JCSE The Journal of Corrosion Science and Engineering

ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

Corrosion behavior of reinforcing steel in cement with partial replacement of MK

Wafaa A. Ghanem*, Amal S. I. Ahmed ** , Ghalia A. Gaber,**

(*) Central Metallurgical Research and Development Institute (CMRDI), Al-Tabbin, Helwan.

(**) Faculty of science (girls), Al-Azhar University, Cairo, Egypt.

Corresponding Author E-mail: ghaliaasaid@yahoo.com.

Abstract

The effect of different percentages of cement (MK) on the corrosion behavior of embedded reinforcing steel bars was studied in presence of 3.5% NaCl and 5% $MgSO_4$ solutions. A poor Greek kaolin with a low kaolinite content was thermally treated and the produced Metakaolin (MK) was ground to the appropriate fineness. Different electrochemical techniques namely; open circuit potential, linear polarization and electrochemical impedance spectroscopy measurements were used. It is concluded that the use of Metakaolin as a cement replacement 20% w/w, improves the corrosion behavior of reinforcing steel in cement in 3.5 % NaCl solution. While in 5% $MgSO_4$ solution, the 5 % MK replacement is the best one with cement to reduce corrosion rate.

Keywords: Corrosion behavior; Reinforcement; OPC; MK; Electrochemical Techniques.

1. Introduction

The durability of reinforced concrete depends on the surrounding environmental and exposure conditions. The alkaline phase from hydrated cement has a protective action for the embedded reinforcing steel bars. Reinforcement corrosion is one of the major causes of degradation in concrete structure [1]. MK is unique in that it is not the by-product of an industrial process nor it is entirely natural; it is derived from a naturally occurring mineral and is manufactured specifically for cementing applications [2]. Metakaolin, produced by controlled thermal treatment of kaolin, can also be used as a concrete constituent, since it has pozzolanic properties [3].

The studies, regarding the improvement of the mechanical, shrinkage, and some durability properties of the concrete by MK have

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

been carried out by the researchers [4–6]. Batis et al. [3] studied the effect of MK on the corrosion resistance of cement mortar by corrosion potential, mass loss, and corrosion rate using the Linear Polarization method. They reported that the use of Metakaolin, either as a sand replacement up to 20% w/w, or as a cement replacement up to 10% w/w, improved the corrosion behavior of mortar specimens.

The cement which is alkaline (pH 13.5) oxidizes embedded steel bars, forming a chemically and electrically inactive layer (passive film) of ferric oxide [7]. Corrosion of the reinforcing steel bars is initiated to form inactive thin layer which can be broken when immersed in carbonate, chloride or sulphate solutions. Carbonates, chlorides and sulphates media can be found in concrete when using contaminant aggregates, or adding $CaCl_2$ (as an accelerator) during the mixing step or they are found under the effect of sea-water or ground-water on concrete and they can also result from attack of concrete by the surrounding environment in coastal regions [8].Chloride and sulfate are used as aggressive anions. Chloride ions are being present as original constituents of concrete mixture or as a result of penetration from the environment. Sulfate ions, on the other hand, are found to be actively participated in the corrosion of reinforcing steel especially in the area of the Middle East [9].In the present investigation, the corrosion behavior of steel reinforcement in cement has been studied with partial replacement of cement by Metakaolin from 5% to 20%.

2. Experimental procedure

2.1. Materials used

The materials used in this investigation were Ordinary Portland cement (OPC) produced from National Cement Company and MK produced by controlled thermal treatment of kaolin. A poor Greek kaolin with a low kaolinite content was thermally treated at 650 ^{0}C for 3 h and the produced Metakaolin (MK) was ground to the appropriate fineness. The chemical analyses of these raw materials are shown in Table (2.1)

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

Table 2.1: Chemical compositions of raw materials.

Chemical composition (%)	Na_2O	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Fe_2O_3	L.O.I
OPC	0.601	4.227	15.892	0.175	2.539	0.103	67.330	0.510	5.292	-
MK	0.077	28.729	52.002	0.126	0.405	0.136	0.605	4.247	2.348	10.9

2.2. Sample preparations

Cylinder specimens of 60 mm diameter and 100 mm height were cast with an embedded steel bar of 12 mm in diameter and 100 mm in height for corrosion test. The steel bars were mechanically polished to remove the firmly adherent mill scales on the surface and cleaned by deionised water, dried with acetone then coated with epoxy while 1 cm^2 not coated. The chemical compositions of reinforcing steel are shown in Table (2.2).

Table 2.2: Chemical composition of reinforcing steel

Element	**C**	**Si**	**Mn**	**P**	**S**	**Cr**	**Ni**	**Al**
Wt %	**0.323**	**0.169**	**0.782**	**0.0321**	**0.0186**	**0.0188**	**0.0135**	**0.0333**

Different mixes were made by substitution 0, 5,10,15,20 wt. % of cement by MK. The mixes were denoted as M_0, M_1, M_2, M_3 and M_4 as shown in Table (2.3). The cylindrical specimens were vibrated mechanically to assist compaction. After 24 h of setting the cylindrical specimens were demoulded and subjected to water curing for 7 days in order to avoid any contamination.

Table (2.3): Mix composition of the prepared cements, (wt %).

Mix No.	OPC	MK	Water
M_0 (OPC)	100	-	0.24
M_1 (5 % MK)	95	5	0.24
M_2(10 % MK)	90	10	0.24
M_3(15 % MK)	85	15	0.24
M_4(20 % MK)	80	20	0.24

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

2.3. Corrosion measurements

Three different electrochemical methods were used to evaluate the corrosion rate of reinforcing steel bar. The open circuit potential, linear polarization measurements and electrochemical impedance investigations were performed using the voltalab 40 Potentiostat PGZ301 Dynamic EIS Voltammetry"All- in -one"(made in Germany).

2.3.1. Open Circuit Potential (OCP)

OCP measurements were often used as an indication of the corrosion risk of the steel. The reinforcing steel embedded in the cement paste was employed as working electrode and a saturated calomel electrode (SCE) as reference electrode. Bi-weekly readings were recorded for potential till 90 days of exposure period. Before each measurement, the potential was recorded until it reached an almost stable value, which was the corrosion potential, E_{corr}.

2.3.2. Linear polarization Resistance (LPR)

The linear polarization technique was used to determine the polarization resistance and the corrosion rate of reinforcing steel bars embedded in cement paste. The potential of the steel electrode was scanned at a slow rate of 5mV/s. The tests were initiated at 250 mV below the corrosion potential (E_{corr}) and terminated at 250 mV above it, while recording the polarization current (I). The polarization resistance, R_P, of the reinforcing steel is defined as the slope of a potential - current density plot at the corrosion potential (E_{corr}) as follows:

The corrosion current density is calculated from the Stern-Geary equation:

$$I_{corr} = B / R_p \quad \text{and}$$

$$B = \beta a\ \beta c / 2.3\ (\beta a + \beta c)$$

Where; B is a function of the anodic and cathodic Tafel slopes βa and βc. The corrosion rate, C.R. (μm consumption of steel per year) can be computed using Faraday's Law as follows

$$\text{C.R. } (\mu m/year) = 3.3 I_{corr}\ M/zd$$

Where; z = ionic charge (2 for iron), M = atomic weight of metal (55.85 for iron), d = density of iron, 7.9g/cm^3, and $I_{corr.}$ = corrosion current density, μA/cm^2.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

2.3.3. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful technique for investigating electrochemical and corrosion systems. The main advantage of this technique is the use of a purely electronic model (equivalent circuit) to represent the electrode/electrolyte interface. EIS was performed between 100 MHz - 50 kHz frequency range using a frequency response analyzer (voltalab 40 Potentiostat PGZ301 Dynamic EIS Voltammetry). The amplitude of the sinusoidal voltage signal was 10 mV.

3. Results and Discussion

3.1. Open Circuit Potential (OCP)

Fig.1(a and b) shows the potential - time behavior of reinforcing steel bar embedded in cement paste without and with different percentages of MK in 3.5% NaCl and 5% $MgSO_4$ solutions, respectively. The open circuit potential was monitored periodically for a period of 90 days of exposure. The corrosion potential of reinforcing steel bar in Portland cement was found to be good indicator of corrosion activity. If the potential between saturated calomel electrode (SCE) and steel bar was more positive than -200 mV, it is considered a non corrosion (passive) state for steel, while if the value was more negative than -250 mV this indicates active corrosion. Between -200 and -250 mV, the steel surface may be active or passive [10].

Samples immersed in 3.5% NaCl solution, Fig. (1.a), attained active potential and the time of active potential does not depend on the increase of the concentration of MK percentage in the specimen at the end of exposure. In 20 % MK replacement the shift of potential towards positive direction was observed at the end exposure period. Regarding samples immersed in 5% $MgSO_4$ solution, Fig. (1.b) a steady state potential was observed and remained passive in 5 % of MK, while the steady state potential was observed active in the range of 10 - 20 % of MK. It can be observed that the active potential time does not depend on the concentration of MK in 3.5% NaCl solution while in case of 5% $MgSO_4$ solution the active potential time has a significant value for specimens having 5% MK.

Generally sample with low percentage of MK (5%) immersed in 3.5% NaCl solution has more negative potential (about - 500 mV) but it has

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

less negative values (about -120 mV) if immersed in 5% $MgSO_4$ solution. This shows the influence of MK on the micro- structural diffusion properties of blended cemented concrete and also the pore size distribution may be the reasons for the concrete/mortar has significantly reduced the potential, which acts as filler material [11].

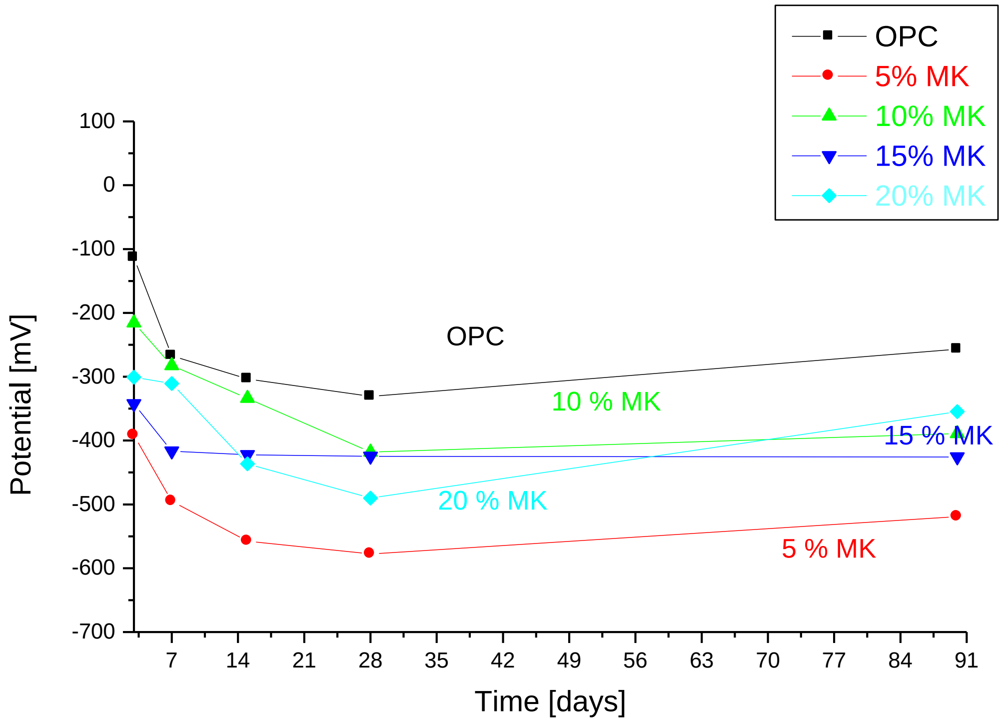


Fig. (1.a). Potential variation with time for Reinforcing Steel presented in different percentage of Metakaolin paste in 3.5 % NaCl.

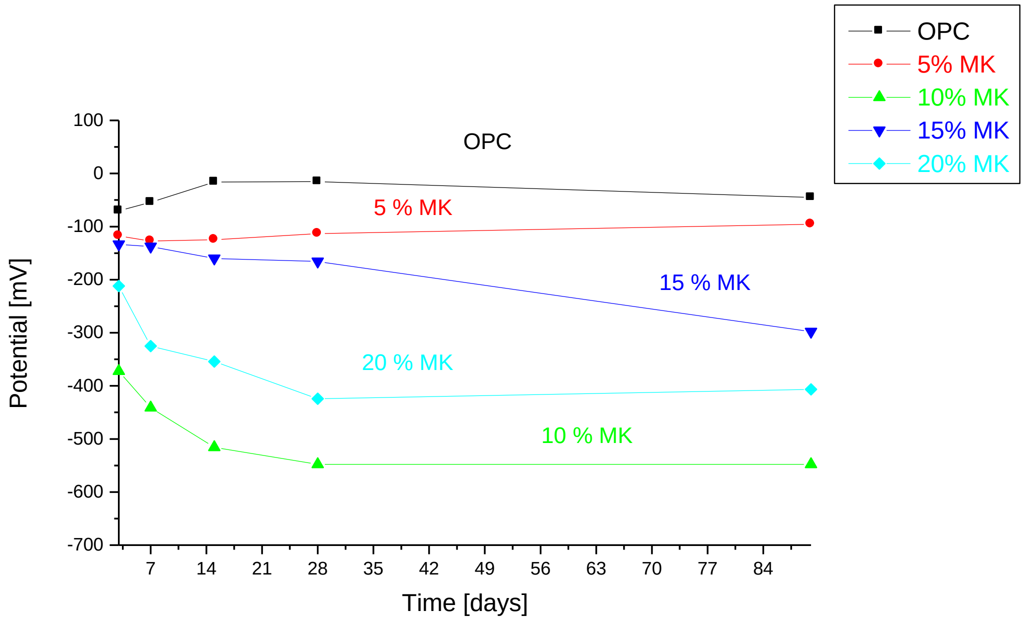


Fig.(1.b). Potential variation with time for Reinforcing Steel presented in different percentage of Metakaolin paste in 5 % $MgSO_4$.

3.2. Linear Polarization Resistance (LPR)

The progress of the corrosion and consequently the performance of the MK admixed concretes can be monitored by means of the corrosion current density and the corresponding corrosion rates were illustrated, respectively. Linear polarization technique had employed at scan 5 mV/S. The linear polarization measurements of reinforcing steel for 90 days in cement paste with and without MK immersed in 3.5% sodium chloride solution are presented in Fig. (2). The values of corrosion parameters, corrosion potential (E_{corr}), corrosion current density (I_{Corr}), polarization resistance (R_p) and corrosion rate (C.R), are recorded in Table (3.1). It can clearly be seen from Fig.(2) and Table (3.1) results, that the control system curve (OPC) without addition of MK has lower corrosion potential than the curves of concretes with MK due to the increase in the amount of MK admixed.

From Table (3.1) also, it is found that there is a nonsystematic decrease in the corrosion current density of the concretes. Also, the corrosion rate values decreased as the concentration of MK increased in 5, 10, and 20 % while the addition of 15% it increased. The polarization resistance values decreased mostly as the concentration of MK increased. The effect of 3.5% NaCl solution on control concrete is more pronounced than MK concretes. These results demonstrate that control concrete shows active corrosion behavior, whereas MK concretes generally stayed in moderate corrosion region. For a given chloride concentration, the utilization of MK especially at 20 % provided good performance to the concrete in terms of corrosion. Since water, oxygen, and chloride ions have considerable roles in the initiation of corrosion of embedded steel and hence causing cracking of concrete, it is obvious that the transport characteristics of concrete is the key for controlling the occurrences of the processes required for corrosion. It is concluded that 20 % addition of MK replacement with cement showed good corrosion resistance property.

Since MK is known for its beneficial contribution on the permeability properties of the concrete [3], one of the main effects in mitigating the harmful effect of chloride ion contamination can be considered as the enhancement of the pore structure of the concrete. Decrease in the average pore size and total porosity of concrete results in reduced capillarity of concrete [3-6, 12, 13].

Table 3.1: linear polarization measurements for reinforcing steel immersed in 3.5% sodium chloride after 90 days.

system	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	R_p ($k\Omega.cm^2$)	Corrosion Rate ($\mu m/y$)
OPC (control)	-316.1	2.7924	15.35	32.66
5 % MK	-644.5	2.8048	10.85	32.80
10 % MK	-510.1	1.6003	19.22	18.71
15 % MK	-506.4	3.5679	12.08	41.73
20 % MK	-461.6	1.0603	31.69	12.40

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

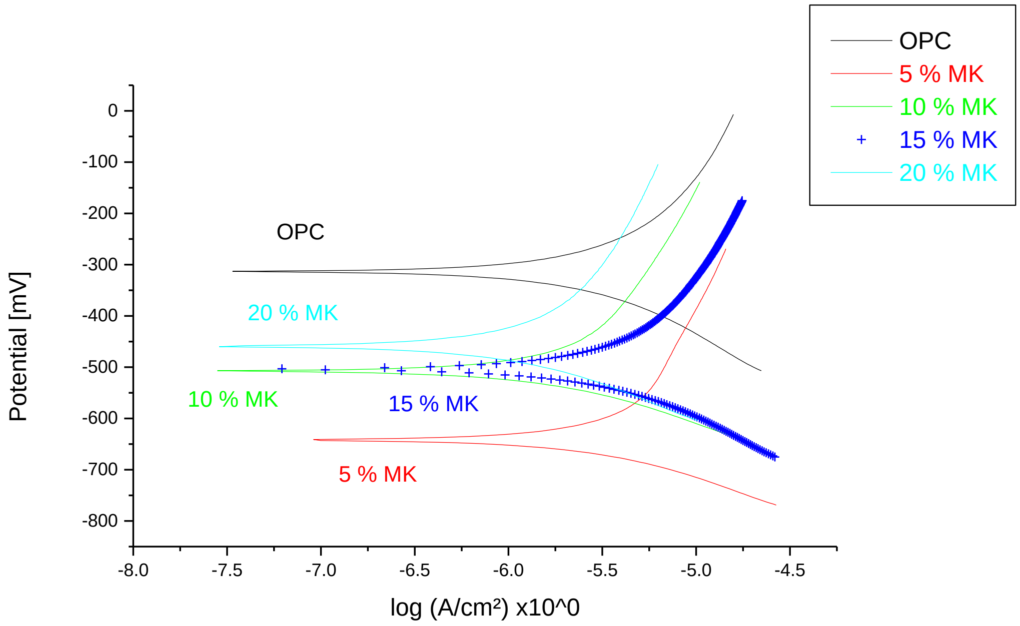


Fig. (2). Linear polarization curves for reinforcing steel immersed in 3.5 % NaCl

The linear polarization curves of reinforcing steel for 90 days in cement paste immersed in 5% magnesium sulfate is presented in Fig.(3). The values of corrosion parameters, corrosion potential (E_{corr}), corrosion current density (I_{Corr}), polarization resistance (R_p) and corrosion rate (C.R), were recorded in Table (3.2).

From Table (3.2), results indicated that the corrosion potential decreased and towards to negative values with additions of MK, compared with control concrete. The addition of 10 % MK showed higher corrosion current and corrosion rate compared to other concrete systems. While the corrosion current and corrosion rate for 5% MK addition was found to be lesser than that of the control system (OPC). In case of 20 % MK addition, corrosion current and corrosion rate was found to be slightly higher than the control system. Therefore, the addition of 5% and 15% MK showed lesser corrosion rates compared to control system (OPC). The polarization resistance values showed lower value with addition of 10 % MK than the OPC , while 5% and 15 % and 20 % MK addition showed higher values of polarization resistance compared to control concrete (OPC). These results can be attributed to the existing original passive film which may be replaced by sulfate ions leading to the formation of ion sulfate film, and reduces the ability of the original passive film [10]. It is concluded that 5% addition of Metakaolin

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

replacement with cement showed to be good corrosion resistance property with concrete in 5% $MgSO_4$.

Finally, from the linear polarization resistance measurements for reinforcing steel for 90 days in cement paste immersed in 3.5% NaCl and 5% $MgSO_4$ solution with and without addition of Metakaolin, it is concluded that 20% addition of Metakaolin replacement with cement showed best corrosion resistance property with concrete in 3.5% NaCl solution while in 5% $MgSO_4$ solution the 5% addition of Metakaolin is the best one addition replacement with cement to reduce the corrosion rate.

Also, it is suggested that chlorides formed metal holes at the film interfaces. The activation by chloride was attributed to dissolution of Portland layer followed by de-stabilization of the film bond by migration through ions; with little or no chemical dissolution of the film occur at this stage [14, 15]. Modification of the original film by sulfate ions may lead to the formation of ion sulfate film, and reduces the ability of the original passive film [16].

Table 3.2: linear polarization measurements for reinforcing steel immersed in 5 % $MgSO_4$ after 90 days.

system	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	R_p ($k\Omega.cm^2$)	Corrosion Rate (μm/y)
OPC (control)	-171	0.8144	29.02	9.525
5 % MK	-246.2	0.3966	48.86	4.639
10 % MK	-639.1	4.504	9.07	52.67
15 % MK	-441.9	0.4487	53.51	5.248
20 % MK	-509.3	0.9381	34.66	10.97

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

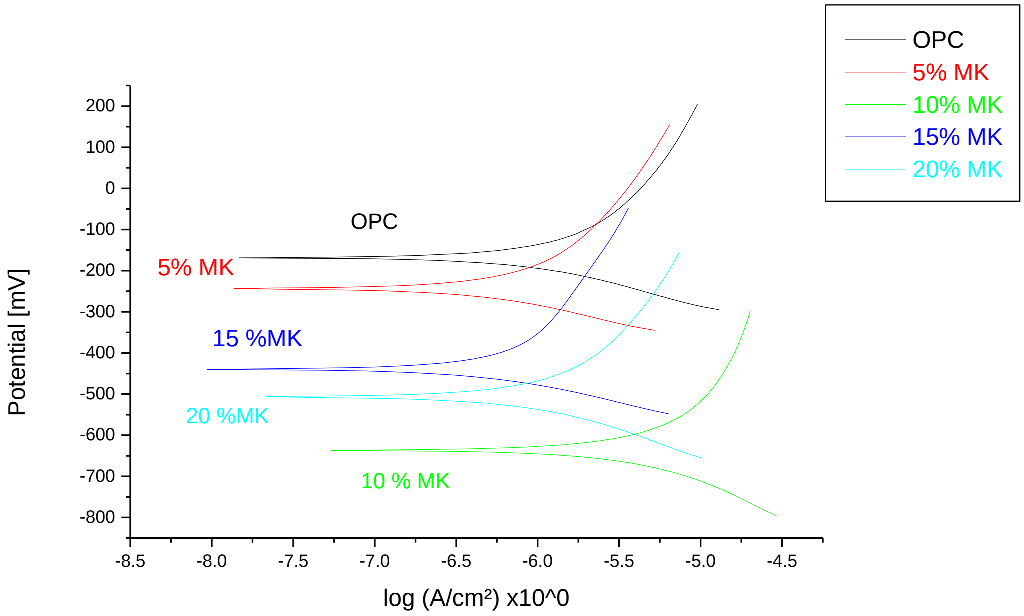


Fig. (3). Linear polarization curves for reinforcing steel immersed in 5 % $MgSO_4$ after 90 days.

3.3. Electrochemical Impedance Spectroscopy (EIS)

The impedance measurements technique has been applied to the study of pitting corrosion and other localized corrosion. The impedance technique has marked advantages in the study of interfacial reactions and other interfacial phenomena.

Fig. 4(a ,b) represents the Nyquist and Bode plots of reinforcing steel with and without different percentage MK after 90 days of immersion in 3.5% NaCl solution. Nyquist plot Fig. 4(a) showed that the corrosion resistance increased by increasing the percentage of Metakaolin. The surface resistance of reinforcing steel without MK is 1.863 k ohm.cm². The resistance slightly increased after addition of 5% MK. Another increase is observed for 10% MK to reach 2.782 k ohm.cm². The highest surface resistance is found for 20% MK (6.029 k ohm.cm²). Bode plot showed that the pitting resistance of the reinforcing steels is generally improved by increasing the Metakaolin content which was confirmed by the relaxation of the impedance spectra Fig. 4(b). The results revealed that the amount of MK and the concentration of NaCl solution (3.5%) had significant effect on corrosion resistance values. It is

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

considered that the increase in the amount of MK resulted in increase in the corrosion resistance values. CEB-192 (Comite Euro- International du Beton) proposes that the likely corrosion rate is negligible for concrete with resistivity higher than 20 k ohm.cm², low for resistivity values in the range of (10-20) k ohm.cm², high for resistivity value in the range (5-10) k ohm.cm², and very high for concrete with resistivity lower than 5 k ohm.cm², [17].

As can be seen from Fig. 4(a), likely corrosion rates of uncontaminated concrete with MK and contaminated with 5-10 % MK are considered as very high, while with 20 % MK is considered as high. However, due to the inclusion of chloride ions, the corrosion behavior has negatively been affected. The lower chloride permeability of concretes containing mineral additives in terms of the lower ionic conductivity (OH^- ions) of the pore fluid and the denser microstructure of the cement paste which may also explain the higher electrical resistivity of these concretes. Therefore, it can be inferred that the higher the ionic conductivity due to the introduction of chloride ions, the lower the electrical resistivity resulting in the susceptibility to initiation of corrosion. It is also reported that the cement pastes incorporating MK had remarkable chloride binding capacity due to high alumina content. MK also provides a denser structure to concrete by microfilling and secondary pozzolanic reactions. The increase in the electrical resistivity with strength of concrete was mainly due to the denser microstructure of concrete [17].

The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

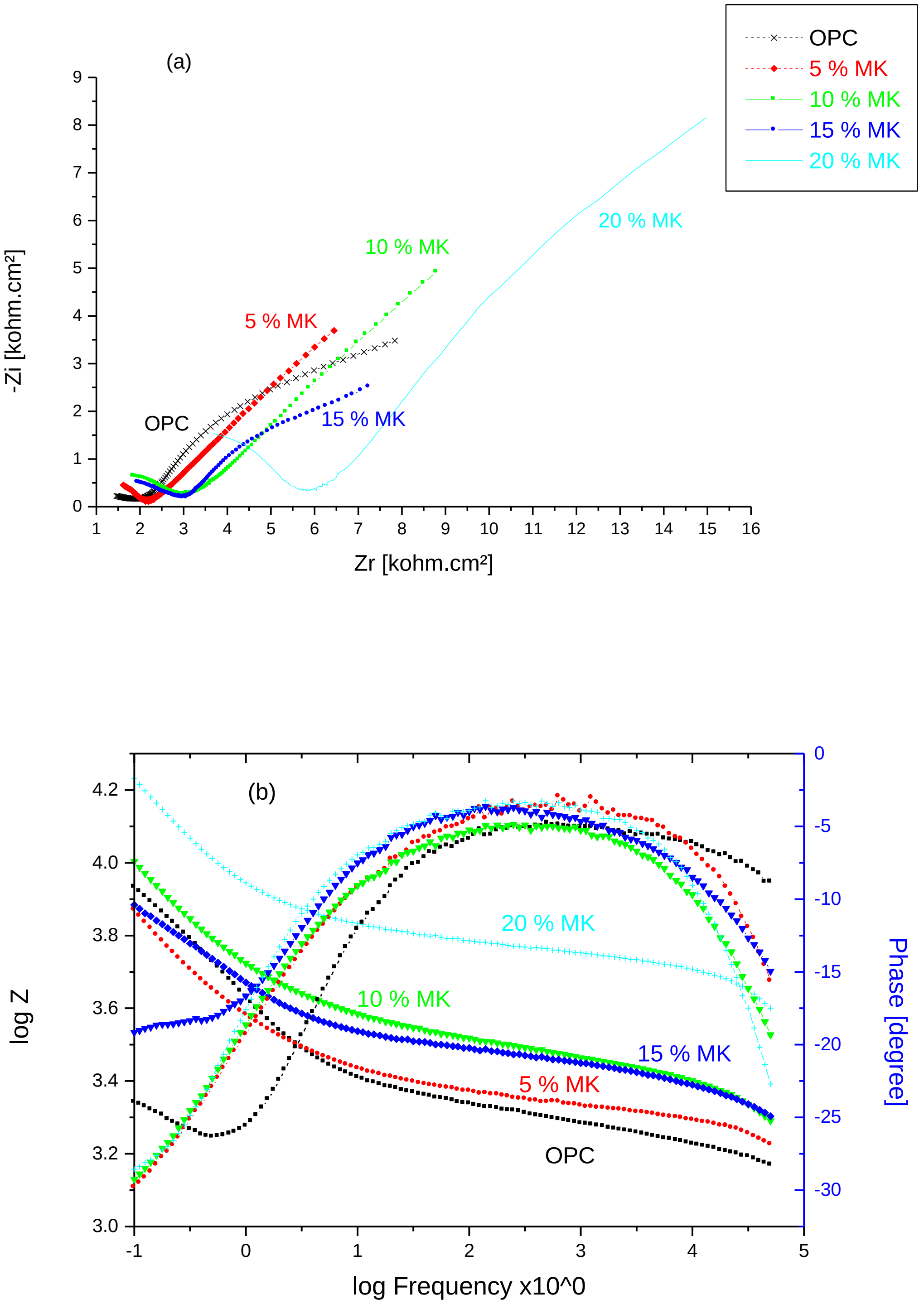
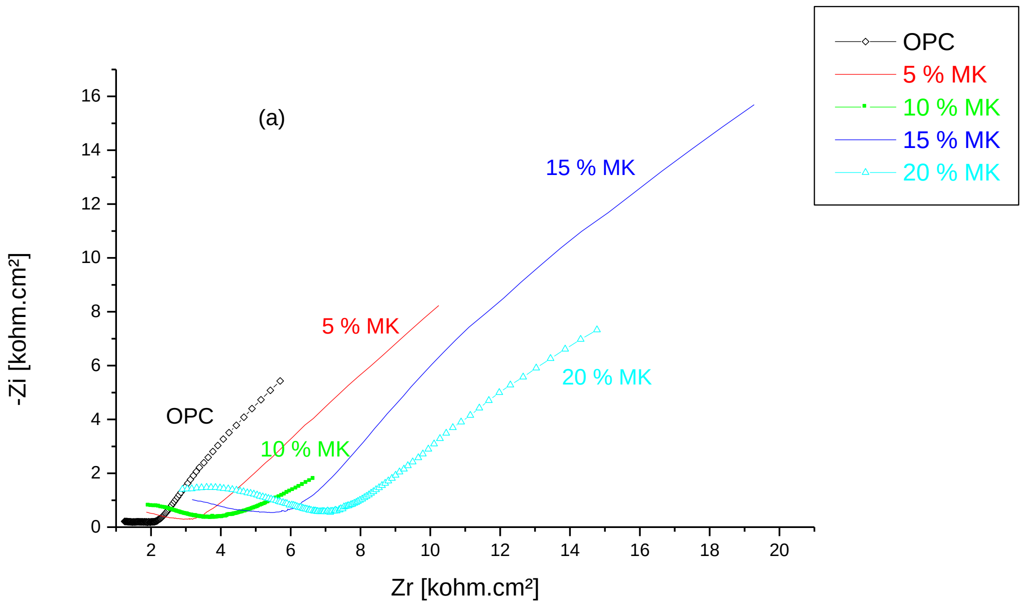


Fig. 4 (a) Nyquist and (b) Bode plots of reinforcing steel with different percentage MK after 90 days of immersion in 3.5% NaCl.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

Fig .5(a and b) represents the Nyquist and Bode plots of reinforcing steel with different percentage MK after 90 days of immersion in 5% $MgSO_4$ solution. Nyquist plot Fig. 5(a), showed that the corrosion resistance increased by increasing percentage of MK. The surface resistance of reinforcing steel without MK is 2.040 k ohm.cm². The resistance slightly increased after addition of 5 % MK. Another increase is observed for 10 % MK to reach 4.578 k ohm.cm². The highest surface resistance is reported for 20 % MK (9.001 k ohm.cm²). Bode plot, Fig.5 (b), showed that the pitting resistance of the reinforcing steel was generally improved as increasing the Metakaolin content which is confirmed by the relaxation of the impedance spectra, Fig. 5(b), this may be attributed to formation of oxide film.

Finally, it is concluded that the effect of addition of different percentage of MK to reinforcing steel immersed in both 3.5 % NaCl and 5% $MgSO_4$ solution, on the corrosion resistance measured by electrochemical impedance microscope is the same feature and confirmed each other. But the corrosion resistance value in 5% Mg SO_4 solution is slightly higher than 3.5% NaCl solution.



JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 16, Preprint 18 submitted 16 April 2013

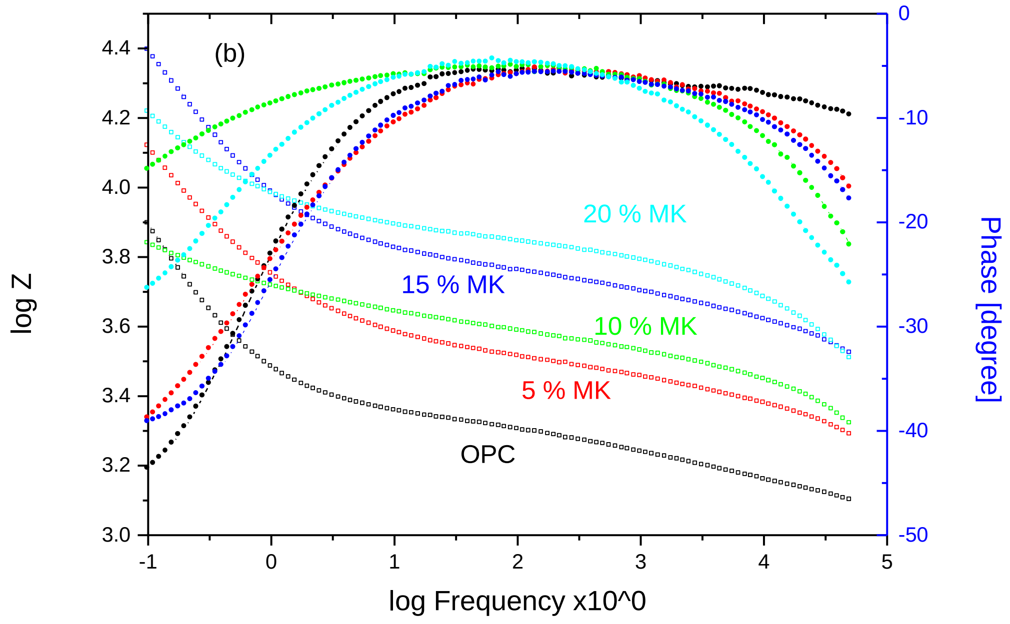


Fig.5 (a) Nyquist and (b) Bode plots of reinforcing steel with different percentage MK after 90 days of immersion in 5% $MgSO_4$.

3.4. Conclusion

The results of the present study showed that each electrochemical technique provide some information about the corrosion resistance of steel bars embedded in cement with and without different percentages of MK in 3.5 % NaCl and 5 % $MgSO_4$ solutions, respectively. From the obtained results it can be concluded that:

1. MK plays an important role in reducing the corrosion of steel in cement which exposed to chloride or sulphate media.

2.The open circuit potential measurements showed that the sample with 5 % MK immersed in 3.5 % NaCl solution has more negative potential while it has less negative values if immersed in 5 % $MgSO_4$ solution. So, chloride ions are more aggressive for steel bar in cement than sulfate ions.

3. The active potential time does not depend on the percentage of MK in 3.5 % NaCl solution while in 5 % $MgSO_4$ solution the active potential time has a significant value for 5 % MK.

4. From the linear polarization resistance results, it is represented that 20 % MK replacement with cement showed best corrosion resistance property with concrete in 3.5 % NaCl solution. While 5 % MK replacement with cement in 5 % $MgSO_4$ solution is the best addition to reduce the corrosion rate.

5. According to EIS measurements, it is showed that the localized corrosion resistance of reinforcing steels in 3.5 % NaCl and 5 % $MgSO_4$ solution increases as the percentage of MK in cement increased.

6. The optimum percentage of MK replacement with cement to control corrosion of reinforcing steel in both chloride and sulphate containing media are 20 % and 5 %, respectively.

Acknowledgements

The authors acknowledge the support extended by Central Metallurgical Research and Development Institute (CMRDI), Al -Tabbin, Helwan.

References

[1].**H.E.Jamil, M.F.Montemor, R.Boulif, A.Shriri, M.G.S.Ferreira**,An electrochemical and analytical approach to the inhibition mechanism of an amino-alcohol-based corrosion inhibitor for reinforced concrete,Electrochimica Acta 48(2003) 3509-3518.

[2]. **G. M. Habeeb, M. S. Essa**, Jornal of Kerbala University, 5(4), 2007.

[3].**G. Batis , P. Pantazopoulou, S. Tsivilis, E. Badogiannis**, The effect of metakaolin on the corrosion behavior of cement mortars, Cement and Concrete Composites ,27 (2005) 458–467.

[4]. **E.Guneyisi , M.Gesog˘lu , K.Mermerdas**, Improving strength, drying shrinkage, and pore structure of concrete using Metakaolin, Mater. Struct. , 41 (2008) 937–949.

[5]. **E. Guneyisi ,M. Gesog˘lu , K. Mermerdas**,Strength deterioration of plain and metakaolin concretes in aggressive sulfate environments. ASCE J Mater. Civ. Eng., 22(2010) 403–407.

[6]. **H.S Kim, S.H Lee, H.Y Moon**, Strength properties and durability aspects of high strength concrete using Korean Metakaolin,Constr. Build. Mater., 21(2007) 1229–1237.

[7]. **G.J. Verbeck**, Mechanism of corrosion of steel in concrete, Corrosion Science, 24 (11) (1986) 21– 30.

[8]. **F.H. Dakhil, R. El Uzzafar, A.S. Al-Gahfani**, Deterioration of concrete structures in the environment of Middle East, Journal of the American Concrete Institute ,1 (1984) 13– 20.

[9].**S.M. Abd El Haleem, S. Abd El Wanees , E.E. Abd El Aal, A. Diab**, Environmental factors affecting the corrosion behavior of reinforcing steel II: Role of some anions in the initiation and inhibition of pitting corrosion of steel in $Ca(OH)_2$ solutions, Corrosion Science 52 (2010) 292–302.

[10].**K. Sakr**, Effect of cement type on the corrosion of reinforcing steel bars exposed to acidic media using electrochemical techniques, Cement and Concrete Research 35 (2005) 1820–1826.

[11].**J. A. Kastuch, G.V. Walters, T.R. Jones**, High performance concrete incorporating metakaolin – a review, concrete 2000. University of Dundee, 1993, p. 1799-1811.

[12]. **J .Ding, Z. Li**, Effects of metakaolin and silica fume on properties of concrete., ACI Mater. J. 99(2002) 393–398.

[13].**E.E. Abd Aal, S.Abd El Waness, A.Diab, S.M. Abd El Haleem**, Environmental factors afeecting the corrosion behavior of reinforcing steel III , Measurement of pitting corrosion current of steel in $Ca(OH)_2$ solutions under natural corrosion conditions, corrosion science 51(2009) 1611-1618.

[14]. **C.Y. Chao, L.F. Lin, D.D. Macdonald**, A point defect model for anodic passive films, part 1. film growth kinetics, part 2. chemical breakdown and pit initiation, Journal of the Electrochemical Society 128 (1981) 1187– 1194.

[15]. **D.S. Leek, A.S. Poole**, The breakdown of the passive film on high yield mild steel by chloride ions, in: C.L. Page, K.W. Treadway, P.B. Bamforth (Eds.), Proc.″Corrosion of Reinforcement in Concrete″, Society of Chemical Industry, Elsevier, London, 1990.

[16]. **J. Tritthart**, Pore solution composition and other factors influencing the corrosion risk of reinforcement in concrete, in: C.L. Page, R.W. Treadawy, P.B. Bamforth (Eds.), Proc. ″Corrosion of Reinforcement in Concrete″, Society of Chemical Industry, Elsevier, London, 1990.

[17]. **E. Güneyisi , M. Gesoğlu, F. Karaboğa, K. Mermerdas**, Corrosion behavior of reinforcing steel embedded in chloride contaminated concretes with and without metakaolin, Composites: Part B 45 (2013) 1288–1295.