Short Communication

Electrochemical Corrosion Behaviour of Carbon Steel Reinforcement in Metakaolin-Limestone Modified Concrete Exposed to Simulated Soil Solution

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Due to environmental and technical needs, partial replacement of cement using pozzolanic materials in concrete structures has received much attention from researchers. In this work, an experimental research was done to study the durability and corrosion resistance of carbon steel rebar in Metakaolin-Limestone (MKLF) modified concrete exposed to simulated soil solution. The present work considered the electrochemical corrosion behavior of carbon steel rebar in simulated soil with and without chloride using open circuit potential, electrochemical impedance spectroscopy and polarization tests. Electrochemical measurements indicated that the addition of MKLF enhances corrosion resistance, decreases the corrosion rate and delays corrosion onset. This improvement in concrete structure can be related to the decrease of the concrete permeability.

1. INTRODUCTION

Soil is the most diverse environment known for metal corrosion [1]. The degree of corrosion of metals in the soil can vary from rapid dissolution to minor effects [2, 3]. Many constructions, such as steel pipelines for natural gas and oil, water mains and sewers, steel containers for gasoline and foul oil, the steel rebars for the foundation of bridges, houses, and buildings, are placed underground and thus exposed to the aggressive action of soil [4-6]. Therefore, studying the effect of the soil nature on corrosion of metals is crucial to the safety and efficiency of our infrastructures [7].

Today, reinforced concretes have been applied in main structures for example bridges, ports, tunnels and marine construction [8, 9]. Though, the durability of steel rebar is typically endangered by corrosion actions. Combining supplementary cementitious materials (SCMs) into a concrete mix reduces its penetrating property and decreases capillary pores in concrete structure [10]. Thus,

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attaining a surface of steel rebar in chloride-contaminated water develops more difficult. Conventional SCMs such as blast furnace slag, silica fume and fly ash [11, 12], today use of metakaolin (MK) seems to be a promising option for the production of environmental materials [13]. Most studies confirm the significant pozzolanic reaction of MK compared to other mineral additives [14-16]. Metakaolin is essentially an artificial pozzolan which may react by Portlandite (CH) from the hydration of cement and create additional C-A-S-H or C-S-H [17]. This allows MK to improve significantly the durability of cementitious materials and mechanical performance.

This work studies the possibility of replacing Portland cement (PC) by mineral additions, although keeping or improving durability and mechanical performances. However, limestone and MK additives have been approved that can improve electrochemical corrosion resistance and reduce specific surface area and permeability, the simultaneous influence of both on corrosion behavior of carbon steel reinforced concrete in soil environment hasn't been previously reported. Thus, in this work, we have considered the effect of limestone and MK admixtures on corrosion resistance of carbon steel rebar exposed to simulated soil solution by an electrochemical technique.

2. MATERIALS AND METHOD

The chemical composition of the Portland cement (PC), metakaolin (MK) and limestone fillers (LF) are shown in Table 1. The cylindrical concrete specimens with 70 mm diameter and 200 mm height were produced by replacement of 20 wt% of PC by MK and LF. The PC was mixed with gravel and sand (1.5:1: 3) to prepare concrete structure. The concrete mixtures were blended by a high-speed mixer machine to obtain a heterogeneous dispersion. The ratio of water to cement was 0.5. The compositions of the used carbon steel are C (0.116 wt%), Si (0.30 wt%), Mn (0.40 wt%), S (0.045 wt%) and P (0.045 wt%). 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.

Table 1. Chemical compositions of PC, LF and MK (% by mass)

Compositions	PC	LF	MK
SiO_2	21.63	0.22	50.73
Fe_2O_3	3.04	0.15	0.96
Al_2O_3	4.75	-	43.96
CaO	63.27	55.16	0.24
MgO	2.54	1.13	0.21
K_2O	0.52	0.02	0.11
Na_2O	0.33	-	0.02
SO_3	2.93	0.09	-
L.O.I	0.85	43.23	0.55

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An analytical grade chemical was used as electrolyte solution in the electrochemical impedance spectroscopy (EIS), open circuit potential (OCP), and polarization studies. The simulated soil solutions were produced at room temperature after one day of stirring through Whatman filter papers. The simulated electrolyte composition of the soil is given in Table 2. In order to determine the corrosion of carbon steel reinforced concrete samples, these samples were exposed to simulated soil solution contaminated with 3.5 wt% NaCl as an aggressive agent.

Table 2. Simulated soil electrolyte composition for electrochemical assessments

Compounds	Mg/l
$CaCl_2.2H_2O$	159
KCl	149
$NaHCO_3$	504
$MgSO_4.7H_2O$	106

A three-electrode cell was used during the electrochemical tests, with carbon steel reinforced concrete and saturated calomel and platinum electrodes as a working, reference, and counter electrodes, respectively. Figure 1 shows a schematic diagram and detailed dimensions for the carbon steel reinforced concrete used as a working electrode in electrochemical experiments.
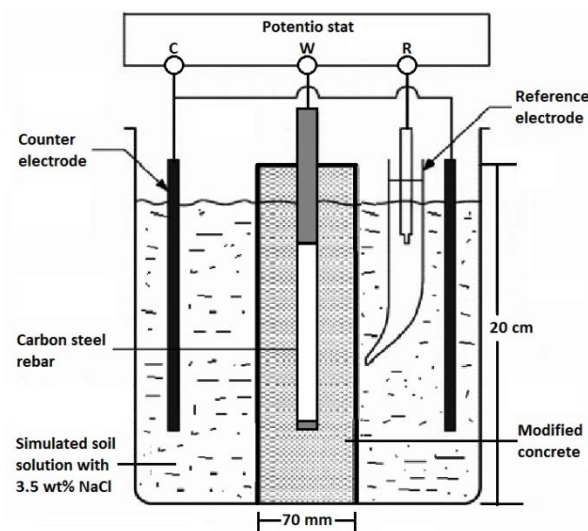

Figure 1. Schematic diagram of the carbon steel reinforced concrete used as a working electrode in electrochemical experiments

The EIS analysis was performed at the frequency wide-ranging between 0.1 MHz and 10 mHz at 10 mV applied AC amplitude. The EIS measurements of samples were recorded after immersing time of 1, 3 and 8 weeks. The potentiodynamic polarization characterizations were done at a scanning rate of 1 mV/s after eight weeks of the immersion times. According to ASTM C642 water absorption values were measured by drying a sample with a constant mass, and then immersing it in water and measuring the mass of standard surface dry. Water absorption was the proportion of the difference

between the two values measured to the dry mass. The surface morphologies of the steel samples were conducted using scanning electron microscope (SEM).
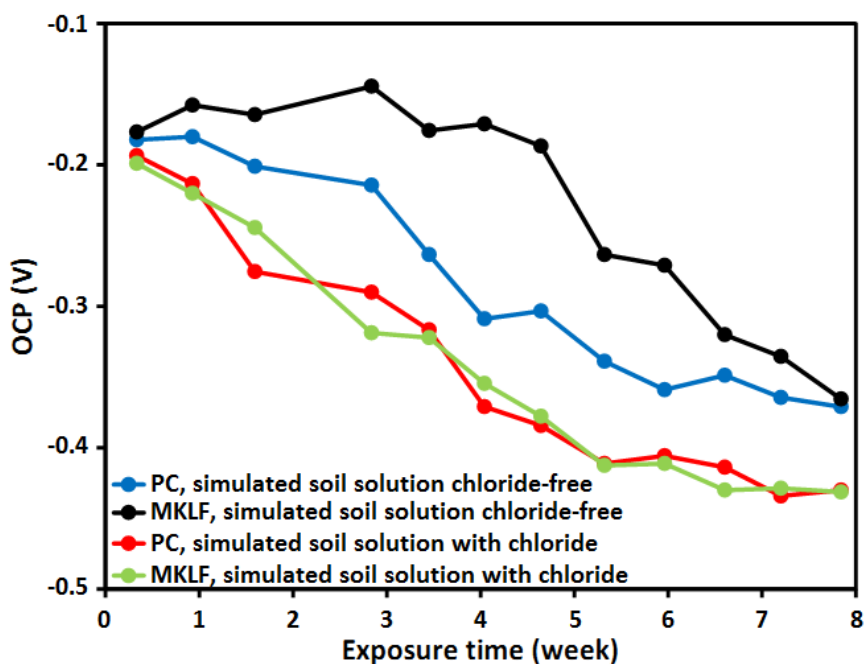
3. RESULTS AND DISCUSSION

Figure 2. OCP of the carbon steel rebars in concrete samples with the various admixtures after 8 weeks exposure time in simulated soil solution with and without chloride

The OCP changes of the carbon steel rebars in concrete samples with the various conditions are shown in Figure 2. Both samples in simulated soil solution without chloride show the most positive values of potential during the initial stages of exposure. Though, after a specified time, the potential value starts to decrease which indicates the onset of corrosion [18]. This occurs after about 3 and 5 weeks of exposure for PC and MKLF, respectively.

Such behavior obviously shows that metakaolin and limestone admixtures delay the time required for corrosion to begin. However, for samples in simulated soil solution with chloride, the values of potential decrease slowly from the initial stages of exposure representing that depassivation of rebar happens much earlier, because the solution was polluted with chloride ions. Furthermore, the values of OCP were approximately the same and the trends were similar, thus indicating that MKLF has no significant effect on the evolution of OCP in both samples. After six weeks all specimens indicated potential values lower than -0.3V, showing active corrosion procedures. Thus, consistent with the OCP results, MKLF contributes to reduce the entrance of Cl ions to the steel rebars.
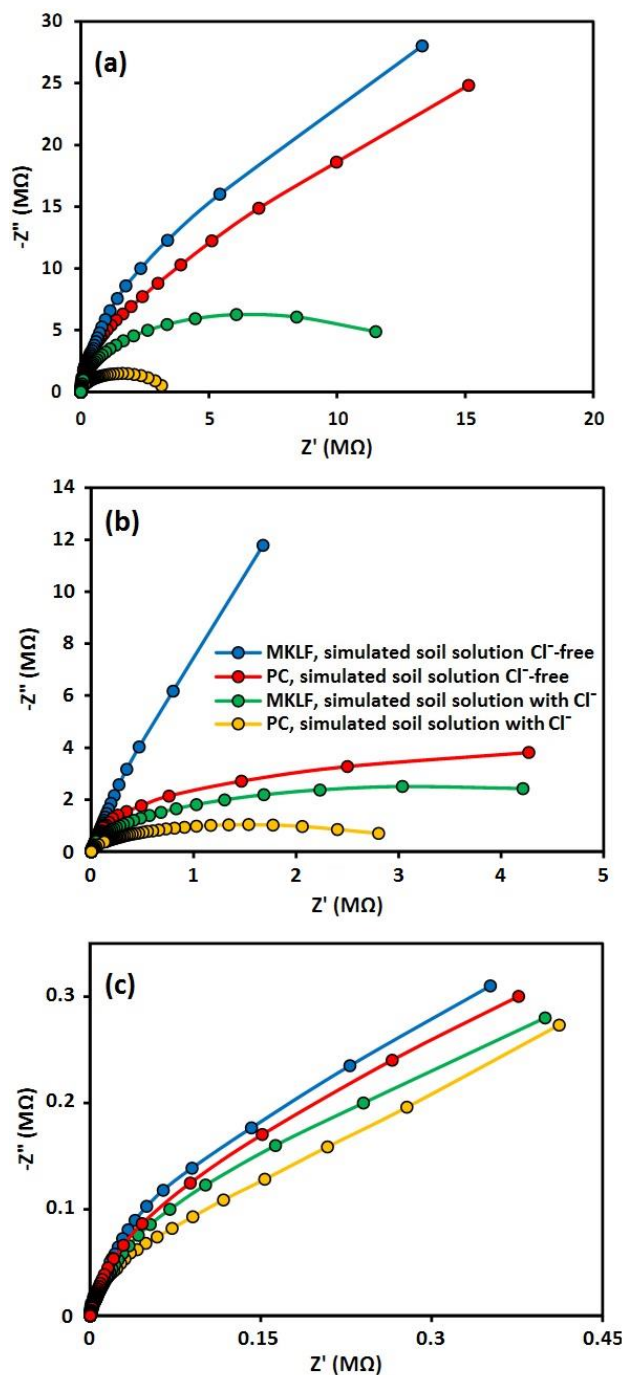
Figure 3. Nyquist plots of the carbon steel rebars in concrete samples with the various admixtures in simulated soil solution with and without chloride after (a) one, (b) three and (c) eight weeks of immersion

The EIS assessment was used to study the electrochemical corrosion behavior of steel rebars [19]. Figure 3 indicates the impedance spectra of the samples after 1, 3 and 8 weeks of exposure. High-frequency response may be associated with the concrete-electrolyte interstitial which indicates an improvement of concrete resistivity. The low and mid-frequency responses are the concrete-steel interface property which can be attributed to the corrosion behavior. At initial stages of the exposure process, the evolution of EIS shows a capacitive response in both samples into a simulated soil

solution without chloride; this effect is more noticeable in the MKLF sample. For PC, the impedance values indicate a significant reduction after one week of immersion whereas for MKLF specimens the capacitive trend may be found until three weeks of immersion. This indicates that the presence of MKLF delays depassivation of steel rebars consistent with the evolution of OCP. The samples into simulated soil solution with chloride exhibited the lowest values of impedance at the initial stages of immersion. The low-frequency impedance values were lower than the samples determined for samples into simulated soil solution without chloride and no significant differences were observed between the PC and the MKLF samples which were in agreement with the OCP findings. At 8 weeks of exposure, all specimens indicated similar values of impedance in the low-frequency range. Different equivalent circuit models may be applied to fit the EIS results. In this work, the circuit model was chosen to analyze the EIS result (Fig. 4). The dielectric property of concrete covered on steel rebar must cause in two-capacitive loops [20]. In this work, this effect is difficult to see due to the limitations of the instrumentation and the low thickness of mortar used. The appropriate equivalent circuit is shown in figure 4. In this figure, CPE_p is the passive film capacitance in high-frequency region, R_p is the passive film resistance, CPE_{dl} is the double layer constant phase element between the carbon steel bar and the concrete in the region of low-frequency and R_{ct} is the charge transfer resistance [21]. R_s is the contribution of electrolyte resistance.
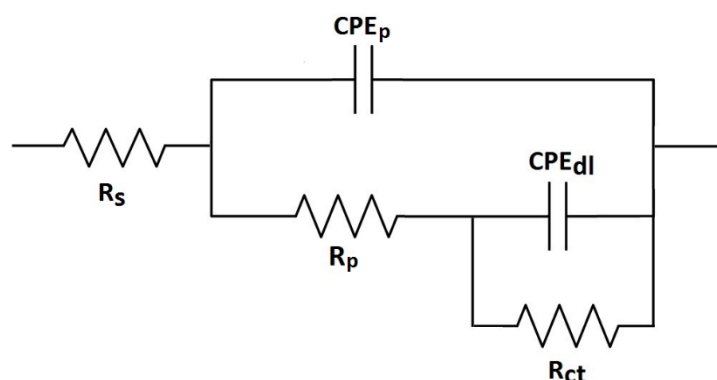

Figure 4. An equivalent circuit model

The R_p/CPE_p indicates the response from the protective film of steel surface. Obtained results of fitting presented in table 3. At the initial immersion, Rp values were similar for all samples (Table 3) which cannot correlate it for the presence of metakaolin and limestone admixtures in concrete. However, the MKLF sample had a tendency to show higher value of electrical resistance until about 3 weeks of exposure. At 8 weeks of exposure, all specimens exhibited a reduction of Rp. The reduction of CPE_p can be associated with the heterogeneous surface of steel with a greater defect in the passive layer, which appeared more for the samples exposed to the simulated soil solution with chloride.

The charge-transfer resistance (R_{ct}) is one of the helpful parameters, because it is proportional to the rate of corrosion in carbon steel rebars [22]. For the samples into a simulated soil solution with chloride, the R_{ct} values were close and reduced gradually with increasing exposure time. No difference was observed in the effect of MKLF in this regard, the addition of MKLF had no negative effect on the corrosion behavior of rebar. Conversely, for samples into simulated soil solutions without chloride, the

effects of MKLF are obviously reflected from the evolution of R_{ct}. In the one week of exposure, the both specimens indicate high values of R_{ct}, which show that the steel rebars are in passive-state [23]. For PC mixture, at the three week of immersion, there is a decrease in R_{ct} which indicates the onset of corrosion. Then, the R_{ct} value gradually reduced and the values were similar to the values obtained from the samples into a simulated soil solution without chloride. This is according to the accumulation of Cl ions in the concrete/rebar interface resulting in corrosion activity.

MKLF specimen indicates the highest values of R_{ct} compared to the other samples during three-weeks of immersion which exhibits the protective role of MKLF on reinforcing steel. Then, there was a gradual reduction of R_{ct} value at eight-weeks of the immersion which was consistent with the evolution of OCP. The resistance of the passive layer increased in the MKLF sample which revealed that the protective property of the passive layer advanced was strong. The MK 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 LFs 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 [26]. The admixtures filled up small cracks and the capillary pores, resulting condensed the structure of cement which enhanced the corrosion resistance of carbon steel rebars in corrosive solutions [27].

Table 3. Electrochemical parameters achieved from the equivalent circuit (Figure 3)

Immersion time	Samples	$R_s(\Omega\ cm^2)$	$R_p(M\Omega\ cm^2)$	$CPE_p(\mu F\ cm^{-2})$	$R_{ct}(M\Omega\ cm^2)$	$CPE_{dl}(\mu F\ cm^{-2})$
1 week	S1	54.2	0.43	11.2	32.8	19.8
	S2	43.8	0.32	18.1	28.7	14.3
	S3	41.7	0.31	22.7	13.4	18.6
	S4	51.6	0.22	17.6	3.3	13.2
3 weeks	S1	38.4	0.75	13.7	15.2	16.1
	S2	55.4	0.45	19.4	8.7	25.4
	S3	34.2	0.48	30.2	5.3	34.3
	S4	45.8	0.17	23.4	2.6	26.7
8 weeks	S1	67.2	0.28	17.8	0.38	37.2
	S2	71.4	0.19	27.1	0.33	29.9
	S3	59.5	0.21	36.9	0.27	54.1
	S4	63.4	0.11	23.8	0.21	76.2

* MKLF sample in simulated soil solution without chloride (S1); PC sample in simulated soil solution without chloride (S2); MKLF sample in simulated soil solution with chloride (S3); PC sample in simulated soil solution with chloride (S4)

The values of CPE_{dl} show that there are overall tendencies to increase values at the beginning of immersion assessment for all samples, which can indicate an enhancement of active-area in interface of solution-metal and more heterogeneous surface of electrode. The highest CPE_{dl} values at 8-weeks immersion times were determined for both samples into simulated soil solution without chloride, which confirms that more heterogeneous and intense corrosion activity is happening.
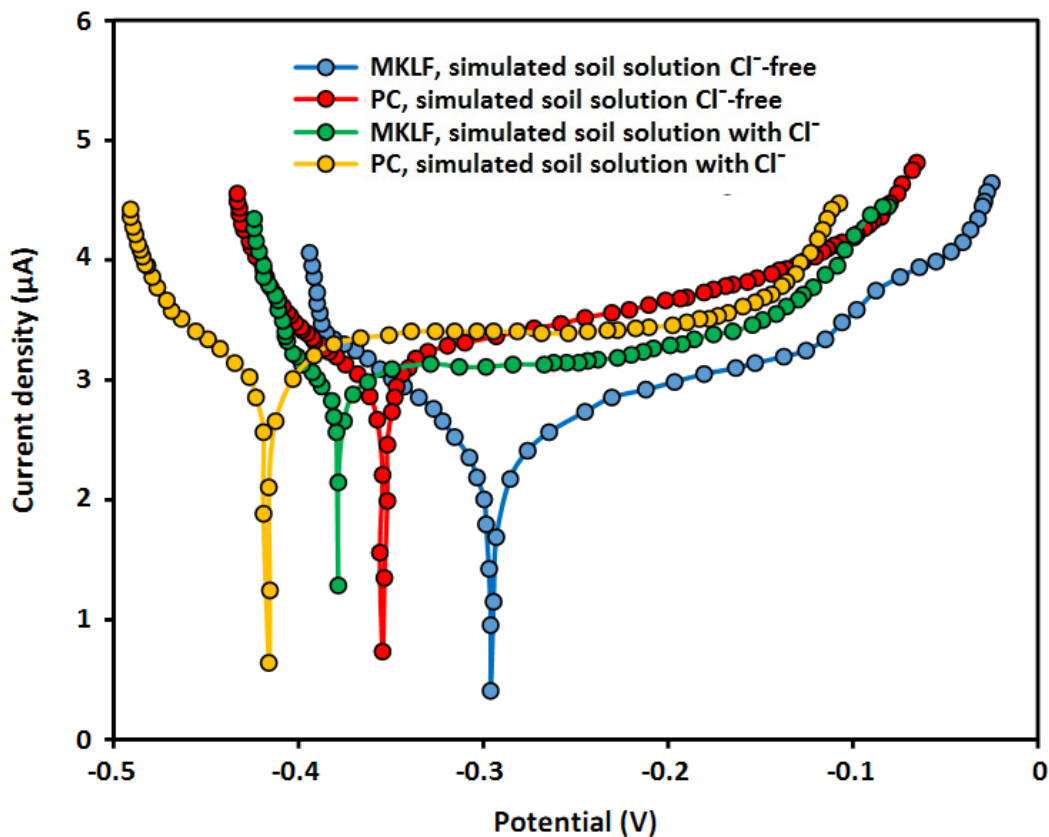
Figure 5. Potentiodynamic polarization curves of the carbon steel rebars in concrete samples with various admixtures in simulated soil solution with and without chloride after eight weeks of the immersion times

Table 4. Corrosion current density and corrosion potential of the carbon steel rebars

Samples	Corrosion current density	Corrosion potential
MKLF sample in simulated soil solution without chloride	2.67 μA	-292 mV
PC sample in simulated soil solution without chloride	3.26 μA	-347 mV
MKLF sample in simulated soil solution with chloride	3.14 μA	-386 mV
PC sample in simulated soil solution with chloride	3.33 μA	-418 mV

A comparison study on the potentiodynamic polarization curves were performed after eight weeks of the immersion times (Figure 5) which indicates that concrete samples with MKLF indicate higher anodic current density, when compared to the relevant specimens without MKLF. The values of the corrosion current density and the corrosion potential are indicated in table 4 which are achieved from the polarization diagrams in Figure 5. The concrete sample without MKLF had the minimum corrosion potential compared to the other concrete specimens. This sample was very susceptible to corrosion. The steel rebar embedded in concrete with MKLF had a lower trend toward corrosion. As

shown in figure 5, MKLF content leads to a significant increase in corrosion potential (E_{corr}). Thus, the potential had shifted to more positive values. Furthermore, corrosion current density (I_{corr}) shifted toward the left side which indicated that there was lower corrosion current on the surface of rebar [28, 29]. The corrosion current density of MKLF samples was lower than that of the other samples (Table 4) which revealed their excellent corrosion resistance of steel rebar in the marine environment.

The permeability of concrete is directly related to the presence of MKLF. On the other hand, lower permeability leads to the production of denser concrete [30]. This means that fewer ions were allowed to enter the concrete samples. Therefore, the I_{corr} will be less and the E_{corr} will be more positive. Corrosion of steel rebar in the concrete specimen with MKLF was intensely decreased after eight weeks exposure in simulated soil solution which was more resistant to corrosion than the other concrete samples. It can be attributed to the amount of MKLF which had a direct effect on the performance of the reinforced concrete. The presence of MKLF moves corrosion potential to more anodic value which proposes that the steel rebar in such an environment shows an improved passivation behavior [31]. Specimen MKLF reveals the lowest value of corrosion current density. Therefore, the polarization results indicate the beneficial role of MKLF in concrete exposed to the simulated soil solution, verifying the prior electrochemical studies.

The electrochemical data show a good agreement, indicating the addition of MKLF in concrete samples leads to enhanced corrosion resistance. The EIS results shows adding MKLF leads to a small enhancement of high-frequency resistance, proposing less permeable and denser concrete structure, created by a higher volume of CSH-gel formed because of pozzolanic reaction including MKLF. The results achieved in this study highlight the effect of MKLF admixture in concrete structures and exhibit a detailed electrochemical data in which the helpful effects of MKLF are referring to delay in the onset of corrosion and reduction of corrosion activity in reinforced concrete immersed to chloride medium.

Figure 6 reveals the surface morphologies of the carbon steel rebar in PC and MKLF mixture exposed to simulated soil solution with chloride after 8 weeks. Figure 6b shows low pitting corrosion on the carbon steel surface. MKLF creates the bridging effect which can improve the flexural and tensile strength. Moreover, the metakaolin and limestone as mineral admixtures in the concrete structures can have the pore blocking effects leading to less permeability. Actually, by reducing the internal conductivity of the pores, it reveals less capillary porosity [32].
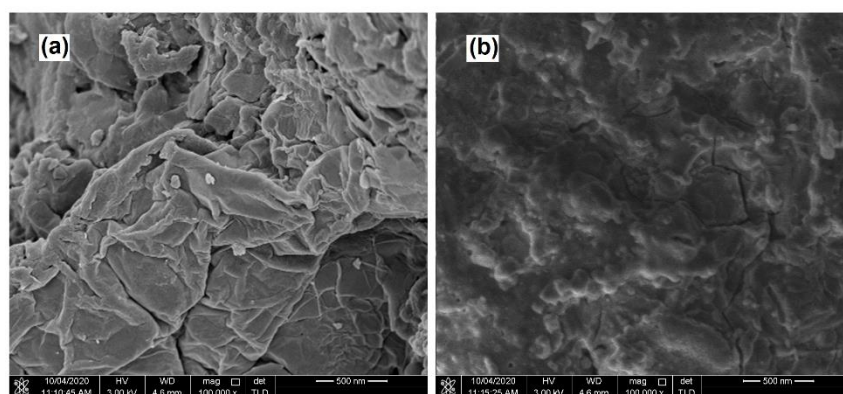

Figure 6. Surface morphologies of carbon steel in various concretes (a) PC mixture, (b) MKLF mixture exposed to simulated soil solution with chloride after 8 weeks.
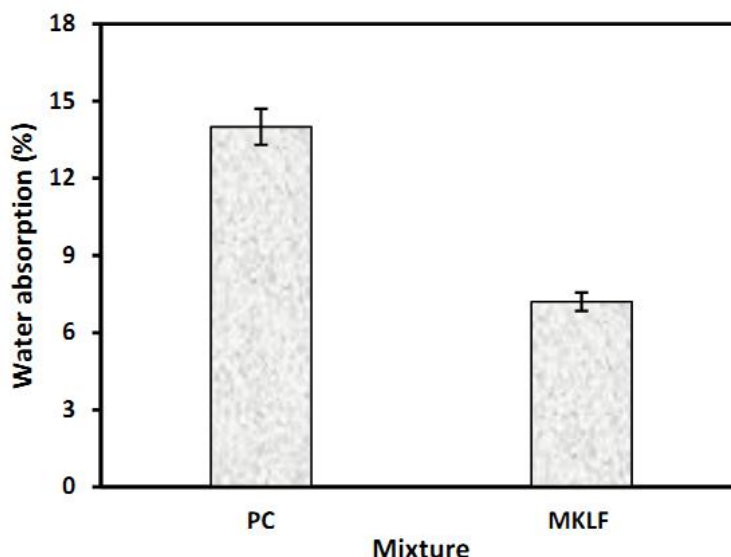
Figure 7. Water absorption of concretes with PC mixture and MKLF mixture exposed to simulated soil solution with chloride after 8 weeks.

In order to study the permeability of specimens, a water absorption assessment was done. Figure 7 exhibited the water absorption of prepared specimens immersed to simulated soil solution with chloride after 8 weeks. It indicates the partial substitution of PC with metakaolin and limestone has considerable effect on lower water absorption of samples. The hydration heat rising from the water-cement reaction reduces due to the existence of high content of Al_2O_3 and SiO_2 in metakaolin [33]. Moreover, limestone as filler decreases the permeability of concrete structure and enhances the durability. Furthermore, it inhibits the aggressive ions from reaching the surface of steel rebar. Also, in MKLF sample, reduction in absorption water can be attributed to low capillary porosity which may relate to the effect of pore blocking. MKLF mix shows the lowest percentage of water absorption than the PC mixture.

4. CONCLUSION

In this work, an experimental research was done to study the durability and corrosion resistance of carbon steel rebar in MKLF modified concrete exposed to simulated soil solution. The present work considered the electrochemical corrosion behavior of carbon steel rebar in simulated soil with and without chloride using OCP, EIS and polarization tests. The EIS results fitted by a suitable equivalent electrical circuit revealed that the highest corrosion resistance was achieved for the MKLF mixture. Electrochemical measurements revealed that the addition of MKLF enhances corrosion resistance, decreases the corrosion rate and delays corrosion onset. This improvement in concrete structure can be related to the decrease of the concrete permeability. Surface morphologies of carbon steel rebar indicated lower pitting corrosion on the MKLF sample compared to the PC sample which was in agreement with the electrochemical results.

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