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Short Communication

Electrochemical Corrosion Behaviour of Carbon Steel in Concrete with Metakaolin Admixture Exposed to Soil with High Concentration of Chloride Ions

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One of the most useful construction materials is concrete. Cementitious materials blended with some admixtures have been used to improve durability, sustainability and reduction of production cost. In recent years, the use of metakaolin as one the most efficacious pozzolans in concrete has received remarkable interest. On the other hand, chloride ions in different environments play a significant role in corrosion reaction. To evaluate the effects of soil environment, especially the soil with high concentration of chloride ions on the corrosion of carbon steel in concrete with metakaolin admixture, investigations were carried out. In this study, electrochemical corrosion behavior of carbon steel in concrete with metakaolin replacement in different ratios (5 wt%, 10 wt%, 15 wt% and 20 wt%) was discussed. Electrochemical corrosion behavior was studied by monitoring of corrosion potentials, polarization measurement and electrochemical impedance spectroscopy (EIS) and also the surface morphology was studied by scanning electron microscopy (SEM). EIS results indicated that the concrete containing metakaolin, especially the sample with 15 wt% MK revealed higher corrosion resistance compared to the ordinary Portland cement (OPC). Furthermore, polarization measurements showed that the lowest corrosion current density and the highest corrosion potential belonged to the 15 wt% Mk sample which was consistent with EIS results. Scanning electron microscopy revealed that the mixture containing 15 wt% MK is denser and more uniform with less porosity than that of the OPC sample.

Keywords: Corrosion resistance; Electrochemical Impedance spectroscopy; Metakaolin; Polarization; Carbon steel in concrete mixtures

1. INTRODUCTION

Concrete is one of the most important materials in construction of infrastructures [1, 2]. Durability and performance of the concrete are affected by its corrosion resistance. The chemical and physical protection of steel in concrete concrete leads to more structure durability. Concrete has a porous structure and the penetration of aggressive ions may cause less durability. For instance, the chloride ions can diffuse by the concrete to the carbon steel bar and lead to depassivation of the protecting layer and beginning the corrosion process [3, 4]. One of these ways of transmission is from the soil into the concrete. Some parameters such as the environmental conditions, the chemistry of the mixture and also microstructure can affect the protection. Hence, strength and durability of concrete can be improved by using sustainable supplementary materials [5]. It has shown that adding admixtures such as metakaolin (MK) affects the corrosion behavior of concrete [6, 7].

Metakaolin (MK) has been studied due to its capability in reaction with Ca(OH) by-products which occurs during the hydration of cement [8-10]. With adding MK, the durability and mechanical properties of materials based on cement increase because of the high pozzolanic activity of MK [11, 12]. Studies have shown that MK improves the resistance of the lime and cement paste against the entrance of ions with changing the pore structure of them, because MK acts as an effective pozzolan[13]. In addition, alumina phases and tobermorite gel are produced as a result of the reaction between calcium hydroxide (CH) and MK. The stability of produced phases may result in a dense interfacial transition zone. Therefore, porosity decreases and microstructural compactness is achieved [14]. Studies showed that partial replacement of Portland cement by weight of 5-20% of MK has the positive effects on the properties of concrete by filler effect in concrete and also acceleration of the hydration of cement [15, 16]. Studies indicated that high amount of calcium hydroxide (CaOH) was consumed during the hydration process of cement and MK, the presence of C-S-H gel and crystalline calcium alumino-silicate can help to improve the microstructure, and refinement of pore structure resulted in reducing the pore sizes [17]. The research revealed that the tensile and compressive strengths of the concrete were increased by the partial replacement of cement with 15wt% MK [18]. Ramezanianpour carried out an investigation about the relationship between chloride permeability and compressive strength of concrete [19].

Very few studies have been done on the evaluation of the corrosion behavior of concrete including MK in soil environments. Thus, the aim of this work is to study electrochemical corrosion behavior of carbon steel in concrete with metakaolin in different ratios (5 wt%, 10 wt%, 15 wt% and 20 wt%) exposed to soil with 3% NaCl using EIS and polarization measurements.

2. MATERIALS AND METHOD

The control sample and samples containing different percentages of MK were placed in containers filled with soil with 3% NaCl by weight of soil to evaluate effects of the addition of MK on the corrosion behavior of carbon steel in concrete. These cylindrical concrete specimens with size of 75 × 150 mm and with steel bars with 12 mm diameter were produced by replacement of 5 wt%, 10 wt%, 15 wt% and 20 wt% of ordinary Portland cement (OPC) by metakaolin. The used MK was a commercially available natural pozzolan. The chemical compositions of OPC and MK are given in Table 1. The compositions of concrete mixtures are shown in table 2 where the ratio of water to cement ratio was 0.48. The compositions of the used Q235 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 preparationof a higher homogeneous dispersion, the concrete mixtures were mixed at a high speed.

Table 1. Chemical composition of Ordinary Portland cement (% by mass)

Composition	OPC	MK
SiO_2	21.63	50.73
Fe_2O_3	3.04	0.96
Al_2O_3	4.75	43.96
CaO	63.27	0.24
MgO	2.54	0.21
K_2O	0.52	0.11
Na_2O	0.33	0.02
SO_3	2.93	---
L.O.I	0.85	0.55

Table 2. Compositions of prepared mixtures (kg/m^3)

Sample	Cement	MK	Water	Fine aggregates	Coarse aggregates
OPC	400	---	192	940	692
M5	380	20	192	940	692
M10	360	40	192	940	692
M15	340	60	192	940	692
M20	320	80	192	940	692

All electrochemical measurements were carried out by a triple-electrode system connecting to a potentiostat coupled to PC (Ivium, Netherlands) which contains the steel bar embedded in concrete as the working electrode, a platinum wire and a saturated calomel electrode (SCE) as an auxiliary and a reference electrode, respectively. It took about 60 minutes for stabilization before each measurement. The electrochemical impedance spectroscopy (EIS) was performed in the frequency range between 0.01 Hz and 100 kHz with a 10 mV amplitude signal with reference to the open circuit. Zview software was used to fit the EIS data to a suitable electric circuit. The potentiodynamic polarization measurement was performed with a rate of 1 mV s^{-1}. The corrosion current density (i_{corr}) and the corrosion potential (E_{corr}) were obtained from the Tafel extrapolation of polarization curves (50-100 mV away from E_{corr}) [20, 21]. The surface morphologies of specimens were studied by Zeiss Sigma 300 VP scanning electron microscope. All the electrochemical measurements were done at environment temperature.

3. RESULTS AND DISCUSSION

The obtained results of monitoring corrosion potentials (E_{Corr}) of carbon steel in the concrete samples without and with MK exposed to soil with chloride ions are shown in figure 1. Corrosion probability can be estimated according to ASTM C876 standard test as for potential values which are less than -350 mV the corrosion probability is very high, the values between -200 mV and -350 mV show uncertain state for probability of the presence of active corrosion [22]. Figure 1 indicates that initially corrosion potential values of almost all samples are approximately -380 mV. As seen, corrosion potential of carbon steels embedded in concrete mixtures containing MK in compared to the OPC sample show the positive values. There is a large increase for potential values when the ratio of MK is 15 wt%. The steel rebarin the M15 and M20 samples show the more passive behavior than the OPC sample while remaining in the uncertain region during the exposure time. The corrosion potentials of carbon steel bars in M5 and M10 mixtures after the eight weeks are in the uncertain region and remain there for the rest of the exposure period. Furthermore, corrosion potentials of the OPC sample which shows the lowest values remain in the active region during 12 weeks. It can be concluded that corrosion still continues for the OPC sample during the exposure time. According to these results, carbon steels in concrete with MK admixture present more positive potential values and lower corrosion tendency. This indicates the influence of Mk as a filler material on the properties of microstructural and diffusion and also the distribution of pore size [23].

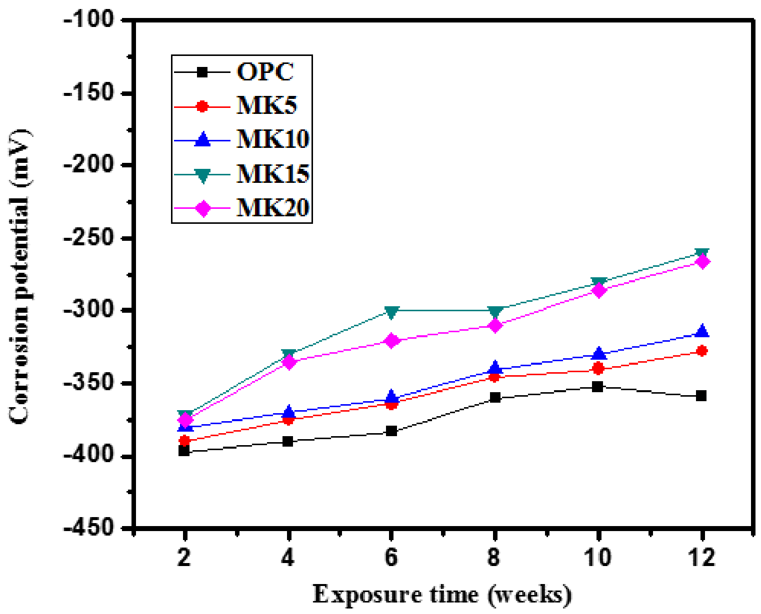

Figure 1. Corrosion potentials of carbon steel in concrete immersed into the soil containing 3 wt% chloride

EIS measurements of the samples were carried out after exposure to chloride enriched soil (3% NaCl) for 8 weeks. Figure 2 displays Nyquist and Bode plots corresponding to the concrete samples containing different ratios of MK. It can be seen that the radius of the capacitive loop increases with increasing the amount of MK, which indicates an enhancement in the corrosion resistance of the concrete samples.

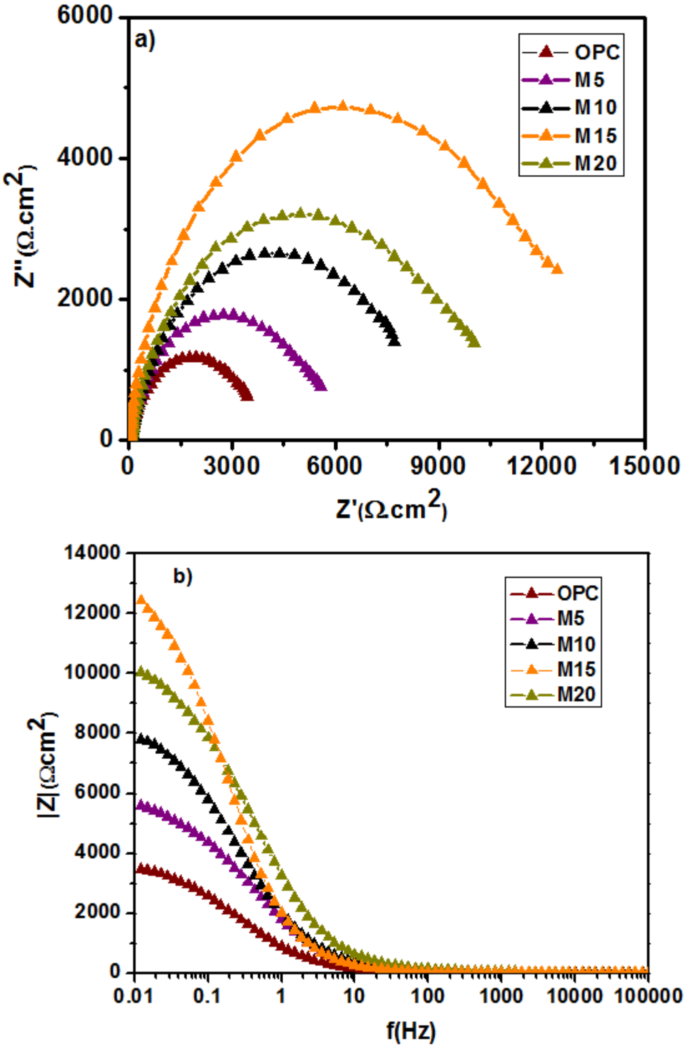

Figure 2. a) Nyquist and b) Bode plots of steel bars in concrete containing different metakaolin contents exposed to soil with a chloride concentration of 3%

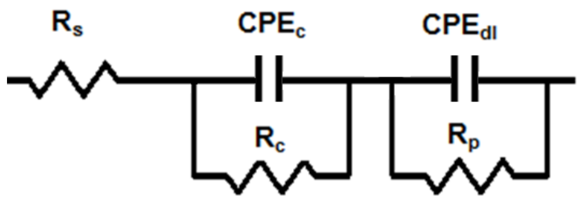

Figure 3. The used equivalent circuit for fitting of EIS data

The appropriate equivalent circuit used for fitting the EIS data is shown in figure 3. In this figure, $CPE_c$is the constant phase element between the soil and concrete in high frequency region, R_c is the concrete 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_P is the polarization resistance [24]. Obtained results of fitting presented in table 3 indicate that with increasing metakaolin replacements into the concrete, R_{ct} and R_c increase and also CPE_{dl} and CPE_c reduce. These results show that corrosion resistance of the concrete samples enhances with increasing of metakaolin replacements and reaches the highest value for the concrete containing 15 wt% (M15). It can be due to the filler effect of particles of MK in pores or interface zone between cement paste and aggregate. Furthermore, the other reason can be a pozzolanic reaction between metakaolin and $Ca(OH)_2$ produced during the hydration of cement which creates additional $C_3S_2H_3$ gel. Corrosion resistance is reduced for 20 wt% MK that this reduction can be due to pelleting of the metakaolin particles around the cement particles at higher ratio replacement which prevents the process of hydration of cement [23]. Moreover, with increasing the amount of MK content porosity of samples decreases that results in lower permeability and thus it protects the carbon steel in concrete from the aggressive environment [25]. This decrease can be as a result of reducing pore structure of the samples. Decreasing in porosity can be attributed to a denser phase which results in increasing the strength. Also, the effect of fine-grained MK filler yields denser microstructure and discontinuation of the capillary porosity[26].

Table 3. Obtained electrochemical parameters of fitting the Nyquist plots with an appropriate equivalent cuircuit

Sample	$R_s(\Omega)$	$R_c(\Omega)$	CPE_c (μFcm^{-2})	n_c	$R_p(\Omega)$	CPE_{dl}(μFcm^{-2})	n_{dl}
OPC	16	900	70.2	0.60	2700	16.1	0.72
M5	13	1000	59.3	0.64	4725	10.7	0.79
M10	12	1400	28.1	0.71	7000	9.5	0.83
M15	11	4533	12.6	0.82	7967	4.6	0.9
M20	13	2800	19.5	0.74	7625	8.9	0.88

The behavior of corrosion and also the performance of the concrete samples containing different ratios of metakaolin (5 wt%, 10 wt%, 15 wt% and 20 wt%) were studied by means of corrosion current density and corrosion potential. Polarization curves of carbon steel in concrete with different percentages of Mk exposed to soil with 3wt% NaCl for 8 weeks are shown in figure 4. The values of corrosion potential (E_{Corr}) and corrosion current density (I_{Corr}) are presented in table 4. It can be observed that the corrosion potential of steel rebar in various concrete specimens containing MK indicates a positive shift relative to OPC sample. Thus, corrosion resistance of the samples can be enhanced and tendency towards corrosion is reduced.In addition, the values of corrosion current densities of steel rebars in different mixtures containing MK are lower than that of in concrete without admixtures. The lowest value associated to this parameter obtains for the concrete with 15 wt% MK among samples containing MK. In fact, enhancement of corrosion resistance of the mixtures may be related to production of additional hydrate phases which obtain from pozzolanic reaction between calcium hydroxide and metakaolin and related filler effect that leads to a denser structure. On the other hand, decreasing the corrosion resistance related to the MK20 sample may be due to reduction of pH in pores as a result of consumption of $Ca(OH)_2$ in pozzolanic reaction [7]. Results are consistent with previous studies which showed the resistance to chloride penetration is improved by using of MK and also increasing of the MK content in comparison with the OPC [27]. These results are consistent with the obtained EIS results.

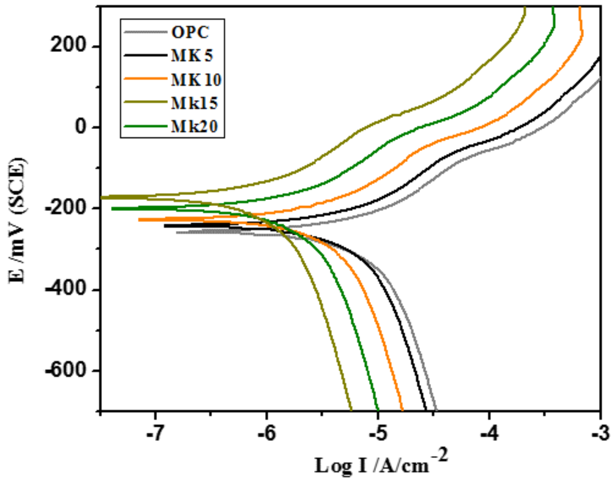

Figure 4. Polarization curves of steel bars in concrete containing different metakaolin contents exposed to soil with a chloride concentration of 3%

Table 4. Corrosion parameters of steel rebar obtained from polarization curves

Mixtures	E_{Corr}/mV (SCE)	i_{Corr}(μA/cm^2)
OPC	-256	3.1
MK5	-242	2.6
MK10	-225	1.9
MK15	-173	0.8
MK20	-199	1.3

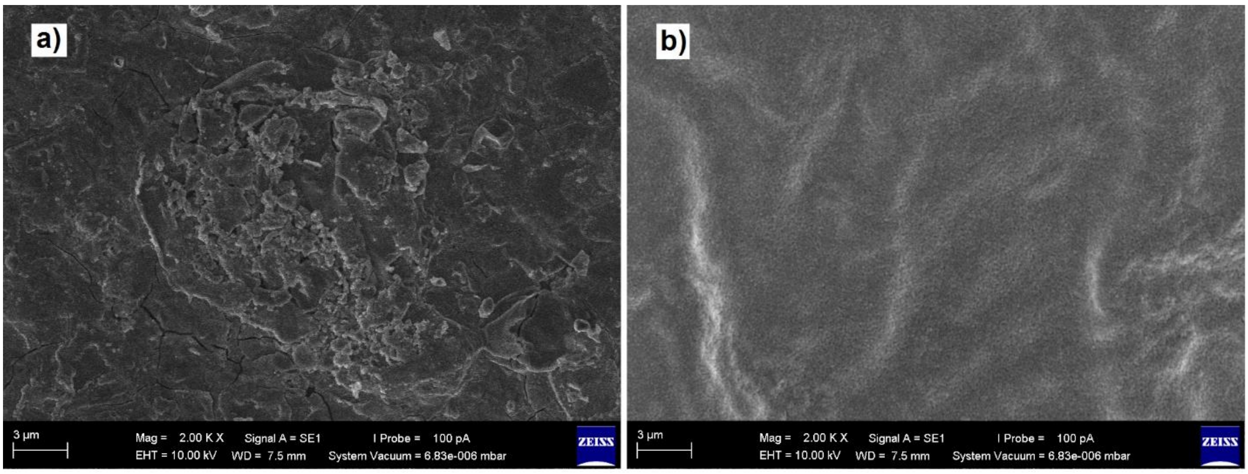

Figure 5. SEM imagesof concrete specimens, (a) OPC sample and (b) concrete sample containing 15 wt% metakaolin exposed to soil with a chloride concentration of 3% after 4 weeks

Microstructures of the OPC and the sample including metakaolin 15 wt % (M15) after 4 weeks are presented in figure 5. Figure 5b indicates that the mixture containing 15 wt% MK is denser and more uniform with less porosity than that of the ordinary Portland cement [27].

4. CONCLUSION

In this study, electrochemical corrosion behavior of carbon steel in concrete with metakaolin replacement as one the most efficacious pozzolans in different ratios (5 wt%, 10 wt%, 15 wt% and 20 wt%) exposed to the soil with high concentration of chloride ions was investigated. EIS results indicated that the concrete containing metakaolin especially the sample with 15 wt% MK revealed higher corrosion resistance compared to the ordinary Portland cement (OPC). Moreover, polarization measurements showed that the lowest corrosion current density and the highest corrosion potential belonged to the 15 wt% Mk sample which was in consistent with EIS results. Scanning electron microscopy revealed that the mixture containing 15 wt% MK is denser and more uniform with less porosity than that of the OPC sample. It can be concluded that with increasing the amount of MK content, porosity of specimens decreases that results in lower permeability and thus it protects the carbon steel in concrete from the corrosive environment. Decreasing in porosity can be attributed to a denser phase which results in increasing the strength. Also, the effect of fine-grained MK filler yields denser microstructure and discontinuation of the capillary porosity.

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