Int. J. Electrochem. Sci., 15 **(2020)** 9003 – 9012, doi: 10.20964/2020.09.35

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Portland Cement Partially Replaced by Blast Furnace Slag and Multi-Walled Carbon Nanotubes: Effect on Corrosion Resistance of Carbon Steel Reinforcement in 3% NaCl

Yang Ming[1,2,3], *Ping Chen*[1,2,3,*], *Ling Li*[1,2,3*], *Cheng Hu*[1,2,3]

[1] Guangxi Key Laboratory of New Energy and Building Energy Saving, Guilin 541004, China;
[2] College of Civil and Architecture Engineering, Guilin University of Technology, Guilin 541004, China;
[3] Guangxi Beibu Gulf Engineering Research Center for Green Marine Materials,Guilin 541004, China;
[*]E-mail: chenping8383@188.com and aileen540220@sina.com

Received: 13 May 2020 / *Accepted:* 30 June 2020 / *Published:* 10 August 2020

A partial replacement for Portland cement (PC) through supplementary cementitious materials is an alternative technique to reduce carbon steel corrosion in reinforced concrete under exposure to marine environment. Here, the effect of blast furnace slag (BFS) and carbon nanotubes (CNTs) admixtures into PC on the electrochemical corrosion resistance of carbon steel reinforced concrete was assessed by electrochemical impedance spectroscopy (EIS) and polarization systems during immersion in 3.5 wt% NaCl media. The higher compressive strength was observed for BFS-CNT sample which can be attributed to the pozzolanic reaction of BFS filler, the formation of denser microstructure and acceleration of the hydration process. The polarization results show that the concrete samples containing CNTs admixture had a lower value of corrosion current density and corrosion rate revealing the superior performance than the other samples. The EIS measurements indicated that BFS-CNT sample was most effective for enhancing the corrosion resistance of the steel rebar due to the decrease of water absorptivity and chloride ion permeability.

Keywords: Carbon nanotubes; Blast furnace slag; Portland cement; Corrosion resistance; Electrochemical characterizations

1. INTRODUCTION

The corrosion behavior of reinforced concrete is an important factor affecting its durability. Low corrosion resistance can predictably lead to expensive and significant repair work into the concrete[1, 2]. Pore structures of a concrete includes gel pores, capillary pores and air voids [3, 4]. As one of the main features of concrete materials, the structure of the pores has a certain ratio in concrete and has significant consequences on the transfer properties [5, 6]. Parameters of pore structure including the distribution pore size porosity are the main components of microstructure. Previous research had shown that the pore structure affects physical mechanical performance, frost resistance and permeability of concrete [7, 8].

Mineral additives are usually used in several applications such as high performance concrete building sand bridges. Famous mineral additives include fly ash, rice husk ash, and silica fume [9-12]. The addition of these materials in the concrete production have positive environmental effects and minimizing problems related to its disposal.

Recently, blast furnace slag (BFS) had been utilized in concrete as a partial replacement material in cement for several economic and environmental reasons[13].The pozzolanic reactions assistance to fill up in pore structures and make the concrete denser [14, 15]. Thus, partial replacement of Portland cement (PC) with BFS can considerably reduce the risk of chloride penetration, alkali-silica reactions and sulfate attack and increase compressive strength[16].

Recently, application of nanostructures in the construction industry have received special attention. Studies reported that Al2O3, SiO2,Fe2O3 and CuO are generally used nanomaterials in concrete [17-20].Among that, carbon nanotubes (CNTs) reveal that the hybrid effect of CNTs improved the compressive strength and resist the formation of crack in concrete [21, 22].

Previous studies have been conducted solely to describe the unique properties of concrete materials, and very little research had been done on the development of the durability and microstructure of concrete by combining various additives, including BFS and CNTs.

This work focused on the effects of BFS and CNTs admixture on compressive strength, pore structure and corrosion behavior of reinforced concrete in marine environment.

2. MATERIALS AND METHODS

In this work, the reinforced concrete mixture ratio which included various cementitious components such as blast furnace slag (BFS), multi-walled carbon nanotubes (MWCNTs) and Portland cement (PC) were studied. The composition of PC and BFS is summarized in Table 1. The MWCNTs have fibrous structures that are closely related to each other. MWCNTs purchased from Sigma-Aldrich was used for the study.

Table 1. Chemical composition of BFS and PC

	PC (wt%)	BFS (wt%)
SiO_2	20.65	34.27
Al_2O_3	4.74	9.42
Fe_2O_3	3.02	1.15
CaO	64.25	45.24
MgO	2.04	7.42
SO_3	2.96	1.26
LOI	0.88	0.24

Table 2 indicates various ratios of the concrete mixture. The PC was blended with sand, gravel, and water (1.5: 3: 1: 0.5) to produce concrete structure. The fresh mixture was poured into the cylindrical plastic molds with 25 cm height and 10 cm diameter at room temperature and 80% relative humidity for 24 h. The samples were cast and then the molds were removed after one day.

The compressive strength assessment was done according to ASTM C109-16a[23].The compressive strength was considered by the following equation:

$$F_{cc}\ (N/mm^2) = \text{Ultimate load (N)/ Sample area } (mm^2) \qquad (1)$$

Table 2. The ratios of the concrete mixture

Sample	PC (g)	Gravel (g)	Sand (g)	Water (g)	BFS (g)	MWCNTs (g)
PC	750	500	1500	250	0	0
BFS	675	500	1500	250	75	0
BFS-CNT	600	500	1500	250	75	75

In order to study the effect of BFS and CNTs admixtures on corrosion resistance of the steel reinforced concretes, electrochemical tests were performed on carbon steel rebar after one month exposure to 3.5 wt% NaCl solution. The chemical composition of carbon steel bar is shown in Table 3.

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

Carbon	**Mn**	**Si**	**Cu**	**Al**	**Cr**	**Ni**	**Fe**
0.13	0.75	1.5	0.34	0.017	0.09	0.10	Residual

The three-electrode electrochemical system was applied to study corrosion behavior of the steel rebar by electrochemical impedance spectroscopy (EIS) technique. Carbon steel rebar, a standard copper/copper sulfate and graphite electrodes were used as a working electrode, reference and counter electrodes, respectively. All analysis were performed in a 3.5 wt% NaCl environment. The EIS was done at a frequency range of 10 mHz to 0.1MHz. The polarization tests were done at a potential range of -700 mV to 100 mV with 1 mV/s scanning rate. The surface morphologies of samples were considered by scanning electron microscope (SEM, Zeiss Sigma 300 VP).

3. RESULTS AND DISCUSSION

Figure 1a shows FESEM images MWCNTs with 10 to 20 µm length and 150 to 200 nm diameter which were used in this study. BFS was obtained by quenching molten iron blast furnace slag (Fig. 1b). The BFS powder can improve the later strength, reduce the hydration heat in concrete, and increase the microstructure of concrete which was used as partial replacement in the PC.

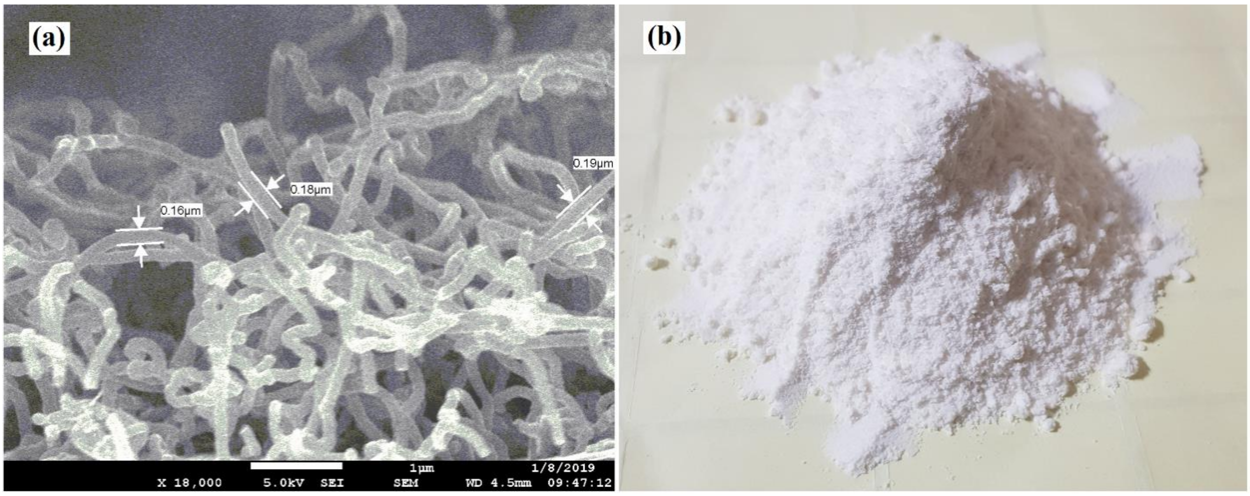

Figure 1. FESEM images (a) MWCNTs and (b) BFS

The compressive strength results attained for different samples after one month of curing is shown in figure 2. As shown, the mixture containing CNT nanostructures had superior compressive strength than the other samples which was 94% higher than the PC. The enhancement in compressive strength for BFS-CNT sample can be ascribed to the use of BFS as a filler in improving microstructure. Moreover, the BFS as an activator contributed to the pozzolanic reaction which form a denser microstructure and accelerated the hydration process, enhancing the compressive strength [24]. On the other hand, the crystal growth of carbon matrix enhanced the compressive strength of concrete containing CNTs [25].

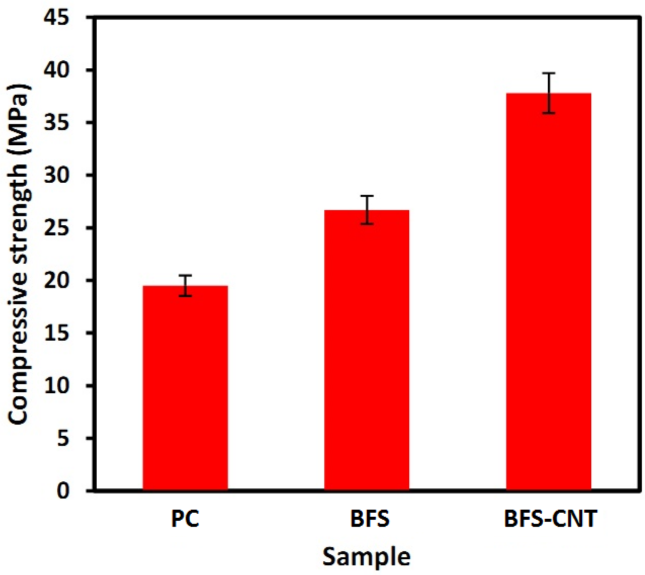

Figure 2. Compressive strength of different samples after one month of curing

The water absorption of different samples after one month exposure to 3.5 wt% NaCl solution were obtained 11.9%, 6.8% and 4.3% for PC, BFS and BFS-CNT, respectively. It was found that the admixtures had significantly affected the water absorption results which indicated the use of BFS and CNTs as cement replacement strangely varied water absorption of the concrete. This finding could be directly useful in justifying the corrosion behavior of carbon steel reinforced concrete.

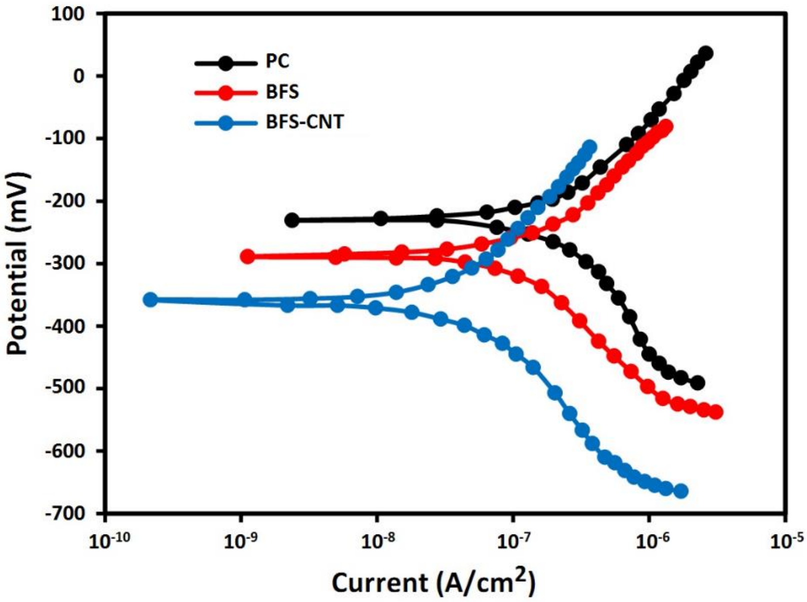

Figure 3. Polarization plots of carbon steel rebar in different concrete specimens immersed to 3.5 wt% NaCl media after one month exposure time

Figure 3 indicates Polarization plots of carbon steel rebar in different concrete specimens immersed to 3.5 wt% NaCl media after one month exposure time. The corrosion parameters attained from polarization curves are summarized in Table 4. As shown, the sample containing CNTs was revealed to have a higher corrosion potential value which can be attributed to the higher electrical conductivity of the CNTs. The excellent conductivity of partial replacement cement using MWCNTs was attained as the CNTs were aligned in a certain direction and optimum CNTs loading were selected[26]. Furthermore, it was found that the BFS-CNT sample had lesser value of current density compared to the PC and BFS samples. The better performance of BFS-CNT samples was caused by the combined effect of CNTs and BFS admixtures which accelerated the hydration reaction because of the reactivity and high specific area of the nanostructures. It can form a denser concrete and decreased the mortar permeability and reduced the current flow [27]. On the other hand, the lower current density in the BFS-CNT sample can be attributed to the change in the structure or the thickness of the passive layer on the steel rebars [28]. Moreover, the concrete sample containing CNTs admixture had the lowest corrosion rate with 5.48 times smaller than the PC sample. The results show that BFS-CNT sample had a lower value of corrosion concrete and the corrosion rate revealed a superior performance than the other samples.

Table 4. The corrosion parameters attained from polarization curve

Mixture	Corrosion potential (mV)	Corrosion current density (μA/cm^2)	corrosion rate (MMPY) × 10^{-3}
PC	-242	0.32	3.4
BFS	-293	0.09	1.1
BFS-CNT	-356	0.06	0.62

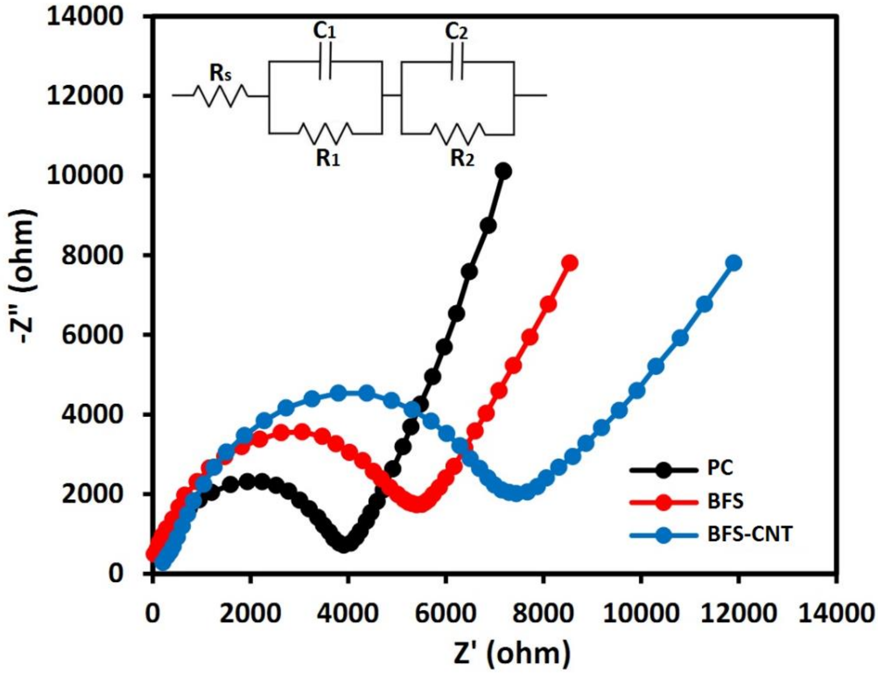

Figure 4. Nyquist diagrams of carbon steel embedded in different concrete samples immersed to marine environment. The inset shows an equivalent circuit model used to fit EIS data

EIS technique was used to evaluate the corrosion resistance of low carbon steel rebar embedded into the concretes with various admixtures in 3.5 wt% NaCl solution. Figure 4 shows the Nyquist plots reached by the EIS analysis. The equivalent circuit used to fit EIS data is shown in the inset of Fig. 4. Where R_s is the solution resistance.C_1 and R_1 reveal the capacitance and resistance of the coated concrete, respectively. C_2 and R_2 are the double-layer capacitance and the charge transfer resistance of steel rebar surface, respectively [29, 30]. The obtained data are shown in table 5.

Table 5. The attained data from the equivalent circuit used to fit EIS data

Mixture	R_s (Ω)	R_1 (Ω)	C_1(μF cm^{-2})	R_2 (Ω)	C_2(μF cm^{-2})
PC	38.4	2896	9.59	4056	12.25
BFS	28.8	3947	7.32	5974	10.63
BFS-CNT	32.7	5643	5.89	7985	8.25

These findings reveal that by the suitable replacement of BFS and CNTs in the PC, R_1 increases and C_2 reduces, which indicates an improvement in the stability of the passive film and corrosion resistance on the carbon steel rebar [31]. Due to the high surface area of the BFS, it can form a strong adhesion to hydrated cement, causing a better growth inhibition of the calcium hydroxide[32]. The admixtures fill the tiny cracks and capillary pores and ultimately shrink the structure of cement. These agents enhance the corrosion resistance of carbon steel rebars in aggressive solutions. Furthermore, comparing C_2 and C_1, it was observed that C_1 was lower than C_2 in all specimens which had proven that the formation of double and passive layers at the interfaces had high capacitive behavior[33].

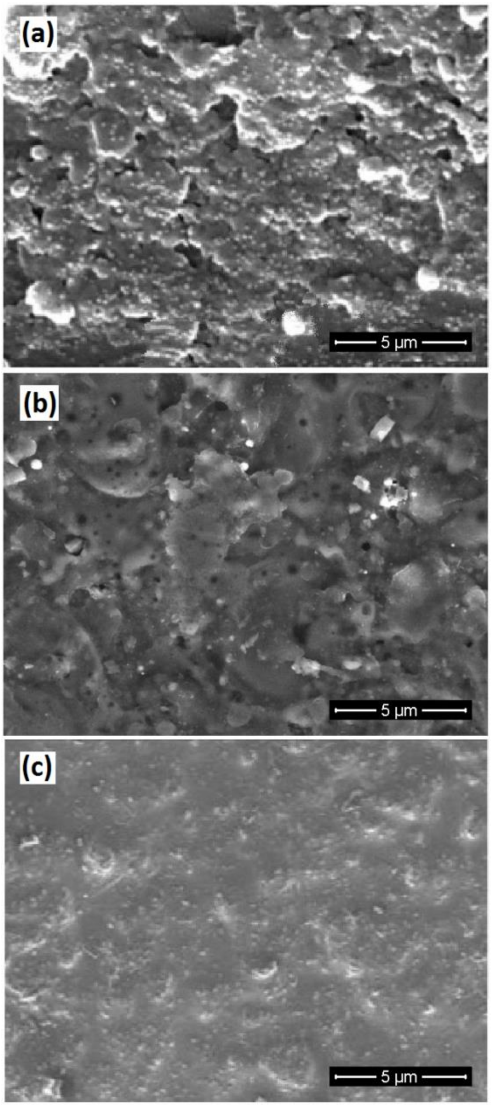

Figure 5. FESEM images of carbon steel surface for (a) PC, (b) BFS and (c) BFS-CNT samples after one month immersed to 3.5 wt% NaCl environment

Figure 5 shows the SEM images of carbon steel surface for PC, BFS and BFS-CNT samples after one month immersion in a 3.5 wt% NaCl environment. The surface of BFS-CNT indicates low pits and corrosion products, showing a mild pitting corrosion happened on the surface of carbon steel rebar, which was in accordance to the results derived from electrochemical experiments. It can be associated to the water reduction and decrease of chloride ion permeability into the concrete. The reaction of BFS with calcium hydroxide may produce hydration products that considerably reduce the porosity of concrete. Moreover, the structure of concrete can be affected by mixing of CNTs in the concrete. However, the entire porosity cannot be eliminated by the addition of the BFS and CNTs, but the large pores may be turned into smaller pores and thus changing the microstructure of the cement paste. These results indicate that partial replacement of BFS and CNTs simultaneously in PC led to a reduction in corrosion rate and improved corrosion resistance of carbon steel rebar because of the decrease of chloride ion and water permeability[34].

4. CONCLUSIONS

In this work, the effect of BFS and CNTs admixtures into PC on the electrochemical corrosion resistance of carbon steel reinforced concrete was assessed by EIS and polarization systems during immersion in 3.5 wt% NaCl media. The higher compressive strength was observed for BFS-CNT sample which can be attributed to the pozzolanic reaction of BFS filler, the formation of a denser microstructure and the acceleration of the hydration process. The polarization results show that the concrete samples containing CNTs admixture had a lower value of corrosion current density and corrosion rate revealing a superior performance than the other samples. The EIS measurements indicate that BFS-CNT sample was most effective for enhancing the corrosion resistance of the steel rebar due to the decrease of water absorptivity and chloride ion permeability. The SEM image of the samples indicate low pits and corrosion products of BFS-CNT, showing a mild pitting corrosion happened on the surface of carbon steel rebar, which was in accordance to the results derived from electrochemical experiments.

ACKNOWLEDGEMENT
This work was sponsored by Guangxi construction new energy and energy conservation Key Laboratory Project (GKN 19-J-21-7, GKN 19-J-21-12)

References

1. F. Rubino, A. Nisticò, F. Tucci and P. Carlone, *Journal of Marine Science and Engineering*, 8 (2020) 26.
2. S. Kakooei, H.M. Akil, M. Jamshidi and J. Rouhi, *Construction and Building Materials*, 27 (2012) 73.
3. S.-H. Kang, S.-G. Hong and J. Moon, *Construction and Building Materials*, 172 (2018) 29.
4. H. Karimi-Maleh and O.A. Arotiba, *Journal of colloid and interface science*, 560 (2020) 208.
5. W. Ren and J. Xu, *Journal of Materials in Civil Engineering*, 29 (2017) 04016244.

6. J. Rouhi, C.R. Ooi, S. Mahmud and M.R. Mahmood, *Electronic Materials Letters*, 11 (2015) 957.
7. R. Zhang, P. Liu, L. Ma, Z. Yang, H. Chen, H.X. Zhu, H. Xiao and J. Li, *International Journal of Concrete Structures and Materials*, 14 (2020) 10.
8. H. Karimi-Maleh, M. Sheikhshoaie, I. Sheikhshoaie, M. Ranjbar, J. Alizadeh, N.W. Maxakato and A. Abbaspourrad, *New Journal of Chemistry*, 43 (2019) 2362.
9. N.S. Msinjili, W. Schmidt, A. Rogge and H.-C. Kühne, *African Journal of Science, Technology, Innovation and Development*, 11 (2019) 417.
10. O.A. Mohamed and O.F. Najm, *Frontiers of Structural and Civil Engineering*, 11 (2017) 406.
11. H. Shan, Z. Wang, J. Xu and L. Jiang, *International Journal of Electrochemical Science*, 13 (2018) 1120.
12. Z. Shamsadin-Azad, M.A. Taher, S. Cheraghi and H. Karimi-Maleh, *Journal of Food Measurement and Characterization*, 13 (2019) 1781.
13. A. Mehta and R. Siddique, *Journal of cleaner production*, 205 (2018) 49.
14. H.-L. Ho, R. Huang, W.-T. Lin and A. Cheng, *Construction and Building Materials*, 160 (2018) 278.
15. F. Tahernejad-Javazmi, M. Shabani-Nooshabadi and H. Karimi-Maleh, *Composites Part B: Engineering*, 172 (2019) 666.
16. E. Özbay, M. Erdemir and H.İ. Durmuş, *Construction and Building Materials*, 105 (2016) 423.
17. R. Ismael, J. Silva, R. Carmo, E. Soldado, C. Lourenço, H. Costa and E. Júlio, *Construction and Building Materials*, 125 (2016) 1080.
18. R. Ortega-Villar, L. Lizárraga-Mendiola, C. Coronel-Olivares, L.D. López-León, C.A. Bigurra-Alzati and G.A. Vázquez-Rodríguez, *Journal of environmental management*, 242 (2019) 487.
19. M. Yildirim and E. Derun, *Materiales de Construcción*, 68 (2018) 161.
20. H. Karimi-Maleh, F. Karimi, S. Malekmohammadi, N. Zakariae, R. Esmaeili, S. Rostamnia, M.L. Yola, N. Atar, S. Movagharnezhad and S. Rajendran, *Journal of Molecular Liquids*, (2020) 113185.
21. M.O. Mohsen, R. Taha, A.A. Taqa and A. Shaat, *Construction and Building Materials*, 150 (2017) 395.
22. M. Alimanesh, J. Rouhi and Z. Hassan, *Ceramics International*, 42 (2016) 5136.
23. E. Gomaa, S. Sargon, C. Kashosi and M. ElGawady, *Journal of King Saud University-Engineering Sciences*, 29 (2017) 356.
24. P. Duan, Z. Shui, W. Chen and C. Shen, *Journal of Materials Research and Technology*, 2 (2013) 52.
25. S. Feng, H. Xiao, R. Zhang and C. Yang, *Construction and Building Materials*, 250 (2020) 118830.
26. X. Gao, L. Liu, Q. Guo, J. Shi and G. Zhai, *Materials Letters*, 59 (2005) 3062.
27. R. Yu, P. Spiesz and H. Brouwers, *Construction and Building Materials*, 65 (2014) 140.
28. Y. Chou, J. Yeh and H. Shih, *Corrosion Science*, 52 (2010) 2571.
29. S.B. Aoun, M. Bouklah, K. Khaled and B. Hammouti, *International Journal of Electrochemical Science*, 11 (2016) 7343.
30. J. Rouhi, M.R. Mahmood, S. Mahmud and R. Dalvand, *Journal of Solid State Electrochemistry*, 18 (2014) 1695.
31. S. Kakooei, H.M. Akil, A. Dolati and J. Rouhi, *Construction and Building Materials*, 35 (2012) 564.
32. Q. Wang, S. Li, S. Pan, X. Cui, D.J. Corr and S.P. Shah, *Construction and Building Materials*, 198 (2019) 106.
33. K. Sarkar, A. Mondal, A. Chakraborty, M. Sanbui, N. Rani and M. Dutta, *Surface and Coatings Technology*, 348 (2018) 64.

34. W. Aperador, A. Delgado and J. Bautista-uiz, *International Journal of Electrochemical Science*, 11 (2016) 2297.