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Short Communication

Microsilica and Waste Glass Powder as Partial replacement of Portland Cement: Electrochemical Study on the Corrosion Performance of Steel Rebar in the Blended Concrete

Guangjuan Gu[1,2,*], *Hongling Song*[2]

[1] Key Laboratory of Building Structure of Anhui Higher Education Institutes (Anhui Xinhua University), Anhui Hefei 230088,China
[2] Anhui Xinhua University Civil and Environmental engineering College, Anhui Hefei 230088,China
[*]E-mail: umbraler2020@sina.com and guguangjuan@axhu.edu.cn

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Today, steel reinforced concrete has been extensively used as building material which is typically exposed to corrosive media, causing corrosion of steel rebar. Here, a partial replacement by microsilica (MS) and Waste Glass Powder (WGP) in ordinary Portland cement (OPC) were used to produce reinforced concrete and its effects were investigated on corrosion resistance of carbon steel rebar in 3.5 wt% NaCl solution. Electrochemical impedance spectroscopy measurements were used to study the electrochemical corrosion behavior of carbon steel rebar. The absorption results revealed that the mixtures containing 10% MS and 10% WGP (10MS10WGP) considerably improved water absorption of concrete structure. Partial replacement of OPC by MS, either with or without WGP, revealed a significant increase in both one and four-week compressive strengths. The electrochemical results indicated that the 10MS10WGP specimen has higher value of corrosion resistance than the other samples. The surface of 10MS10WGP shows low corrosion products and thin pits which can be related to the decrease of water absorption and Cl^- ion permeability into the concrete structure.

Keywords: Partial replacement; Microsilica; Waste glass powder; Ordinary Portland cement; Electrochemical corrosion; compressive strengths

1. INTRODUCTION

The **c**hloride ion penetration into the surface of steel leads to its corrosion and thus, decreases durability of reinforced concrete structures [1]. Thus, research into reducing the permeability of concrete, which can reduce corrosion, has received much attention.

There are various techniques to prevent corrosion in reinforced concrete such as cathodic protection, corrosion inhibitors and epoxy coatings [2-4]. However, these techniques are not very inexpensive and effective.

Partial replacement of Portland cement (PC) with supplementary cementitious materials (SCM) may be another viable and ecological option for corrosion resistance [5, 6]. SCM reduces the porosity and permeability of the concrete due to the formation of cementitious compounds by a pozzolanic reaction with the calcium hydroxide of the cement hydration [7].

Mineral admixtures are typically used in numerous applications for example high performance concrete bridges, buildings and on-shore and off-shore structures. Well-known mineral admixtures include silica fume, rice husk ash, and fly ash [8, 9]. The addition of these additive materials in the production of concrete has a positive environmental property and minimizes the problems associated with its disposal.

Micro silica (MS) is a byproduct of ferro silicon and silicon production, which is mostly from SiO_2 amorphous in the morphology of spherical particles with an average diameter of 100 nm to 200 nm [10]. It has a very reactive pozzolana behavior [11, 12]. Moreover, it has significant potential for improving some of the properties of hardened and fresh concrete required for many engineering applications.

Glass is recognized as a transparent material that is prepared by melting a mix of materials such as $CaCO_3$, soda ash, and silica at high temperature. The waste glass reuse is the most important issue because of the increase in solid wastes into the landfills and indivisible nature of its disposal [13]. Numerous studies have revealed that waste glass which is screened and crushed is an economical, safe and strong alternative to sand utilized in concrete. The use of waste glass in the construction of concrete is advantageous because the cost of concrete production will reduce [14].

Replacement of fine aggregates may cause enhanced stability using pore refinement and improved resistance to the release of harmful agents. Many studies have shown that the mineral admixtures strangely increase the resistance to diffusion of chloride in SCM [15-17]. Given that the simultaneous effects of waste glass powder (WGP) and MS on the corrosion behavior of steel reinforced concrete have not been previously reported. In this work, a study on corrosion resistance of carbon steel rebar in concrete with partial replacement of cement by WGP and MS was done. The electrochemical method was used to investigate corrosion properties of the specimens in marine environments.

2. MATERIALS AND METHOD

In this work, concrete was produced under controlled conditions at room temperature by mixing ordinary Portland cement (OPC), water, coarse aggregates and fine. The cement replacement was performed with waste glass powder (WGP) and micro silica (MS) admixtures. The content of binder mixtures was 500 kg/m^3. The ratio of water to cement (w/c) was 0.45. The chemical composition of OPC, WGP and MS are shown in Table 1.

The composition of the various mixtures are shown in Table 2. The prepared mixtures were transferred into the cuboid molds with Length, breadth and height of 10 cm, 10 cm and 30 cm, respectively at 90% relative humidity and 25 ^{o}C temperature for 24 h. Three cubic samples were used to measure four-week compressive strength. An average of three values have been reported as a result of measuring compressive strength. In order to study the replacement effect of WGP and MS on corrosion behavior of carbon steel rebars, electrochemical tests were done on carbon steel rebar in 3.5 wt% NaCl environment. The composition of the used steel rebar is presented in Table 3.

Table 1. Chemical composition of OPC, WGP and MS

	OPC (wt%)	MS (wt%)	WGP (wt%)
SiO_2	21.55	87.81	71.43
Al_2O_3	4.17	-	-
Fe_2O_3	3.25	0.94	-
CaO	63.15	2.32	10.31
MgO	2.56	6.55	3.75
K_2O	0.47	3.18	-
Na_2O	0.74	1.53	14.51
SO_3	2.43	2.86	-
LOI	0.87	6.20	-

Table 2. Composition of different concrete mixture (kg/m^3)

Mixture	OPC	MS	WGP	Water	Fine aggregates	Coarse aggregates
OPC	500	0	0	225	730	1075
20MS	400	100	0	225	715	1020
20WGP	400	0	100	225	715	1020
10MS10WGP	400	50	50	225	715	1020

Table 3. The composition of used steel rebar (wt%)

Carbon	Mn	P	Si	S	Ni	Cr	Fe
0.16	0.43	0.004	0.22	0.015	0.11	0.13	Residual

A three-electrode electrochemical system, including the steel rebar, platinum wire and a saturated calomel electrode were used as the working, counter and reference electrodes, respectively. All analysis were done in the 3.5 wt% NaCl solution as a simulated marine environment. Electrochemical impedance spectroscopy (EIS, Wuhan CorrTest Instruments Corp., Ltd.) were done at 10 mV amplitude with a scanning range of 0.01 Hz to 0.1 MHz. Value of water absorption was considered by drying a specimen with constant mass. Then the sample is exposed to water and determines the mass of saturated surface-dry. The water absorption is the ratio of difference between two-values determined to the dry mass.

3. RESULTS AND DISCUSSION

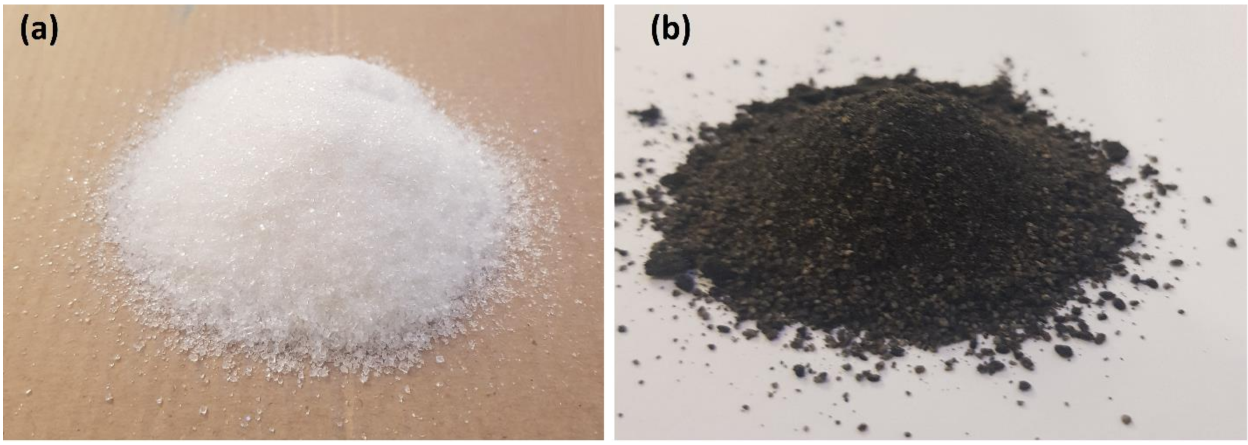

Figure 1. Images of (a) WGP and (b) MS

Figure 1 shows images of WGP and MS were used in this work. The particle shape and size of WGP and MS are observed in Fig. 1. The WGP had 75µm particle size. The MS powder can improve the strength, decrease the hydration heat into the concrete, and enhance the structure of concrete that was utilized as partial replacement into the OPC.

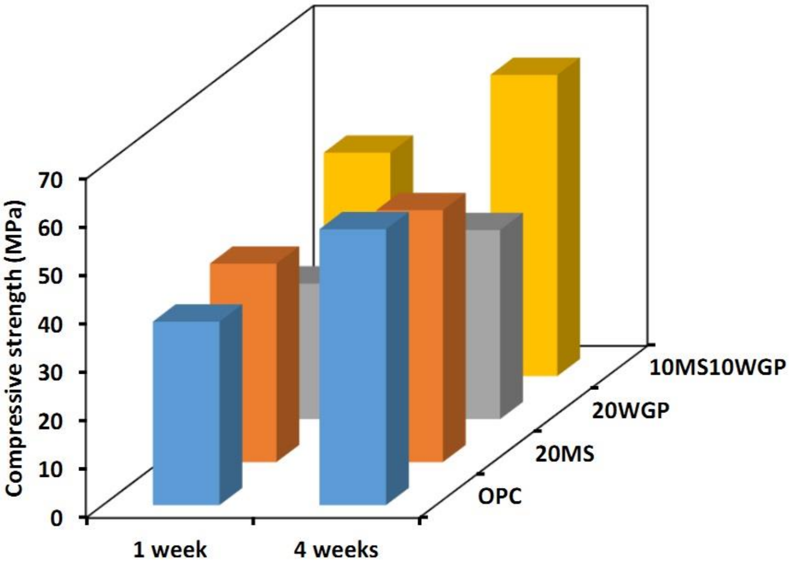

Figure 2. Compressive strength of partial replacement of OPC with WGP and MS.

Figure 2 indicates compressive strengths of partial replacement of OPC with WGP and MS. Similar trends are found in both one and four-week compressive strengths. As shown in fig. 2, partial replacement of OPC with WGP decreases the compressive strength, while incorporation of MS led to increase in strengths. Furthermore, any substitution by MS, either with or without WGP, always shows a significant increase in both one and four-week compressive strengths. MS is a highly reactive pozzolan. The reaction of MS with calcium hydroxide leads to the formation of extra calcium silicate hydrates as secondary reaction products which could efficiently densify the structure of cement paste and thus, strengthen its mechanical activities [18]. Therefore compressive strength increases after 4-week because of the formation of extra calcium silicate hydrate. The separation of cement grains and water absorption capacity of MS could significantly decrease the reactions of cement hydration and therefore weaken the four-week compressive strength [19]. Interestingly, mixtures containing 10 % MS and 10 % WGP indicate approximately the same four-week compressive strengths. Hence, the OPC can be replaced by using a suitable mixture of MS and WGP to improve the strength behavior with a constant W/C ratio and without dispersion.

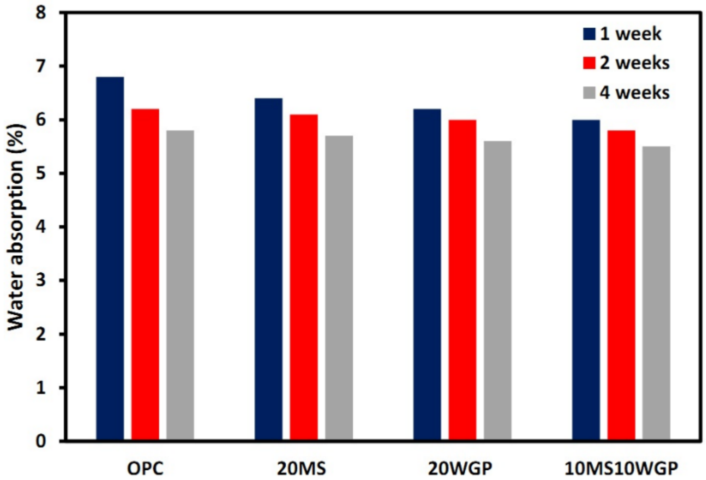

Figure 3. Water absorption of partial replacement of OPC with WGP and MS after 1, 2 and 4 weeks exposed to a marine environment.

The water absorption of partial replacement of OPC with WGP and MS after 1, 2 and 4 weeks exposed to 3.5 wt% NaCl environment are shown in Fig. 3. As revealed, all the samples with WGP and MS show a reduction in water absorption by increasing exposure period compared to the OPC concrete. This means that WGP and MS admixture in OPC can decrease the water absorption of reinforced concrete after being exposed to marine environment. Thus, water absorption of the specimens reduces when the mixtures contain 10 % MS and 10 % WGP. Moreover, it can be concluded that WGP and MS admixtures in OPC had no significant effect on water absorption compared with other properties.

However, the existence of water into the initial stages of corrosion is needed, permeability and adsorption of the samples do not have a major role into the corrosion behavior of steel reinforced concrete which was compatible with previous studies [20]. Actually, it is important to study the oxygen and chloride diffusions for cathodic and anodic reactions, respectively.

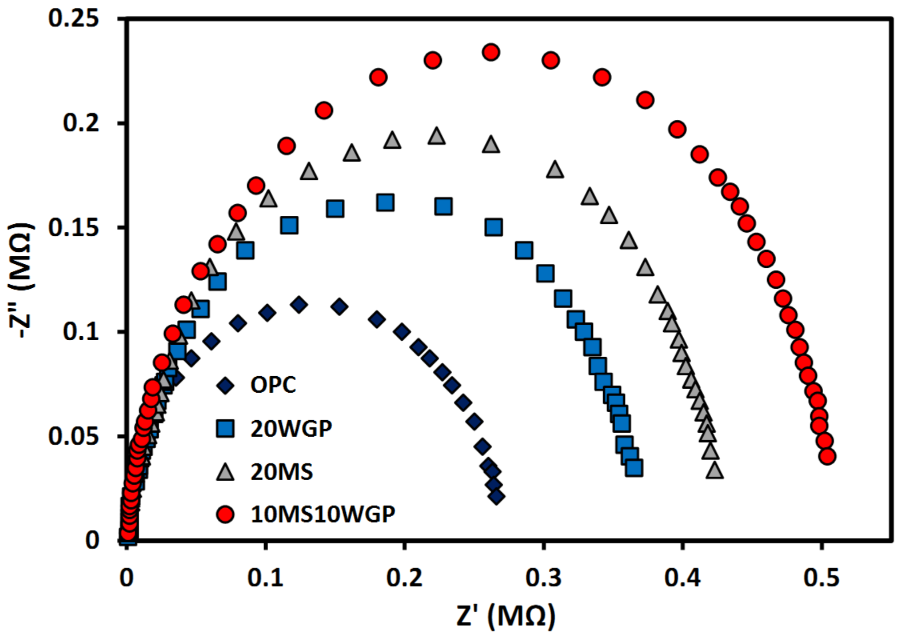

Figure 4. EIS diagram of steel rebar embedded in concrete with partial replacement of OPC by WGP and MS after four-week exposure time in 3.5 wt% NaCl solution

Electrochemical systems have been broadly employed in the investigation of the passive film because of its capability to analyze redox reactions of carbon steel rebar in 3.5 wt% NaCl solution. EIS was used to characterize the corrosion behavior of carbon steel rebar in various concrete specimens with passive films in 3.5 wt% NaCl environment after four-week exposure time. Figure 4 indicates Nyquist diagrams of the specimens. The changes in concrete admixtures had caused a radius variation of the capacitive loop that revealed an improvement of corrosion resistance for carbon steel rebar. Figure 5 shows an equivalent circuit model used for the impedance spectra. Where R_s is solution resistance. R_f and C_f indicate the resistance and the capacitance of coated concrete, respectively [21]. C_{dl} and R_{ct} are the double-layer capacitance and the charge transfer resistance of the carbon steel surface, respectively [22].

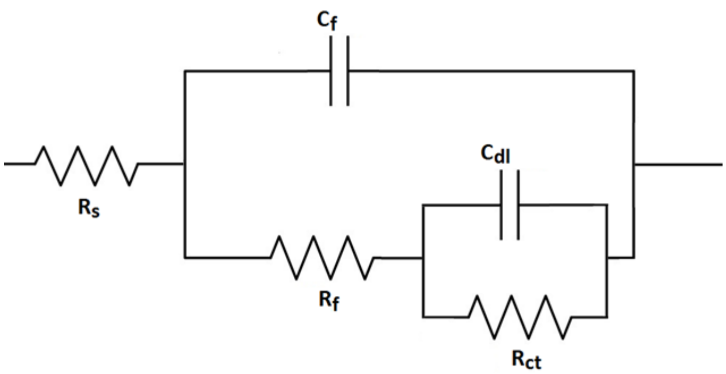

Figure 5. Fitted circuit model with the experimental data

Polarization resistance (R_p) is an assessable indicator to study the corrosion resistance of steel rebar in the aggressive environment [23]. Therefore, the high value of R_p shows more corrosion protection of the specimen.

Table 4. EIS parameters from the fitted circuit model for carbon steel rebar embedded in various concrete specimens after four weeks exposure time into 3.5 wt% NaCl solution

Admixtures	R_s (Ω cm^2)	R_f (MΩ cm^2)	C_f (μF cm^{-2})	R_{ct} (MΩ cm^2)	C_{dl} (μF cm^{-2})	R_p (MΩ cm^2)
OPC	61.3	0.143	2.3	0.278	3.2	0.428
20WGP	65.8	0.196	2.0	0.383	2.5	0.579
20MS	51.1	0.266	1.6	0.422	2.2	0.688
10MS10WGP	59.6	0.301	1.3	0.527	1.6	0.817

Table 4 indicates EIS parameters from the fitted circuit model for carbon steel rebar embedded in various concrete specimens after four weeks exposure time into 3.5 wt% NaCl solution. As shown, the 10MS10WGP sample indicates a considerable enhancement in R_p value showing higher corrosion resistance in marine environments. Furthermore, the value of C_{dl} reduced for the mixtures containing 10 % MS and 10 % WGP, which exhibits that the thickness of passive layer enhanced and the causing protective capacity increased when the concrete mixtures were containing both MS and WGP. Moreover, the resistance of the passive layer increased in the 10MS10WGP sample which revealed that the protective property of the passive layer advanced was strong. The MS had a pozzolanic reaction with calcium hydroxide and produced an monolithic, dense and insoluble gel of $Ca(OH)_2$ crystals [24, 25]. On the other hand, the WGP can form a strong adhesion to hydrated cement due to the high surface area that led to a well inhibition for the growth of calcium hydroxide. The admixtures filled up small cracks and the capillary pores, resulting condensed the structure of cement [26] which enhanced the corrosion resistance of carbon steel rebars in corrosive solutions. Compared to C_f and C_{dl}, it was observed that C_f was lower than C_{dl} in all specimens which indicated the formation of the double layer and passive thin film at the interfaces with high capacitive behavior.

Admixture efficiency (AE) was calculated with the following equation:

$$AE (\%) = 100 \times (R_{ct} - R_{ct}^*)/ R_{ct} \qquad (1)$$

where R_{ct} is the charge-transfer resistance for samples with admixtures and R_{ct}* the charge-transfer resistance for samples without admixtures.

Table 4 shows the AE comparison of concretes with different admixtures as mentioned in the literature. The results indicated that the AE of OPC replacement with both WGP and MS for corrosion resistance of carbon steel were comparable with other admixtures obtained from the literature.

Table 4. AE Comparison of concretes with different admixtures for corrosion inhibitor of carbon steel

Admixtures	Environment	AE (%)	Ref.
Silicon Fume and Fly Ash	3.5 wt% NaCl	47.1	[27]
Diatomite	Acidic solution	44.6	[28]
Blast furnace slag cement	10 % NaCl	59.2	[29]
Bagasse Ash	3.5 wt% NaCl	67.0	[30]
WGP and MS	3.5 wt% NaCl	47.2	This work

Given that electron conductive paths can be formed by addition of WGP, thus the electrical resistivity and the current density of the steel rebar had decreased. Furthermore, the side effects of WGP on corrosion resistance of steel reinforced concrete can be offset by adding MS, which has no notable effect on resistivity of WGP concrete but can decrease the water absorptive and porosity. Furthermore, MS can optimize the WGP dispersion in concrete. Therefore, the addition of the MS and WGP simultaneously assistance to promote a concrete structure that decreases the absorption of water and chloride ions on the steel rebar and also can be introduced as one of the appropriate solutions to decrease the negative effects of adding any mineral additives.

Figure 6 indicates polarization curves of steel rebar in different concrete samples exposed to 3.5 wt% NaCl solution after four weeks exposure time. As shown in figure 6, the anodic branch of polarization diagrams are considered by passive regions at all reinforcement steels, indicating that the passive films had obviously formed on the steel surface when they were exposed to the corrosive environment [31]. Furthermore, a significant shift appeared in corrosion potential towards a positive direction which indicated that the anodic metal dissolution retarded efficiently by changing the content of concrete [32]. Compared to all the samples, the passive region is much wider at the sample 10MS10WGP which indicated a tendency of the steel rebar to passivate. It can be attributed to the dissolution and formation of the oxide film [33]. Moreover, the greater decrease in passive current density in sample 10MS10WGP was due to a change in structure or an increase in thickness of the passive film [34].

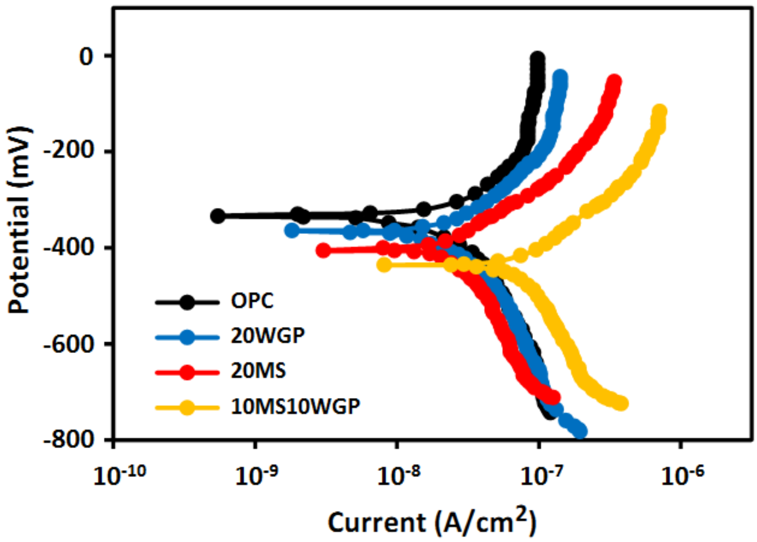

Figure 6. Polarization of steel rebar in different concrete samples exposed to 3.5 wt% NaCl solution after four weeks exposure time

Table 5. Corrosion potential and current density of the steel rebar

Admixtures	Corrosion current density(μA/cm^2)	Corrosion potential (mV)
OPC	0.106	-423 V
20WGP	0.086	-408 V
20MS	0.078	-356 V
10MS10WGP	0.056	-324 V

The values of corrosion potential and corrosion current density are revealed in table 5 which is obtained from the polarization curves in Figure 6. The level of corrosion can be defined in four levels provided by the Durar Network Specification [35]. However, the corrosion current density of the 10MS10WGP sample in the 3.5 wt% NaCl environment was lower than that of the other specimens (Table 5). Therefore, except the OPC sample, all steel reinforced concretes stayed in the passive state during the experiment process which indicated their excellent corrosion resistance of steel rebar in the marine environment [36].

Figure 6 indicates the FESEM images of carbon steel rebars embedded in OPC and partial replacement of OPC with 10% WGP and 10% MS after immersing into 3.5 wt% NaCl media for four weeks. The surface of 10MS10WGP shows low corrosion products and thin pits, indicating a small pitting corrosion occurred on the carbon steel surface, which is consistent with the results obtained from electrochemical tests. It can be related to the decrease of water absorption and Cl^- ion permeability into the concrete structure.

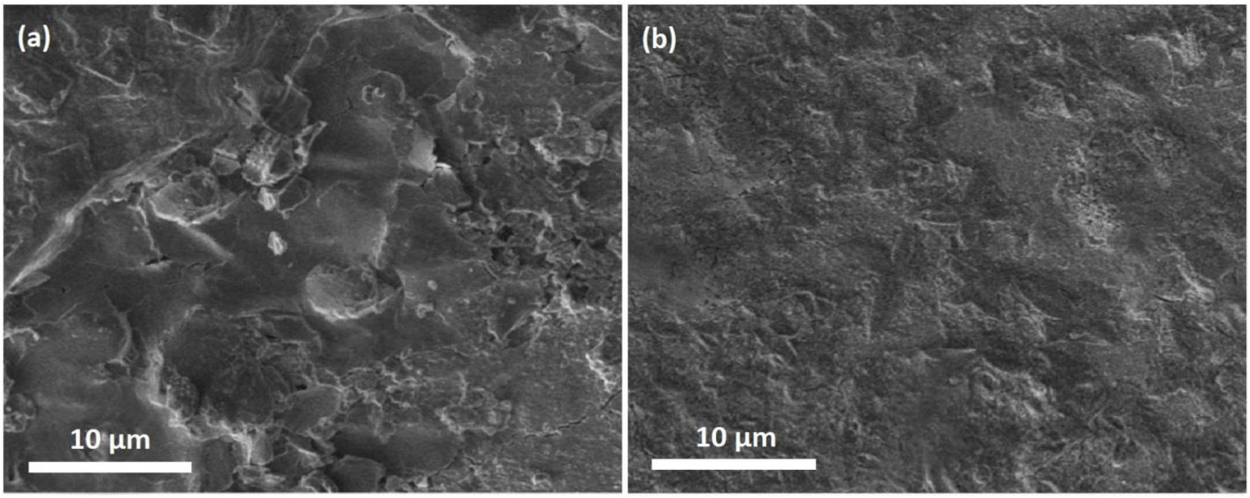

Figure 6. FESEM images of carbon steel rebar embedded in (a) OPC and (b) mixtures containing 10 % MS and 10 % WGP after 4-weeks immersion time into 3.5 wt% NaCl solution

4. CONCLUSIONS

The **c**hloride ion penetration into the surface of steel leads to its corrosion and thus, decreases durability of reinforced concrete structures. Hence, research into reducing the permeability of concrete, which can reduce corrosion, has received much attention. Here, partial replacement of MS and WGP in OPC were used to produce reinforced concrete and its effects were investigated on corrosion resistance of carbon steel rebar in 3.5 wt% NaCl solution. The water absorption of the specimens reduces when the mixtures contain 10 % MS and 10 % WGP. The changes in concrete admixtures had caused a radius variation of the capacitive loop in EIS results that revealed an improvement of corrosion resistance for carbon steel rebar. The electrochemical results indicated that the 10MS10WGP specimen has higher value of corrosion resistance than the other samples. The surface of 10MS10WGP shows low corrosion products and thin pits which can be related to the decrease of water absorption and Cl- ion permeability into the concrete structure.

References

1. W. Aperador, A. Delgado and J. Bautista-uiz, *International Journal of Electrochemical Science*, 11 (2016) 2297.
2. M. Balonis, G. Sant and O.B. Isgor, *Cement and Concrete Composites*, 101 (2019) 15.
3. A.M. Aguirre-Guerrero, R.A. Robayo-Salazar and R.M. de Gutiérrez, *Applied Clay Science*, 135 (2017) 437.
4. H. Karimi-Maleh and O.A. Arotiba, *Journal of colloid and interface science*, 560 (2020) 208.
5. K. Kupwade-Patil, C. De Wolf, S. Chin, J. Ochsendorf, A.E. Hajiah, A. Al-Mumin and O. Büyüköztürk, *Journal of cleaner production*, 177 (2018) 547.
6. M. Alimanesh, J. Rouhi and Z. Hassan, *Ceramics International*, 42 (2016) 5136.
7. G. Girskas and G. Skripkiūnas, *Construction and Building Materials*, 142 (2017) 117.
8. N.S. Msinjili, W. Schmidt, A. Rogge and H.-C. Kühne, *African Journal of Science, Technology, Innovation and Development*, 11 (2019) 417.
9. O.A. Mohamed and O.F. Najm, *Frontiers of Structural and Civil Engineering*, 11 (2017) 406.
10. R. Garg, M. Bansal and Y. Aggarwal, *International Journal of Electrochemical Science*, 11 (2016) 3697.
11. N.K. Lee, K. Koh, M.O. Kim and G. Ryu, *Cement and Concrete Research*, 104 (2018) 68.
12. J. Rouhi, S. Kakooei, M.C. Ismail, R. Karimzadeh and M.R. Mahmood, *International Journal of Electrochemical Science*, 12 (2017) 9933.
13. A.A. Aliabdo, A.E.M.A. Elmoaty and A.Y. Aboshama, *Construction and Building Materials*, 124 (2016) 866.
14. Y. Jiang, T.-C. Ling, K.H. Mo and C. Shi, *Journal of environmental management*, 242 (2019) 440.
15. A. Bahurudeen, K. Wani, M.A. Basit and M. Santhanam, *Journal of Materials in Civil Engineering*, 28 (2016) 04015095.
16. K. Kiran and I.S. Kishore, *International Journal of Civil Engineering and Technology*, 8 (2017) 452.
17. J. Rouhi, S. Mahmud, S.D. Hutagalung and S. Kakooei, *Journal of Micro/Nanolithography, MEMS, and MOEMS*, 10 (2011) 043002.
18. K. Kupwade-Patil, A.F. Al-Aibani, M.F. Abdulsalam, C. Mao, A. Bumajdad, S.D. Palkovic and O. Büyüköztürk, *Construction and Building Materials*, 113 (2016) 423.
19. M.A. Rasol, *International Journal of Scientific & Engineering Research*, 6 (2015) 170.
20. G. De Schutter and K. Audenaert, *Materials and structures*, 37 (2004) 591.
21. K.M. Emran and H. AL-Refai, *International Journal of Electrochemical Science*, 12 (2017) 6404.

22. N. Naderi, M. Hashim, K. Saron and J. Rouhi, *Semiconductor Science and Technology*, 28 (2013) 025011.
23. P. Shao, X. Duan, J. Xu, J. Tian, W. Shi, S. Gao, M. Xu, F. Cui and S. Wang, *Journal of hazardous materials*, 322 (2017) 532.
24. S. Kakooei, H.M. Akil, A. Dolati and J. Rouhi, *Construction and Building Materials*, 35 (2012) 564.
25. J. Setina, A. Gabrene and I. Juhnevica, *Procedia Engineering*, 57 (2013) 1005.
26. F. Husairi, J. Rouhi, K. Eswar, C.R. Ooi, M. Rusop and S. Abdullah, *Sensors and Actuators A: Physical*, 236 (2015) 11.
27. C. Zhang and F. Zhang, *International Journal of Electrochemical Science*, 15 (2020) 3740.
28. H. Gerengi, M. Kurtay and H. Durgun, *Results in Physics*, 5 (2015) 148.
29. D. Koleva and K. Van Breugel, *Bulgarian Chemical Communications*, 44 (2012) 1.
30. Q. Zhang, H. Li, H. Feng and T. Jiang, *International Journal of Electrochemical Science*, 15 (2020) 6135.
31. R. Antunes, M. De Oliveira and I. Costa, *Materials and Corrosion*, 63 (2012) 586.
32. S. Kakooei, J. Rouhi, E. Mohammadpour, M. Alimanesh and A. Dehzangi, *Caspian Journal of Applied Sciences Research*, 1 (2012) 16.
33. C. Li, S. Hu, L. Yang, J. Fan, Z. Yao, Y. Zhang, G. Shao and J. Hu, *Chemistry–An Asian Journal*, 10 (2015) 2733.
34. Y. Chou, J. Yeh and H. Shih, *Corrosion Science*, 52 (2010) 2571.
35. W. Zhao, J. Zhao, S. Zhang and J. Yang, *International Journal of Electrochemical Science* 14 (2019) 8039.
36. A.T. Yousefi, S. Ikeda, M.R. Mahmood, J. Rouhi and H.T. Yousefi, *World Applied Sciences Journal*, 17 (2012) 524.