Durar-Network Specification [19]. Though, the corrosion current density (i_{corr}) of the 10M10L sample in 5 wt% sulfuric acid solution was lower compared to other samples. Hence, except the PC specimen, all steel rebars remained in passive state during the electrochemical corrosion process which revealed their great corrosion resistance of carbon steel rebar in the acidic environment.

Furthermore, as indicated in table 4, cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) values change in different concrete samples. The variation in the values of Tafel slopes can be utilized to recognize the inhibition mechanism of carbon steel, the working electrode composition, the concentration of electrolyte solution, and charge-transfer coefficient [20]. As shown in table 4, the β_c values are unchanged in the different concrete samples, meaning that its effect on the cathodic reaction does not modify the hydrogen discharge mechanism [21]. However, the β_a values change in various concrete specimens revealing an obstruction at anodic reaction sites. Moreover, the β_a value increases in 10M10L specimen which indicates that the MSNs and limestone admixtures in concrete structure can help the corrosion resistance of carbon steel rebars in 5 wt% H_2SO_4 solution.

Table 5. Permeability of concrete samples with different admixtures exposed to 5 wt% H_2SO_4 solution after different immersion time

K_T ($\times 10^{-16}$ m^2)				
Time	**Admixtures**			
	PC	**20L**	**20M**	**10M10L**
1-week	8.754	5.123	1.471	0.967
1-month	6.416	2.514	0.719	0.596
2-months	2.346	0.828	0.453	0.358
4-months	1.122	0.089	0.074	0.063

The compared permeability results from different concrete samples with various admixtures exposed to 5 wt% H_2SO_4 solution after 4 months are indicated in Table 5. High permeability values in the first month may be associated with the wrong performance of the specimens when removing the samples from the mold [22]. Though, it was found that concrete samples with additives had less permeability than samples without admixtures. It can be related to the Connection Bridge formation by mineral admixtures which inhibit the crack growth in concrete. As shown in Table 5, the 10M10L concrete sample clearly had more appropriate K_T than the other samples. Thus, this sample indicated lower permeability of anions in reinforced concrete structure which indicated an alternative additive for the enchantment in durability and corrosion behavior of carbon steel reinforced concerts.

Measuring the mass loss during immersion period offers a relatively accurate forecast for construction life. Figure 2 displays the mass loss of carbon steel rebars in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months. As shown in Fig 2, with increasing immersion time, the mass loss increases. The 10M10L concrete sample indicated a lower value of mass loss for carbon steel rebar than the other samples which was in accordance with the obtained polarization results.

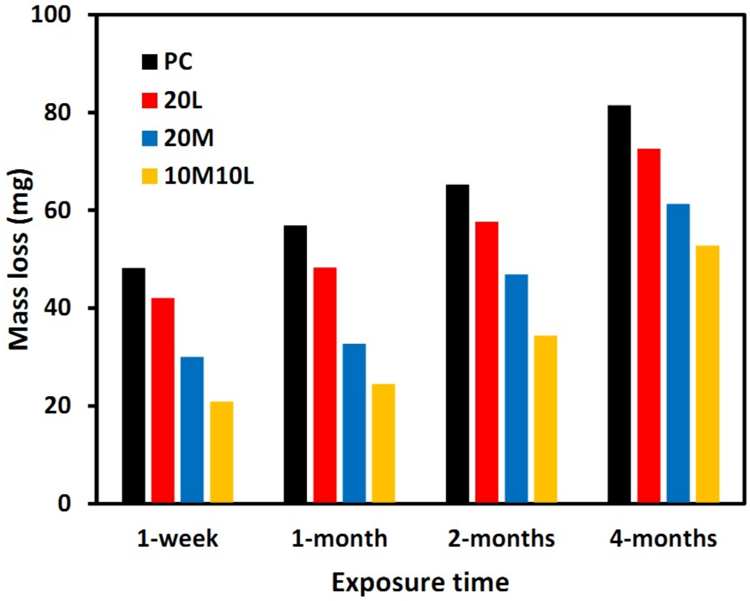

Figure 2. Mass loss of carbon steel rebars in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after different immersion time

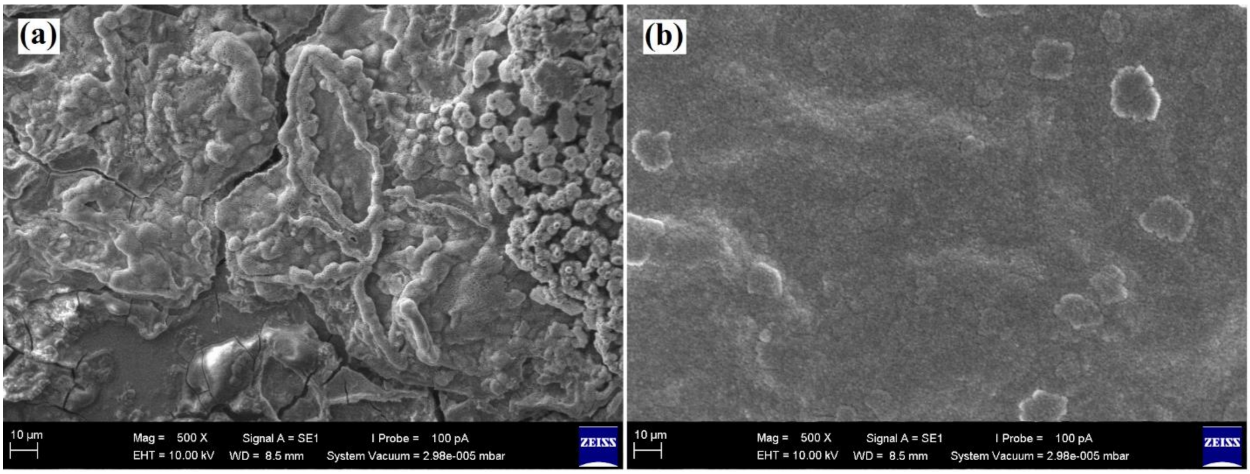

Figure 3. FESEM images of steel reinforcement in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months

Figure 3 indicates the FESEM images of steel reinforcement in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months. Figure 3b indicates that the carbon steel rebar embedded in concrete including both limestone and MSNs admixtures was more uniform compared to the PC specimens which is consistent with previous studies [23, 24]. The MSNs reduce the hydration heat which led to reaction of water-cement [25]. Moreover, the limestone as a filler decreases concrete permeability and enhances durability of concrete structures and inhibits the corrosive anions from reaching the carbon steel surface.

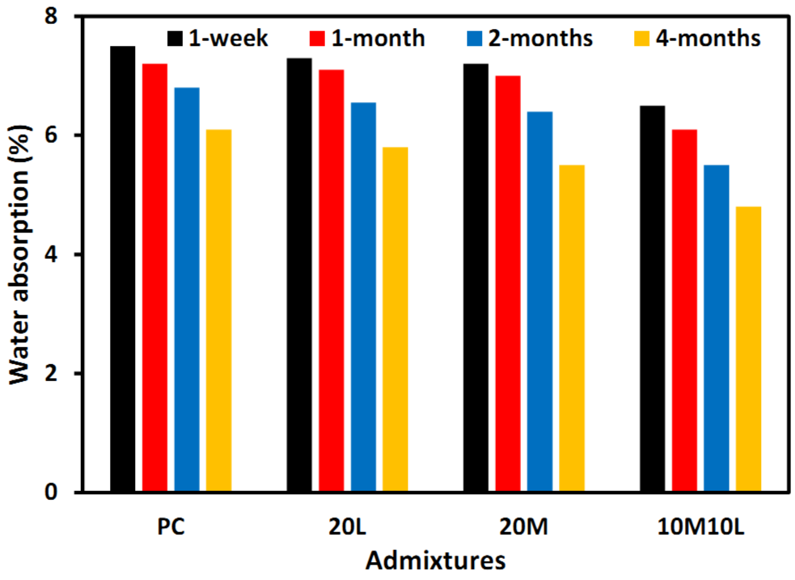

Figure 4. Water absorption of concrete samples with different admixtures exposed to 5 wt% H_2SO_4 solution after 1-week, 1-month, 2-months and 4-months

The water absorption (WA) of concrete samples with different admixtures exposed to 5 wt% H_2SO_4 solution after 1-week, 1-month, 2-months and 4-months are shown in Fig. 4. As revealed, all the specimens with admixtures indicate a reduction in water absorption by increasing immersion time than the PC concrete sample. This means that admixtures in concrete structures can reduce the WA of concrete after being immersed in an acidic environment. The 10M10L specimen indicates lower WA than the other samples, showing considerable effect on WA by the addition of both limestone and MSNs admixtures in PC concrete.

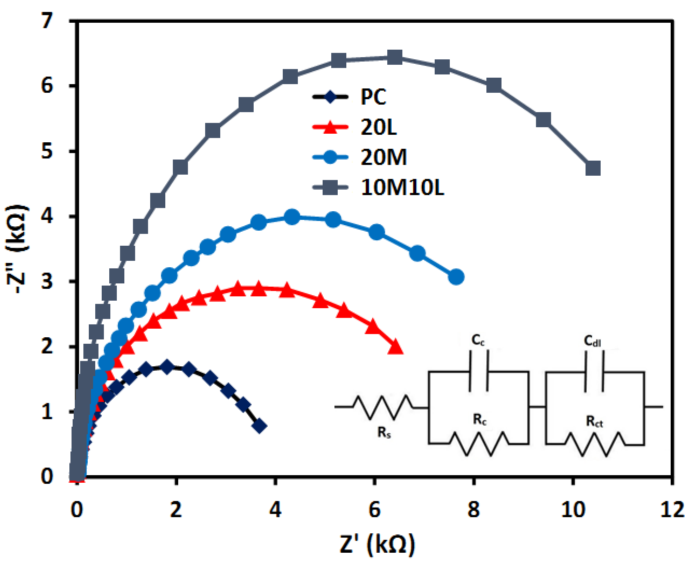

Figure 5. Nyquist diagram of carbon steel rebar in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months. Inset shows the used equivalent circuit

The EIS system has been widely employed in the investigation of the passive film on steel rebars because of its ability to evaluate redox reactions of steel reinforcement in a corrosive environment [26]. The EIS was used to study the effect of additive materials in PC on the corrosion resistance of steel reinforced concrete with passive films in the acidic solution (Figure 5). The variations in concrete content caused changes in the capacitive loop radius which exhibited an improvement in the corrosion resistance of carbon steel rebar. Inset of Figure 5 shows an equivalent circuit model with two-times constants which proposed to simulate the electrochemical process of carbon steel rebars applied by other researchers. R_s indicates the solution resistance [9]. R_c and R_{ct} indicate the passive layer and the charge-transfer resistances, respectively. C_c and C_{dl} represent the passive layer/solution interface and double-layer capacitances, respectively [27]. The obtained data are indicated in Table 6. As indicated in table 6, the value of C_{dl} decreases in a 10M10L sample, which exhibits that the thickness of passive layer enhanced, resulting protective capacity was increased once was used both MSNs and limestone admixtures into the reinforced concrete. Polarization resistance (R_p) is an assessable indicator to study the corrosion resistance of carbon steel rebars into the corrosive media. The higher value of R_p reveals higher corrosion resistance in the specimen.

Table 6. Electrochemical parameters derived from Fig. 5 for carbon steel rebar in concrete with different admixtures exposed to 5 wt% H_2SO_4 solution after 4 months

Admixtures	R_s (Ω cm^2)	R_c(kΩ cm^2)	C_c(μF cm^{-2})	R_{ct} (kΩ cm^2)	C_{dl} (μF cm^{-2})	R_p (kΩ cm^2)
PC	34.7	2.23	8.3	4.22	11.7	6.45
20L	33.8	4.13	6.9	7.98	9.4	12.11
20M	28.5	5.69	5.1	10.21	7.6	15.90
10M10L	32.4	7.82	4.7	13.32	6.8	21.14

As shown in table 6, the 10M10L sample indicates a significant improvement in R_p value showing a higher corrosion resistance compared to the other samples.

4. CONCLUSIONS

In this study, corrosion behavior of carbon steel rebar embedded in concrete structures containing Limestone and MSNs as partial replacement materials of PC in 5% sulfuric acid solution were investigated. Polarization analysis, EIS measurement, water absorption test and mass loss evaluation were utilized to investigate the corrosion resistance of carbon steel rebars. The 10M10L concrete sample indicated a lower value of mass loss for carbon steel rebar than the other samples which caused superior corrosion behavior of steel reinforced concrete. The 10M10L specimen indicates lower WA than the other samples, showing considerable effect on WA by the addition of both limestone and MSNs admixtures in PC concrete. The passive current density in the 10M10L sample was lower compared to the other samples, indicating the enhanced corrosion resistance of carbon steel reinforced concrete containing both MSNs and limestone admixtures. The EIS result reveals that the variations in concrete content caused changes in the capacitive loop radius which exhibited an improvement in the corrosion resistance of carbon steel rebar. The FESEM images indicate that the carbon steel rebar embedded in the 10M10L concrete sample was more uniform compared to the PC specimen which is consistent with previous studies reported.

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