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Effect of Partial replacement of Portland cement with micro-silica on mechanical characteristics of concrete and corrosion behavior of mild steel in 1M HCl

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The effect of micro-silica (MS) as Portland cement (PC) replacement on corrosion resistance of mild steel rebar were considered by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and water absorption analysis after exposure to 1M HCl solution. Compressive strength tests were done to investigate the mechanical property of the concrete samples. By increasing immersion time, all concrete samples containing MS indicated a reduction in water absorption value compared to the concrete sample without MS. The samples with 8 wt% MS exhibited the highest compressive strength after 8 weeks exposure time in a 1M HCl solution. The value of OCP for the steel reinforced concrete specimens with 8 wt% MS remained in the uncertain or low corrosion zone during the process. The EIS results showed that the 8 wt% MS sample had a higher the concrete resistance and charge-transfer resistance compared to other samples, showing lower porosity of concrete structure and thus more improvement in corrosion resistance of the mild steel surface. The SEM images of mild steel rebars revealed that the steel reinforced concrete with 8 wt% MS content had low corrosion and minimum pit products, indicating the slight pitting corrosion shaped on the surface of mild steel rebar, which was in agreement with the results obtained from electrochemical study.

Keywords: Partial replacement; Micro-silica; mild steel rebar; Electrochemical corrosion; Compressive strength; Water absorption; Acidic environment

1. INTRODUCTION

Reinforced concrete structures are the most common material in construction industries [1, 2]. Production of Portland cement (PC) is an extremely energetic process, and emits carbon dioxide during the calcination which has an important effect on global warming [3, 4]. Thus, it is necessary to find eco-friendly concrete preparation with low PC content but high efficiency in durability and strength [5, 6].

An economically and technically based selection of the most appropriate rheology modifiers, additives and fillers plays a main role here. The use of mineral admixtures is one of the important approaches in reducing the environmental impact of the concrete industry [7, 8]. The first approach includes replacing cement with variable volumes of industrial by-products [9, 10]. Pozzolanic materials such as calcined clays, sewage sludge ash, metakaolin and fly ash have been used effectively in cement production, although their use is not prolonged [11-15].

Recently, the use of micro particles has received special attention in the construction application particularly in cement concrete and mortar [16]. Among various manufactured micro particles, micro-silica (MS) has recently been indicated as an improved pozzolan to advance the stability and microstructure of cement-based systems [17].

MS is a non-crystalline polymorph of silicon dioxide (SiO_2). It is an extremely fine powder collected as a by-product of ferrosilicon and silicon composite production and consists of spherical particles with 150 nm of average particle diameter [18, 19].

Nowadays, hydrochloric acid (HCl) has been shown to be a destructive chemical for reinforced concrete structure. HCl is used in almost all fields, such as the production of iron-steel, organic material and the food industry. Moreover, concrete is associated with HCl in the manufacturing process [20, 21].

Given that the effect of acidic environment on the mechanical and electrochemical corrosion properties of reinforced concrete containing MS have not been previously reported. In this work, the electrochemical investigation on corrosion resistance of mild steel reinforced concrete blended with MS as partial replacement of PC were studied. Open-circuit potential (OCP) monitoring, electrochemical impedance spectroscopy (EIS), compressive strength and water absorption measurements were used to consider the corrosion behavior and mechanical property of reinforced concrete samples.

2. MATERIALS AND METHODS

In this work, concrete structures were made under controlled conditions using PC, water, coarse and fine aggregates at room temperature. Micro-silica with concentration of 0-16 wt% was replaced in PC. Table 1 indicates the chemical compositions of the PC and MS. The ratios of concrete combination are revealed in Table 2. Water to cement (w/c) ratio was 0.4. The mixed cements were produced through a high-speed mixer to obtain a high-level of homogeneous dispersion. Mild steel rebar with 10 mm diameter and 10 cm long was embedded in a cylinder with a cover of 3 cm. Prior to use, chemical cleaning was utilized on the surface of mild steel. Table 3 reveals the chemical composite of mild steel rebar. After casting the mix into the molds, the vibrator was utilized to decrease the air bubbles. The specimens were demolded after 24 hours and then cured for four weeks.

Table 1. Chemical compositions of PC and MS

	PC (wt%)	**MS (wt%)**
SiO_2	19.65	86.73
Fe_2O_3	3.01	0.99
Al_2O_3	4.75	0.00
MgO	2.04	7.53
CaO	65.23	2.54
Na_2O	0.29	1.38
K_2O	0.65	3.13
SO_3	2.98	2.58
LOI	0.86	6.48

Table 2. The details of concrete mixtures

	PC	2 wt%	4wt%	8 wt%	16 wt%
PC (kg/m^3)	450	441	432	414	378
Micro-silica (kg/m^3)	0	9	18	36	72
Coarse aggregate (kg/m^3)	735	735	735	735	735
Fine aggregate (kg/m^3)	984	984	984	984	984
Water (kg/m^3)	180	180	180	180	180
W/C	0.4	0.4	0.4	0.4	0.4

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

C	**Si**	**S**	**P**	**Mn**	**V**	**Fe**
0.21	0.52	0.03	0.03	1.43	0.03	Bal.

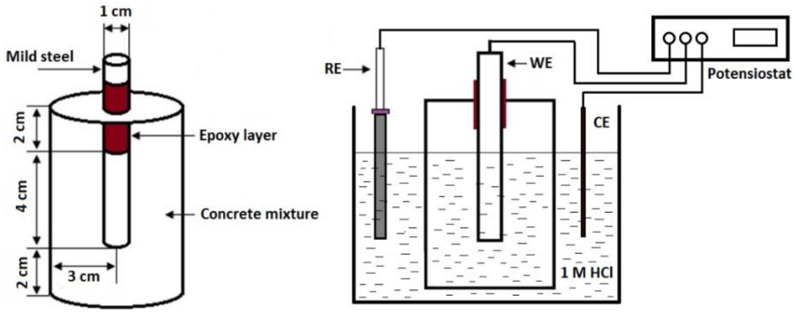

Figure 1. Schematic diagram of the mild steel reinforced concrete used as a working electrode in electrochemical experiments

In order to prepare working electrodes, the concrete mixture was poured into the cylindrical mold, while a steel rebar was placed vertically at the center of the cylinder. Open circuit potential (OCP) was done through a high-impedance voltmeter by an input resistance. EIS as nondestructive monitoring techniques was used to study the corrosion behavior of mild steel rebars. An electrochemical procedure was used with the mild steel rebar, saturated calomel electrode and graphite as a working, reference and counter electrodes, respectively. Figure 1 shows a schematic diagram and detailed dimensions for a reinforced concrete sample. The investigation was recorded after exposure to 1 M HCl as a corrosive environment. The EIS analysis was performed by CorrTest Instruments Corp in a frequency range of 10 mHz to 0.1 MHz.

In order to consider water absorption of mixtures, cylinder-shaped mold with 10 cm diameter and 20 cm height were applied according to ASTM C642. For determination of the water absorption, the samples were exposed to 1 M HCl solution. The water absorption of samples was recorded after immersing time of 1, 2, 4 and 8 weeks which was the average value of three samples. Compressive strength values were attained according to the BS-1881 method. The surface morphologies of the samples were considered with a scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

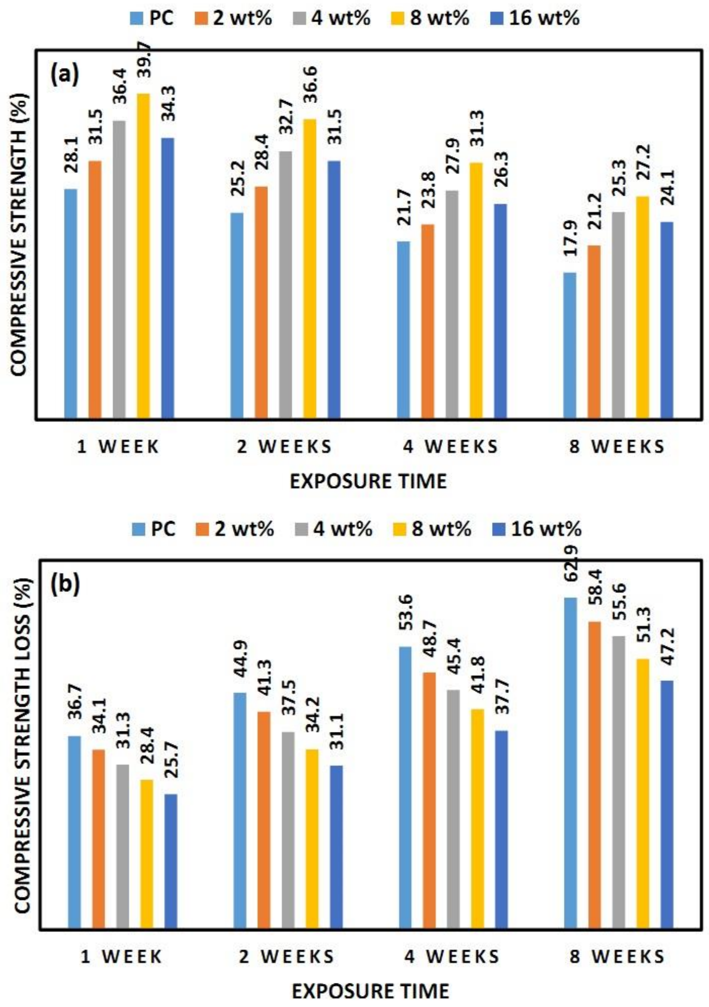

Figure 1. (a) Compressive strength and (b) Compressive strength loss of concrete mixtures with different concentration of MS after 1, 2, 4 and 8 weeks of exposure time in a 1M HCl.

The compressive strength and compressive strength loss of concrete mixtures with different concentrations of MS after 1, 2, 4 and 8 weeks of exposure time in a 1M HCl are shown in Figure 1. As shown in Figure 1a, compressive strength of the concrete mixtures exposed to 1M HCl decreases with increasing exposure time. As seen in figure 1b, the maximum compressive strength loss of all mixtures was found after 8 weeks of exposure time in 1M HCl. The loss was approximately about 60% for all mixtures. This result was in good accordance with previous studies [22]. Moreover, it's observed that the samples with 8 wt% MS indicated highest compressive strength after 1, 2, 4 and 8 weeks of exposure time in a 1M HCl. It can be associated to micro-filler act and improved bonding capability of actual fine MS, which is caused in the microstructure enhancement of concrete matrix. Moreover, the samples with 16 wt% MS revealed the lower strength than the sample with 8 wt% MS after immersing in 1 HCl. This means that a further content of MS as an admixture reduces compressive strength [23]. It can also be related to inferior microstructure of concrete mixtures with higher MS content. On the other hand, it may be attributed to the reaction of HCl by $Ca(OH)_2$ [24]. Once the concrete samples are exposed to HCl solution, an extensive gypsum formation is predicted in areas close to the surface [25, 26]. The samples with 16 wt% MS exhibited a lower compressive strength loss exposure to the 1 M HCl compared to the all samples which can be related to the more dense and compact concrete matrix microstructure because of micro-filler effect of MS.

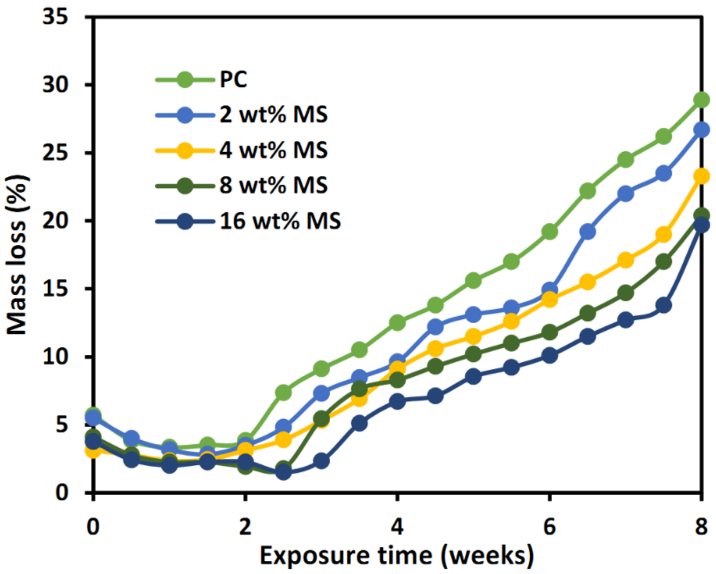

Figure 2. Mass loss of concrete mixtures with different concentration of MS during 8 weeks of exposure time in a 1M HCl

Mass loss of concrete mixtures with different concentration of MS during 8 weeks of exposure time in a 1M HCl is indicated in Figure 2. Concrete mixtures with various ratios of MS revealed a greater resistance to acid attack than PC sample which shows that using MS as an admixture in PC can be studied as an efficient method to enhance resistance of mixtures to acid attack. The findings were in good accordance with former studies [27, 28]. When hydrochloric reacts within the hydration products, hydrogen ions and dissolution of hydrated composites occurs. The process depends on various factors, such as the pH value of solution, hydrochloric acid concentration, porosity of concrete structure and pore structure [24]. Thus, higher resistance of concrete mixtures containing MS can be associated with the enhanced concrete matrix microstructure, which influences the concrete structure. Therefore, using MS as an admixture reduces the porosity of concrete and its pores. As shown in Figure 2, the maximum mass loss was observed after 8 weeks exposure to the HCl acid in all concrete mixtures. As shown in Fig. 2, the PC sample had the worst mass loss of 27% among all samples after 8 weeks of exposure time. When the replacement ratio of MS increases in the concrete mixtures, the mass loss gradually reduces. The result was in good accordance with a previous study [23]. Consequently, samples with 16 wt% MS exhibited best performance of all mixtures.

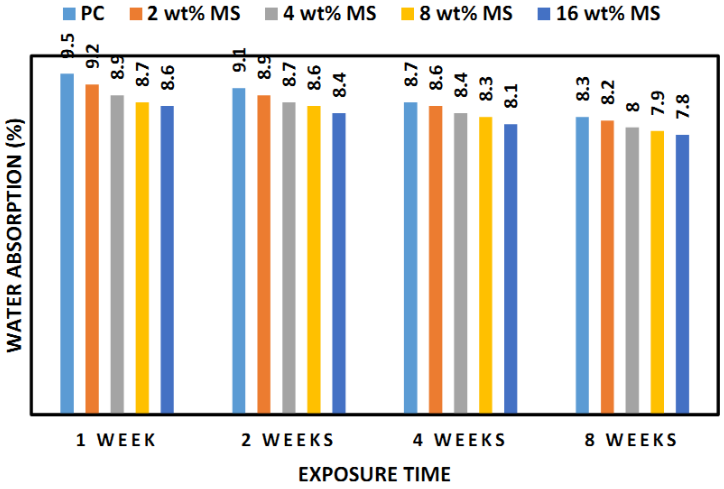

Figure 3. Water absorption of mixtures with different concentration of MS as partial PC replacement after 1, 2, 4 and 8 weeks of exposure time in a 1M HCl

Water absorption of concrete mixtures with different concentrations of MS as partial PC replacement after 1, 2, 4 and 8 weeks of exposure time in a 1M HCl is shown in Figure 3. As revealed in Figure 3, water absorption in all mixtures containing MS was lower than that of PC sample which shows that using MS as an admixture in concrete sample can reduce water absorption of concrete sample after immersed to corrosive environments. Indeed, the water absorption of concrete during exposure to 1M HCl reduce as the MS content increases.

Figure 4 indicates the OCP values of mild steel rebars in concrete samples with different content of MS after 8 weeks exposure time in 1M HCl solution. Dashed lines in Figure 4 separate the various regions of potential corrosion risk. In accordance with ASTM C876-91 [29], three zones can be differentiated as corrosion risk is investigated. Thus, the OCP values lower than -350 mV/CCS indicate the strong corrosion possibility.

Hydrochloric acid may react by the calcium aluminate hydrates or calcium hydroxide and produce calcium chloride dihydrate-ettringite and gypsum. Formation of ettringite and gypsum can cause a considerable deterioration of concrete structure. Furthermore, it can increase concrete structure porosity and then the anions and water can certainly reach the surface of mild steel rebar. Moreover, the samples with 8 wt% MS exhibited a higher OCP value compared to the other samples in the HCl solution.

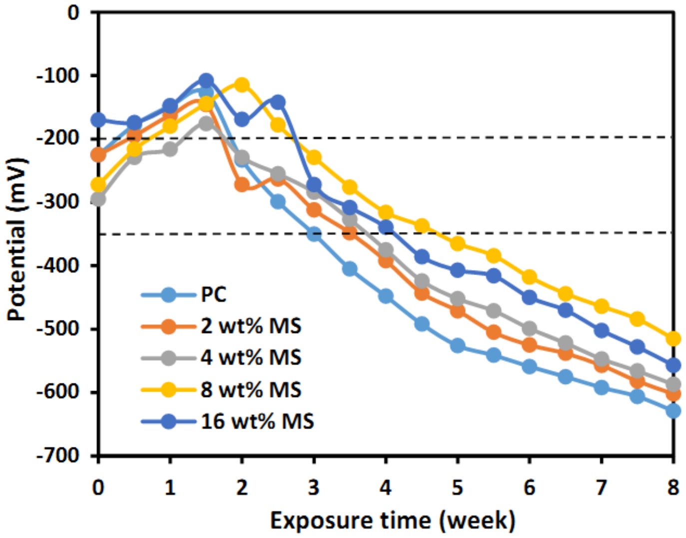

Figure 4. The OCP values of mild steel rebars in concrete samples with different content of MS after 8 weeks exposure time in 1M HCl solution

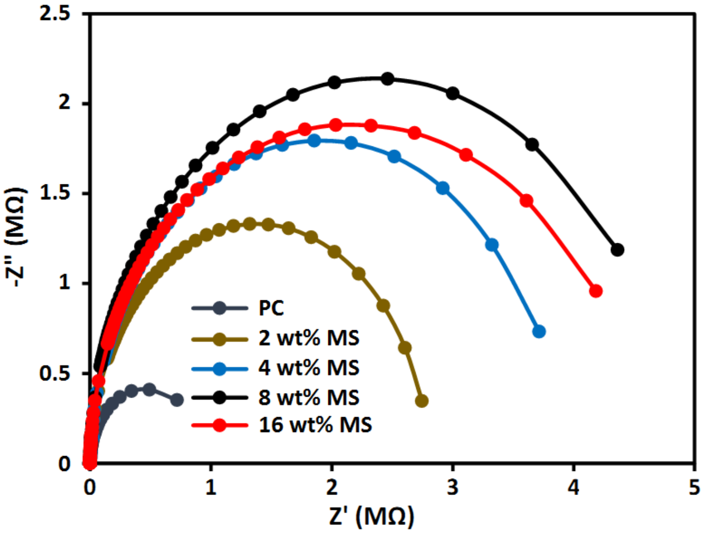

Figure 5. EIS plots of mild steel rebars in concrete samples with different MS content exposed to 1M HCl after exposure time of 8 weeks.

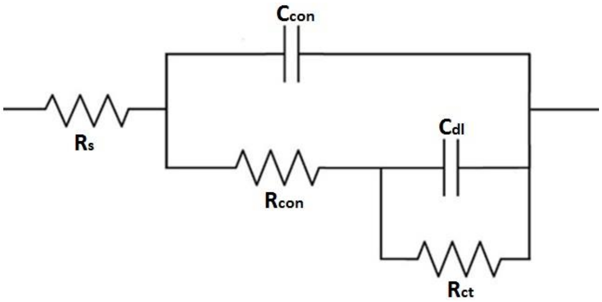

Figure 6. Equivalent circuit model

EIS was used to characterize the corrosion behavior of mild steel rebar in concrete samples with different MS content exposed to 1M HCl after exposure time of 8 weeks. As shown in Fig. 5, all the Nyquist curves had similar configurations which were similar to a half-arch that formed in high-frequency and low-frequency regions have also been reported in previous studies [30, 31]. Qiao et al. [32] gave a description for the pattern shown in Figure 6. The first arch within the high-frequency range is formed by the effect of the concrete matrix [33]. The second arch in the low-frequency range defines the corrosion process on the mild steel surface. The reduction in the size of the arch formed in the high-frequency region is based on the increase in the porosity of the concrete samples and the ion concentration in the cement paste [34].

Figure 6 reveals an equivalent circuit model used in this work. R_s indicates the solution resistance. R_{con} and C_{con} are the resistance of the concrete and the concrete capacitance, respectively. R_{ct} and C_{dl} are the charge-transfer resistance and double-layer capacitance, respectively [35, 36]. As shown in table 4 the arch formed in the low-frequency region changed by increasing the MS admixtures in concrete samples. This difference showed that the porosity of the PC sample was higher than the other samples. Increasing the R_{con} value by increasing the MS content also confirms that the porosity of the concrete has decreased [37, 38]. As shown in table 4, the sample with 8 wt% MS indicates a considerable enhancement in R_{ct} value showing higher corrosion resistance in acidic environments. Furthermore, the value of C_{dl} reduced with increasing MS content up to 8 wt%, which exhibits that the thickness of the passive layer is enhanced on the mild steel surface. The increase in the R_{con} and R_{ct} values of the samples with increasing the MS content in concrete showed that the porosity had decreased and thus, the reinforcement was exposed to fewer corrosive effects.

Table 4. Electrochemical parameters derived from EIS results for different content of MS exposed to 1M HCl solution after exposure time of 8 weeks

Admixtures	R_s (Ωcm^2)	R_{con} (MΩcm^2)	C_{con} (µFcm^{-2})	R_{ct} (MΩcm^2)	C_{dl} (µFcm^{-2})
PC	58.3	0.68	0.96	1.05	1.6
2 wt% MS	62.4	1.25	0.72	2.83	1.2
4 wt% MS	66.7	2.97	0.47	4.11	0.8
8 wt% MS	57.3	3.96	0.28	5.26	0.6
16 wt% MS	63.4	3.23	0.39	4.68	0.7

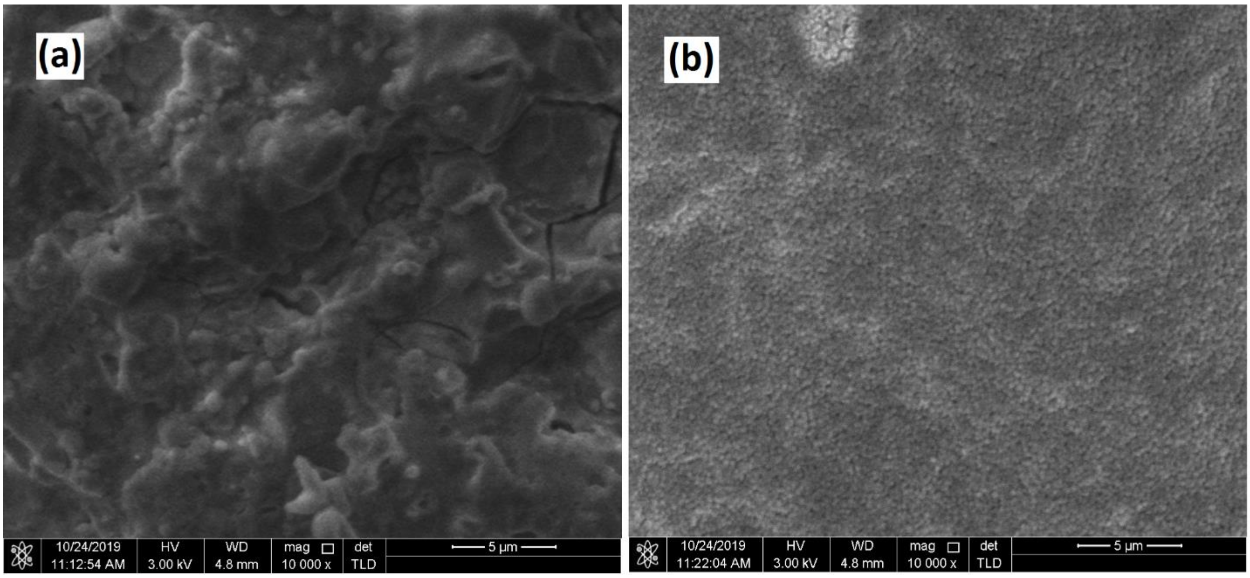

Figure 7. FESEM images of steel surface embedded in concrete samples containing different MS content (a) 0 wt% MS (b) 8 wt% MS after 8 weeks exposed to 1M HCl solution

Figure 7 indicates the FESEM images of steel surface embedded in concrete samples containing different MS content after 8 weeks exposed to 1M HCl solution. The surface of steel reinforced concrete with 8 wt% MS content shows low corrosion and minimum pits products, indicating the slight pitting corrosion shaped on the surface of mild steel rebar, which was in agreement with the results obtained from electrochemical study. It can be associated with reducing water permeability and anions in reinforced concrete samples. The large pores may be improved to smaller pores by addition of MS, causing a variation in the cement paste structure. This results revealed that partial replacement of MS in PC led to a decrease of corrosion rate and improved the corrosion resistance of mild steel rebar due to the reduction of anions and water permeability.

4. CONCLUSIONS

In this work, mechanical property and corrosion behavior of mild steel reinforced concrete containing MS were investigated in 1M HCl solution. To evaluate the effect of MS concentration in the corrosion behavior of the PC concrete, 2 wt%, 4 wt%, 8 wt% and 16 wt% MS replacement levels were performed in concrete production. The compressive strengths revealed that replacement of MS content up to 8 wt% in PC enhanced the mechanical properties of specimens. Moreover, corrosion of mild steel rebar blended in concrete replaced with the MS up to 8 wt% was lower than the other samples. The surface morphology of steel rebar revealed that the reinforced concrete sample containing 8 wt% MS is denser than that of the PC sample. The EIS results showed that 8 wt% MS sample had a higher R_{ct} and R_{con} compared to other specimens, showing lower porosity of concrete structure and thus more improvement in corrosion resistance of the mild steel surface.

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