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Corrosion Protection of Rebar steel in Marine Atmosphere by Nanocoating

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Keywords: Rebar steel, Chloride ion, marine atmosphere, $Mg_3(PO_4)_2$, DLC.

ABSTRACT

Rebar steel is an important building material which is basically used for construction works. This metal is reinforced with concrete for construction of bridges and houses. Such types of bridges and houses face corrosive problems in coastal areas because high concentration of Cl^- ions marine atmosphere. There are several porosities on the surface bridges and houses. The chloride ions enter inside the building materials and develop electrochemical cell on the surface of rebar steel. Rebar steel undergoes process of corrosion reaction and creates several forms of corrosion like galvanic, pitting, stress and crevice. Chlorides ions develop internal and external corrosive effect for rebar steel and concrete hence disbanding occur between building materials. This corrosive ion decreases life of building materials, increase maintenance costs and sometimes major accident takes place. The hydroxides of magnesium and calcium are present in concrete. Chloride ion reacts with these hydroxides and decreases the pH value of concrete thus accelerate the rate of corrosion reaction. Nanocoating of $Mg_3(PO_4)_2$ with DLC filler is applied to control corrosion of rebar steel in marine atmosphere. The uncoated and coated rebar steel with $Mg_3(PO_4)_2$ were exposed to marine atmosphere in different seasons like summer, rainy and winter. The corrosion rate of metal was analyzed in these seasons. The results show that though corrosion rate is minimized it does not produce good results. Porosities are developed on the surface of rebar steel coated with $Mg_3(PO_4)_2$ which is reactive with chlorine ion. DLC is used as filler to close the porosities of coated rebar steel and again the corrosion rate of rebar steel was analyzed in the above mentioned seasons. It is found that this filler has good inhibition effect in marine atmosphere. The corrosion of metal was determined by gravimetric and potentiostatic polarization methods. Coating work was completed with application of nozzle sprays and vapour deposition methods. Coating efficiency, surface coverage area and stability of coating material were calculated with Arrhenius, Langmuir isotherm, Temkin equation, free energy, enthalpy and entropy.

INTRODUCTION

Bridges and houses are very essential for the development of society but these things face corrosive problems in marine atmosphere. In marine atmosphere availability of chloride ion is very high which causes physical and chemical changes in building materials. This pollutant tarnish their facial appearance, corrode building materials and material lose their tensile strength. There are several types of remedial approach developed like proper design of shape, metallic coating, and addition of organic and inorganic inhibitors, polymeric coating, ceramic coating, paint coating and nanocoating to control corrosion in marine atmosphere. These coating methods do not produce good result in chloride environment. Rebar steel coated with Zn, Mg, Al and Cr [1] are used to check corrosion in chloride ion environment. Rebar steel coated by these coated metals did not provide full protection of base metal [2].The chloride ions penetrated the outer surface of building materials and came in contact of coated rebar steel and developed corrosion cell thus coated metal started disintegrating. Different types of polymers were coated on rebar steel to suppress corrosion in marine environment. When polymers coated [3] metal comes into contact with hostile environment of chloride ions, they initiate chemical reaction and disbanding takes place on its surface and finally chloride ions enter into the surface of base metal and corrode it. Organic compounds having nitrogen, oxygen and sulphur functional groups with aromatic and heterocyclic hydrocarbons [4], they produce corrosion mitigation in this environment. These compounds were adhered on the surface of metal by physisorption and chemisorptions bonding, in this way they developed thin film. This thin film is surrounded by chloride ion; its deterioration takes place and rebar steel undergoes corrosion process. Synthetic paints [5] are used for outer and inner surface protection of building material against chloride ion corrosive environment. This protection layer is dissociated by chloride ions and by diffusion process it goes into rebar steel and generates corrosion cell and corrosion reaction occurs on its surface. A nanocoating technique of organic and inorganic materials [6] is applied for protection of rebar steel against chloride ions pollutant. Porosities are developed on the surface of coated metal. Chloride ions enter into the pore of coated materials and starts process of corrosion reaction then after it goes to the base metal corroding it later on. Such types of coating do not produce effective results in marine environment [7]. For this research work Mg3(PO4)2 is used as nanocoating materials for rebar steel and its anticorrosive phenomenon studied in marine atmosphere but this coating did not provide full protection due to porosities. Porosities were blocked by filler of DLC (diamond like carbon) which developed an inert atmosphere.

METHODOLOGY

Rebar steel coupons were cut into size of 5cm height and diameter of 1.6cm where area of test coupon is 10.04cm^2. Its surface was rubbed with emery paper and samples were washed with double distilled water. Finally it was erased with acetone and dried with air dryer and kept into desiccators. The sample was coated with $Mg_3(PO_4)_2$ by nozzle spray and its porosities were filled with DLC. Rebar steel samples without coating, with coating $Mg_3(PO_4)_2$ and DLC (diamond like carbon) filler of $Mg_3(PO_4)_2$ were kept in chloride ions environment for corrosion analysis in different seasons like summer, rainy and winter in marine atmosphere. The corrosion rate was measured by gravimetric method.

The corrosion current density and corrosion rate without and with coating were calculated by potentiostatic polarization technique with help of an EG & G Princeton Applied Research Model 173 Potentiostat. A platinum electrode was used as an auxiliary electrode and a calomel electrode was used as reference electrode with rebar steel coupons [8,9,10,11].

Results and Discussion

The corrosion rates of rebar steel without coating, with coating of $Mg_3(PO_4)_2$ and filler with DLC in summer, rainy and winter seasons were determined by equation1in chloride ions atmosphere.

$$K\ (\text{mmpy}) = 87.6\ W / D\ A\ t \qquad (1)$$

where W = weight loss of test coupon expressed in gm, A = Area of test coupon in square centimeter, D = Density of the material in gm/cm^3.

The surface coverage areas (θ) and the coating efficiencies (CE) were occupied by coated materials and filler were determined by equation 2 and 3.

$$\theta = (1 - K / K_o) \qquad (2)$$

where θ = Surface coverage area, K_o = corrosion rate without coating, K = corrosion rate with coating,

$$CE = (1 - K / K_o) \times 100 \qquad (3)$$

Where K_o is the corrosion rate without coating, K = corrosion rate with coating

The corrosion rates of rebar steel, surface coverage area and coating efficiencies were calculated by equation1, equation2 and equation 3 in different concentrations of chloride ions for summer, rainy and winter seasons and its values were mentioned in Table1 and Table2. The results of Table1 and Table2 were noticed that during winter season corrosion rates were higher in respect of summer and rainy seasons. Rebar steel coupons were coated with $Mg_3(PO_4)_2$ and kept in Cl^- ions environment for the observation of corrosion phenomenon. It is observed that corrosion rate decreased and surface coverage area and coating efficiency increased but these results are not satisfactory. $Mg_3(PO_4)_2$ coated metal was not corrosion free in Cl^-environment because it was further prone to corrosion. To mitigate such corrosion, DLC was used as filler on the coated surface of $Mg_3(PO_4)_2$. The results mentioned in Table2 showed that after DLC filler corrosion rates were highly controlled and surface coverage area and coating efficiency were also improved. DLC coating material enters into the porosities of $Mg_3(PO_4)_2$ and it creates inert atmosphere for Cl^- ions. The Plot of logK Vs. C(concentration of Cl^-), θ(surface coverage area) Vs. C(concentration of Cl^-), CE(coating efficiency) Vs. C(concentration of Cl^-) and log(θ/1- θ) Vs. C(concentration of Cl^-) without coating, with coating of Mg3(PO4)2 and DLC filler were represented in Fig.1, Fig.2, Fig.3 and Fig.4. These plots exhibit straight line so it indicates an anticorrosive character against Cl^- ions.

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Table1: Corrosion of rebar steel in different seasons without and with coating of $Mg_3(PO_4)_2$in marine atmosphere.

Seasons	Summer	Rainy	Winter
Conc.of Cl^- (PPM)	495	553	626
Temperature(0C)	45	35	25
K_0	3.916	5.667	8.361
$\log K_0$	0.592	0.752	0.922
K	1.181	1.926	3.306
logK	0.072	0.284	0.519
θ	0.698	0.659	0.604
(1-θ)	0.302	0.341	0.396
(θ/1-θ)	2.311	1.932	1.525
log(θ/1-θ)	0.363	0.286	0.183
C.E	68.8	65.9	60.4

Table 2: Corrosion of rebar steel in different seasons after coating of $Mg_3(PO_4)_2$over DLC filler in marine atmosphere (Cl^-)

Seasons	Summer	Rainy	Winter
Conc.of Cl^- (PPM)	495	553	626
Temperature(0C)	45	35	25
K_0	3.916	5.667	8.361
$\log K_0$	0.592	0.752	0.922
K	0.340	0.636	1.049
logK	-0.468	- 0.196	0.020
θ	0.913	0.887	0.874
(1-θ)	0.087	0.113	0.126
(θ/1-θ)	10.494	7.849	6.936
log(θ/1-θ)	1.021	0.894	0.841
C.E	91.30	88.70	87.40

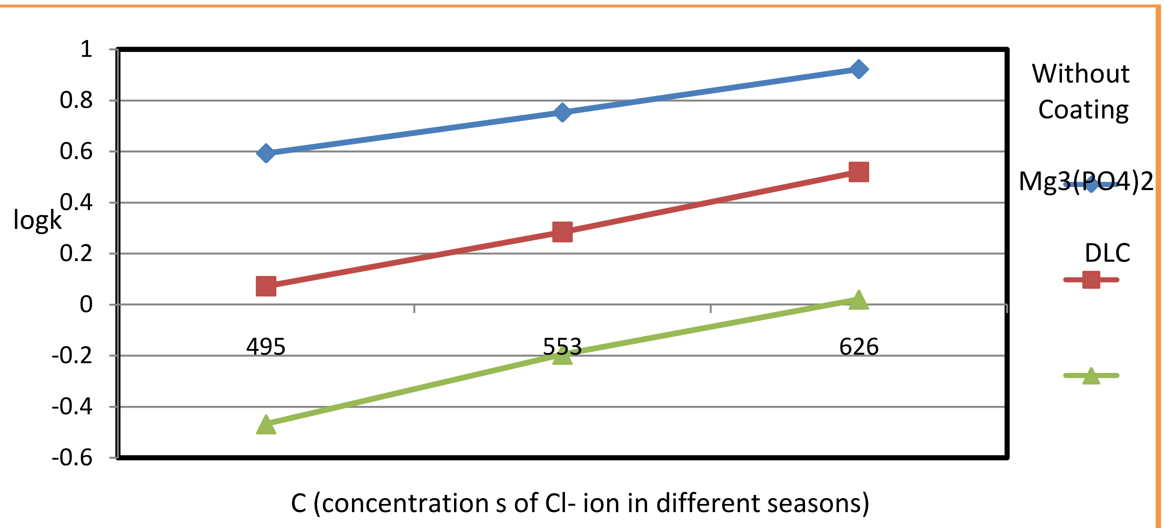

Figure 1: Plot of logK vs. C for rebar steel coated with Mg3(PO4)2 filler DLC

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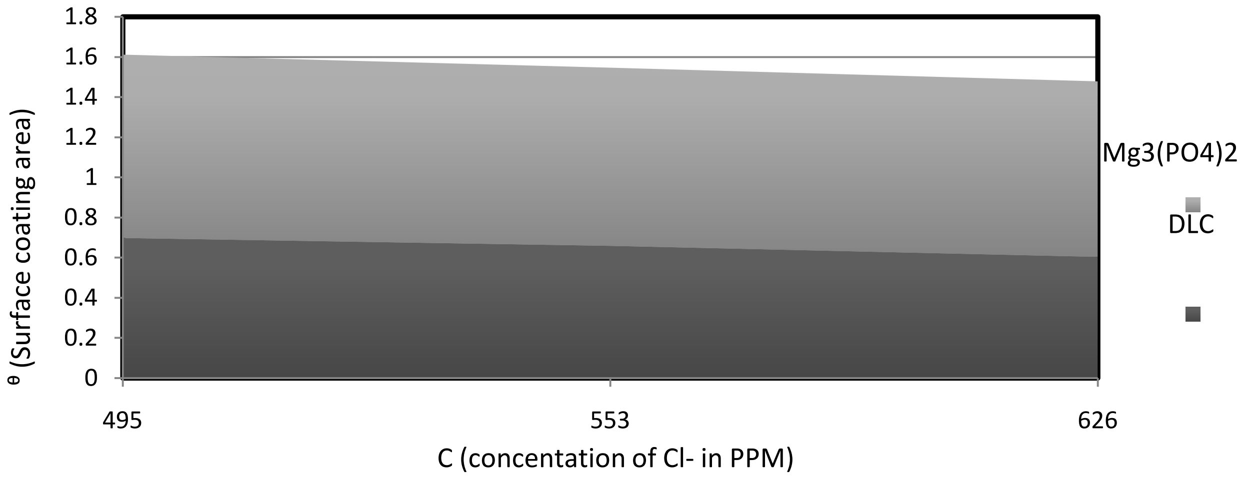
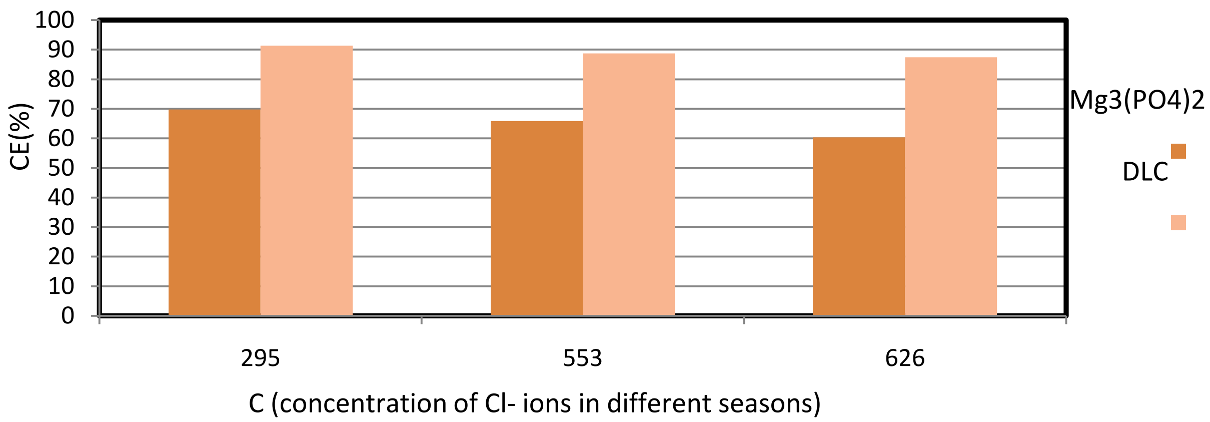


Figure 2: Plot between θ Vs. C in different concentration of Cl- ion in marine



Figture 3: Plot of CE(%) vs C for rebar steel coating with Mg3(PO4)2 filler DLC

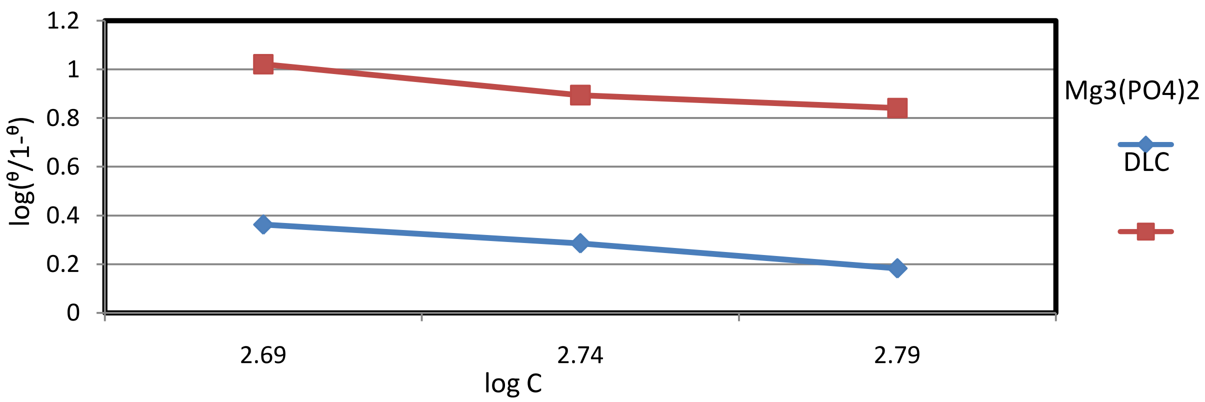


Figure 4: Plot of logK Vs. logC for rebar steel in Cl- ions coating with Mg3(PO4)2 filler DLC

The concentration of Cl^- ions change in different seasons of marine atmosphere due to variation of temperatures. The corrosion rate, surface coverage area and coating efficiencies were calculated in absence and presence of $Mg_3(PO_4)_2$ and DLC in summer, rainy and winter seasons with respect of temperatures and it values were mentioned in Table1 and Table2. The analysis of results of Table 1 and Table2 show that rebar steel coated with $Mg_3(PO_4)_2$ was corroded but filled with DLC corrosion was mitigate. It was observed that corrosion rate was minimized whereas surface coverage areas and surface coating efficiencies were enhanced. The plots between corrosion rate logK vs. 1/T, log (θ/1- θ) vs. 1/T, CE (coating efficiency) vs. T and θ (surface coverage area) vs. T were depicted in Fig.5, Fig.6 and Fig.7. These figures show that $Mg_3(PO_4)_2$ and DLC have good adherence properties in Cl^- ions environment.

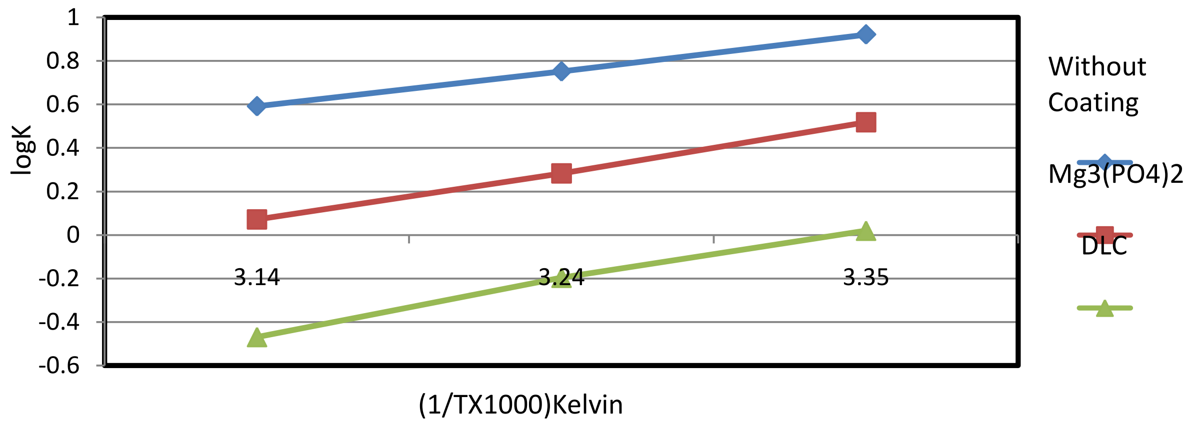


Figure 5: Plot of logK Vs. 1/T for rebar steel in different temperatures of marine atmosphere

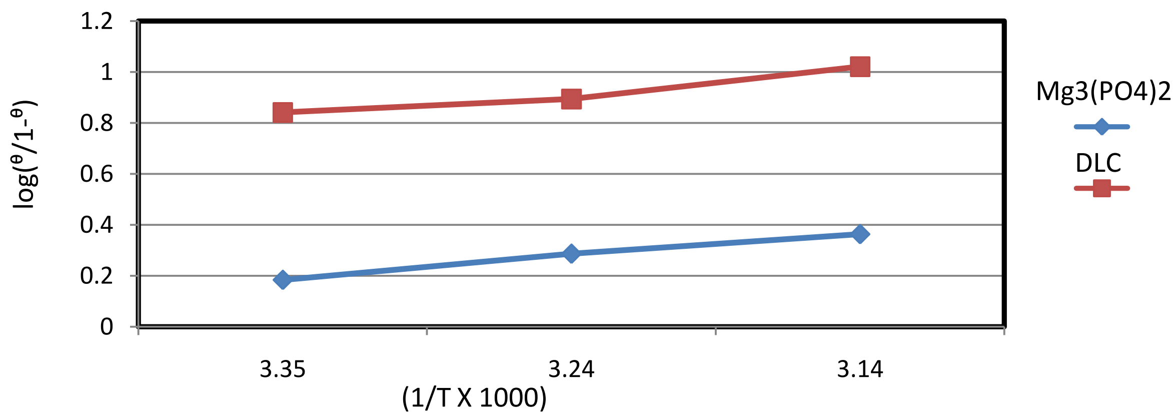


Figure 6: Plot of log (θ/1-θ) Vs. 1/T for rebar steel in different temperatures

The activation energy, heat of adsorption, free energy, enthalpy and entropy for $Mg_3(PO_4)_2$ and DLC were calculated by equation4, equation5, equation6 and equation7 and their values were recorded in Table3 and Table4. The activation energy increased before coating and its values decreased after coating so it indicates that coating materials were effective in Cl^- environment. Heat of adsorption, free energy, enthalpy and entropy values were observed to be negative with $Mg_3(PO_4)_2$ and DLC filler hence these coating and filler materials were strongly bonded with rebar steel. Thermodynamical results of $Mg_3(PO_4)_2$ and DLC reflect that chemical adsorption occurred between coating materials and base metal.

$$d/dt(\log K) = E_a / R T^2 \qquad (4)$$

where T is temperature in Kelvin and E_a is the activation energy

$$\log(\theta/ 1-\theta) = \log(A.C) - (Q_{ads}/ R T) \qquad (5)$$

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where T is temperature in Kelvin and Q_{ads} heat of adsorption

$$\Delta G = -2.303RT [\log C - \log (\theta/1-\theta) + 1.72] \qquad (6)$$

where T is temperature in Kelvin and ΔG free energy

$$K = R\,T / N\,h \log (\Delta S^{\#} / R) \times \log (-\Delta H^{\#} / R\,T) \qquad (7)$$

where N is Avogadro's constant, h is Planck's constant, $\Delta S^{\#}$ is the change of entropy activation and $\Delta H^{\#}$ is the change of enthalpy activation.

The corrosion current density determined in the absence and presence of $Mg_3(PO_4)_2$ and DLC with the help of equation 8 and their values were recorded in Table 5.

$$\Delta E/\Delta I = \beta_a\,\beta_c / 2.303\, I_{corr} (\beta_a + \beta_c) \qquad (8)$$

where ΔE/ΔI is the slope which linear polarization resistance (R_{p}), β_a and β_c are anodic and cathodic Tafel slope respectively and I_{corr} is the corrosion current density in mA/cm^2.

The metal penetration rate (mmpy) was determined by equation9 in absence and presence of $Mg_3(PO_4)_2$ and DLC.

$$C.\,R\,(mmpy) = 0.327\, I_{corr}\, (mA/cm^2) \times Eq.Wt\,(g) / \rho\,(g/cm^3) \qquad (9)$$

where I_{corr} is the corrosion current density ρ is specimen density and Eq.Wt is specimen equivalent weight. The results of Table5 indicate that corrosion current increase without coating and it gets reduced after coating and its value decreases more with DLC filler. Tafel graph was plotted in Figure9 between electrode potential and corrosion current density in the absence and presence of coating materials. Anodic potential, current density and corrosion rate increased without coating but after coating cathodic potential and corrosion current increased and corrosion rate decreased

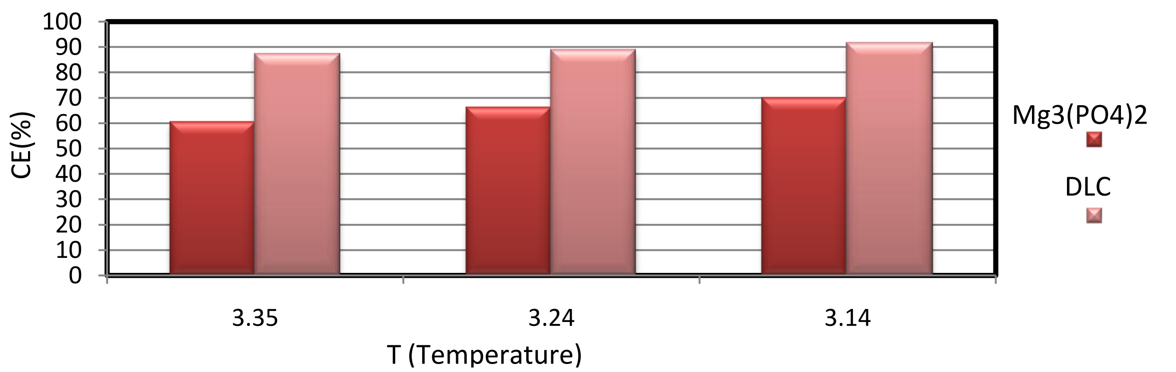
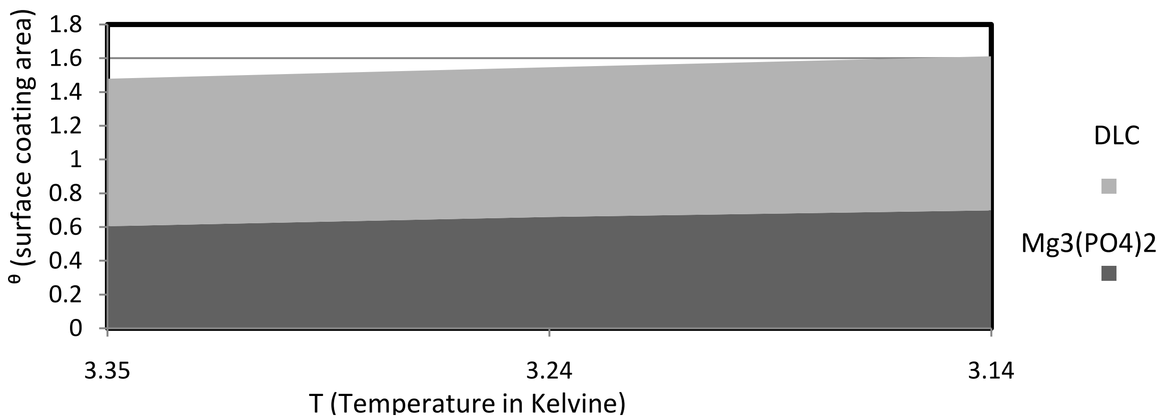


Figure 7: Plot of CE(%) Vs. T for rebar steel in different temperature in Marine environment



Figture 8: Plot of θ Vs. T for rebar steel coating with Mg3(PO4)2 filler DLC in marine atmosphere

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Table 3: Thermodynamical parameters values of coated $Mg_3(PO_4)_2$ on the surface of rebar steel

Seasons	Summer	Rainy	Winter
$E_a(o)$	35.56	46.61	59.08
Ea	29.99	12.14	1.20
Q_{ads}	-23.26	-17.72	-10.99
ΔG	-102.15	-111.93	-122.59
ΔH	28.96	-13.94	-1.32
ΔS	-21.84	-13.94	-38.62

Table 4: Thermodynamical parameters values of coated $Mg_3(PO_4)_2$ with DLC filler on the surface of rebar steel

Seasons	Summer	Rainy	Winter
$E_a(o)$	35.56	46.61	59.08
Ea	29.99	12.14	1.20
Q_{ads}	-65.43	-55.41	-50.51
ΔG	-67.54	-82.18	-92.62
ΔH	-63.67	-43.82	-28.60
ΔS	-30.69	-38.88	-41.78

Table5. Potentiostatic polarization of coated $Mg_3(PO_4)_2$and DLC filler in Cl- ions environment

ΔE(mV)	ΔI	β_a	β_c	$I_{corr.}(mA/cm^2)$	K(mmpy)	$Mg_3(PO_4)_2$ (gm)	DLC (gm)
-650	550	350	250	55.79	4.379	0.00	0.00
-600	475	225	315	45.17	0.354	45	
-575	350	175	325	30.10	0.236		20

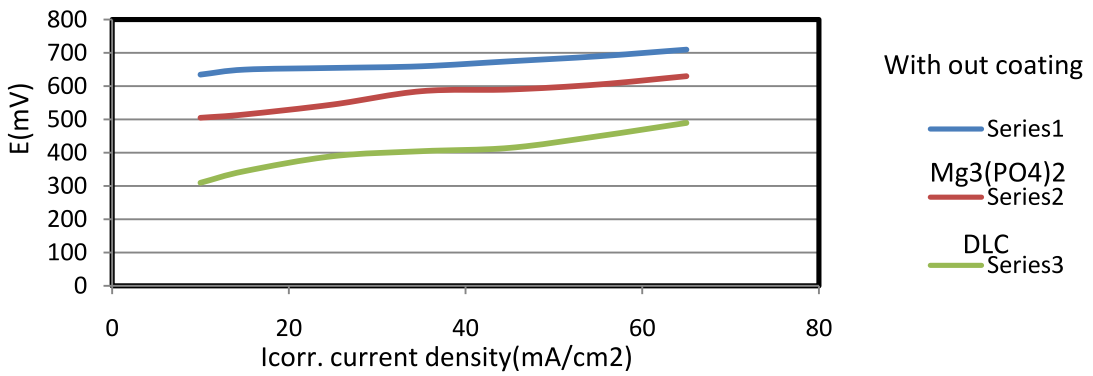

Figure 9: Plot of E(mV) vs. I(mA) for rebar steel coated with Mg3(PO4)2 filler DLC in Cl- ions environment

CONCLUSION

Corrosion is one of the major problems for materials. It is impossible to fully control but it can be minimized with the application of suitable coating materials with application of filler. Rebar steel is an important engineering metal which is used in different appliances of our purposes. It gets corroded badly in Cl^- ions environment. The corrosion protection of rebar steel by nanocoating of $Mg_3 (PO_4)_2$ and DLC as a filler can be used in Cl^- corrosive environment which have highly effective anticorrosive properties. The coated metal coupons by these materials were kept into winter, rainy and summer seasons in Cl^- ions environment for the analysis of corrosion phenomenon. The experimental results collected by the use of gravimetric and potentiostat techniques provide information that this coating and filler materials produce anticorrosive effect in Cl^- ions medium.

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