Research and Reviews: Journal of Pure and Applied Physics

Nanocoating for Corrosion Protection of Metal in SO_2 Environment.

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Research Article

ABSTRACT

SO_2 is a very dangerous corrosive pollutant. This corrosive gas produces dangerous corroding effect with materials. It reacts with moist oxygen to form acids which generates corrosion problems with materials. It changes their physical, chemical and mechanical properties and tarnishes their appearance. Mild steel is a very important engineering metal and it is used for several appliances in day to day life. Mild steel is highly sensitive toward moist SO_2. It develops corrosion cell on the surface of mild steel and undergoes with corrosion reaction. Metal exhibits galvanic corrosion, pitting corrosion, crevice corrosion, and stress corrosion. The concentration of SO_2 gas is increasing day by day in the atmosphere due to industry, transport, road, housing, infrastructure development works and decomposition of living organisms. Its concentration was measured in summer, rainy and winter seasons in industrial areas of different cities and its corrosive effect studied on mild steel. It is observed that concentration of SO_2 gas varies from season to season. Its concentration is more in winter than in summer and rainy. This result shows that mild steel corrodes more in winter seasons with respect of summer and rainy seasons. Nanocoating technique is used to check the corrosion of mild steel in SO_2 environment. For this work, $AlPO_4$ is applied as coating materials and DLC (diamond like carbon) as filler. Nanocoating work completed with nozzle sprays and chemical vapour deposition methods. The corrosion rate and corrosion current density of metal were calculated by gravimetric and potentiostatic polarization techniques. Surface coating phenomena and its stability studied with help of Arrhenius equation and Langmuir isotherm and thermodynamical parameters like activation energy, heat of adsorption, free energy, enthalpy and entropy.

INTRODUCTION

Corrosion is a common problem with materials. It cannot be fully controlled but its effect can be minimized with the help of corrosion protection techniques. It is major setback for economy because huge money expense for repairing, replacement and maintenance of materials. The corrosion protection of materials is a vital issue among scientists. Scientists developed various methods for its protection like designing proper shape; metallic coating [1], non metallic coating [2], inhibitors action [3] anodic and cathodic protection [4] but these techniques do not provide full protection of materials. Metallic coating is used for the corrosion mitigation of materials in SO_2 environment but this type of coating is also not very effective. Paint coating adhered on the surface of metal gets deteriorated in SO_2 environment. Polymeric coating applied in SO_2 environment for the safety of metals but SO_2 disbanded bond connectivity between polymeric materials. It enters into covered metal surface through diffusion and corrodes base metal. Organic coatings [5] are protected metal in above mention corrosive environment. Such organic coatings are disbanded by moist sulphur oxide and it also produces dissolving and swelling attack on their interfaces. Aliphatic and aromatic compounds [6] having nitrogen, oxygen and sulphur atoms are used as inhibitors in different hostile environment. These inhibitors don't mitigate corrosion of metal. Electrochemical technique [7] like anodic and cathodic was applied for corrosion protection of metal but this technique didn't save metal for corrosion. Scavenger's materials [8] were used for minimized concentration of oxygen thus conversion of SO2 into SO3 is controlled. The above mentioned corrosion protection methods give unsatisfactory results in SO_2 environment. The nanocating of inorganic and organic materials [9] exhibit anticorrosive results in this conditions. The nanocoating

materials [10] enter into the matrix of base metal and stopping formation of corrosion cell. Several types of nanocoating techniques [11] were applied for corrosion control of metals like top barrier coating, thermal barrier coating, composite thin film coating and vapour deposition coating. The porosities are developed on surface of coating materials. Corrosive pollutants enter into porosities of coated materials and starts chemical and electrochemical reaction. For this work, the base metal surface was coated with aluminum phosphate and after coating porosities create within coated substance that porosities are blocked by DLC as filler. Nanocoating with DLC filler generates an inert atmosphere for SO_2.

EXPERIMENTAL

Mild steel coupons were cut into size of (10X5X0.01) cm². 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 aluminum phosphate by nozzle spray and its porosities were filled with DLC. Mild steel samples without coating, with coating aluminum phosphate and DLC (diamond like carbon) filler of aluminum phosphate were kept in SO_2 environment for corrosion analysis in different seasons like summer, rainy and winter. 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 mild steel coupons.

RESULTS AND DISCUSSION

The corrosion rates of mild steel without coating, with coating and with DLC filler in summer, rainy and winter seasons were determined by equation1in SO_2 environment.

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

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/cm³.

The surface coverage areas occupied by coated materials were determined by equation 2.

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

where θ = Surface coverage area, K_o = corrosion rate without coating, K = corrosion rate with coating,
The coating efficiencies of coated materials were calculated by using equation2.

$$CE \text{ (coating efficiency)} = (1 - K / K_o) \, X \, 100 \qquad (3)$$

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

The corrosion rates of mild steel, surface coverage area and coating efficiencies were calculated by equation1, equation2 and equation 3 in different concentrations of SO_2 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. Mild steel coupons were coated with $AlPO_4$ and kept in SO_2 environment for the observation of corrosion phenomenon. It observed that corrosion rate decreased and surface coverage area and coating efficiency increased but these results are not satisfactory. $AlPO_4$ coated metal was not corrosion free in SO_2 environment because it was further prone to corrosion. To mitigate such corrosion, DLC was used as filler on the coated surface of $AlPO_4$. The results are mentioned in Table2 showed that after DLC filler corrosion rates were highly controlled and improve surface coverage area and coating efficiency. DLC coating material enters into the porosities of $AlPO_4$ and it creates inert atmosphere for SO_2. The Plot of logK Vs. C(concentration of SO_2), θ(surface coverage area) Vs. C(concentration of SO_2), CE(coating efficiency) Vs. C(concentration of SO_2) and log(θ/1- θ) Vs. C(concentration of SO_2) without coating, with coating of AlPO4 and DLC filler were represented in Fig.1, Fig.2, Fig.3 and Fig.4. These plots indicated that it has anticorrosive characters and improved the life of base metal.

Table1: Corrosion of mild steel in SO_2 environment in without and with coating of $AlPO_4$

Seasons	Summer	Rainy	Winter	Coating Material $AlPO_4$(gm)
Concentration of SO_2 (PPM)	2.85	10.25	15.56	35
logC	0.45	1.01	1.19	
Temperature (^oC)	35	30	25	
K_o	255	507	779	
$logK_o$	2.406	2.705	2.890	
K	128	205	213	
logK	2.107	2.311	2.328	
θ	0.498	0.595	0.721	
(%)CE	49.80	59.50	72.10	
(1- θ)	0.508	0.408	0.279	
($\theta/1-\theta$)	0.980	1.458	2.584	
$log(\theta/1-\theta)$	-0.008	0.163	0.412	

Table 2: Corrosion of mild steel coated $AlPO_4$ in SO_2 environment in presence of DLC filler

Seasons	Summer	Rainy	Winter	Coating Material $AlPO_4$(gm)	DLC filler(gm)
Concentration of SO_2 (PPM)	2.85	10.25	15.56	35	25
logC	0.45	1.01	1.19		
Temperature (^oC)	35	30	25		
K_o	255	507	779		
$logK_o$	2.406	2.705	2.890		
K	82	103	121		
logK	1.913	2.012	2.082		
θ	0.678	0.796	0.844		
(%) CE	67.8	79.6	84.4		
(1- θ)	0.322	0.204	0.156		
($\theta/1-\theta$)	2.105	3.901	5.410		
$log(\theta/1-\theta)$	0.323	0.591	0.753		
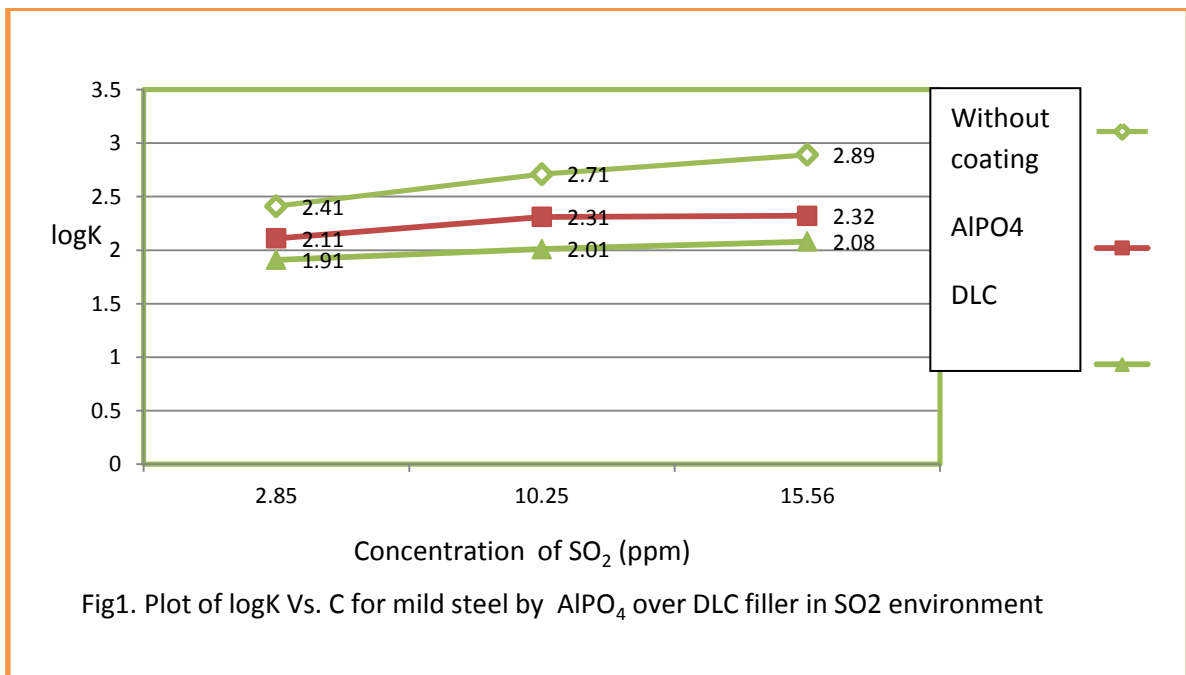
Fig1. Plot of logK Vs. C for mild steel by $AlPO_4$ over DLC filler in SO2 environment
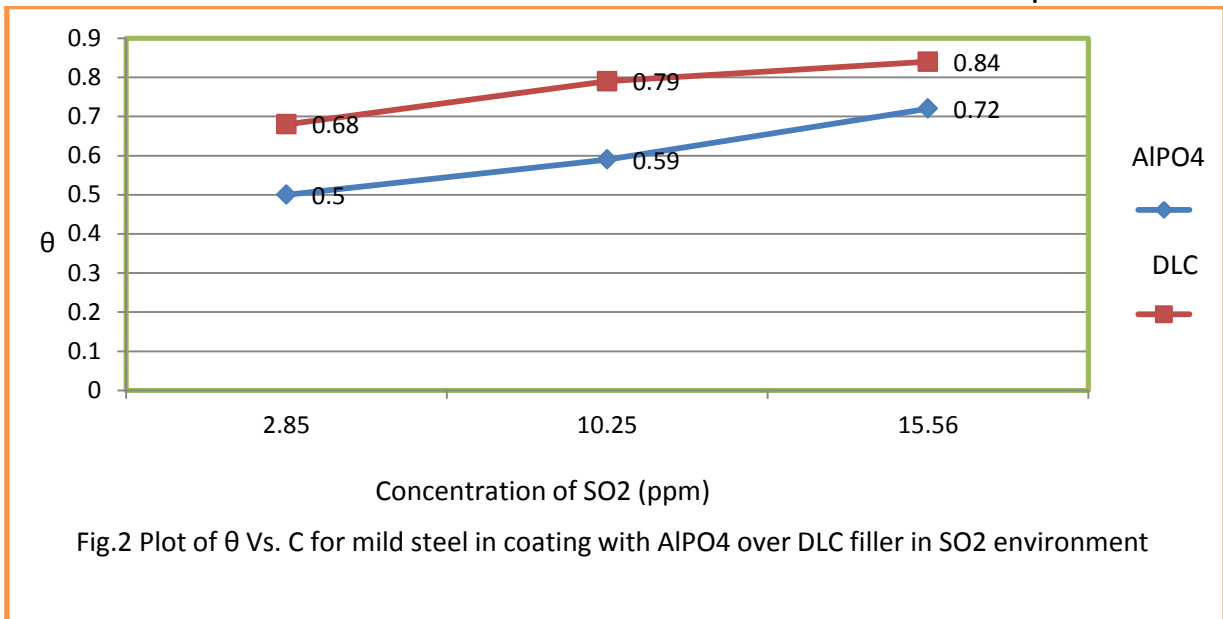
Fig.2 Plot of θ Vs. C for mild steel in coating with AlPO4 over DLC filler in SO2 environment
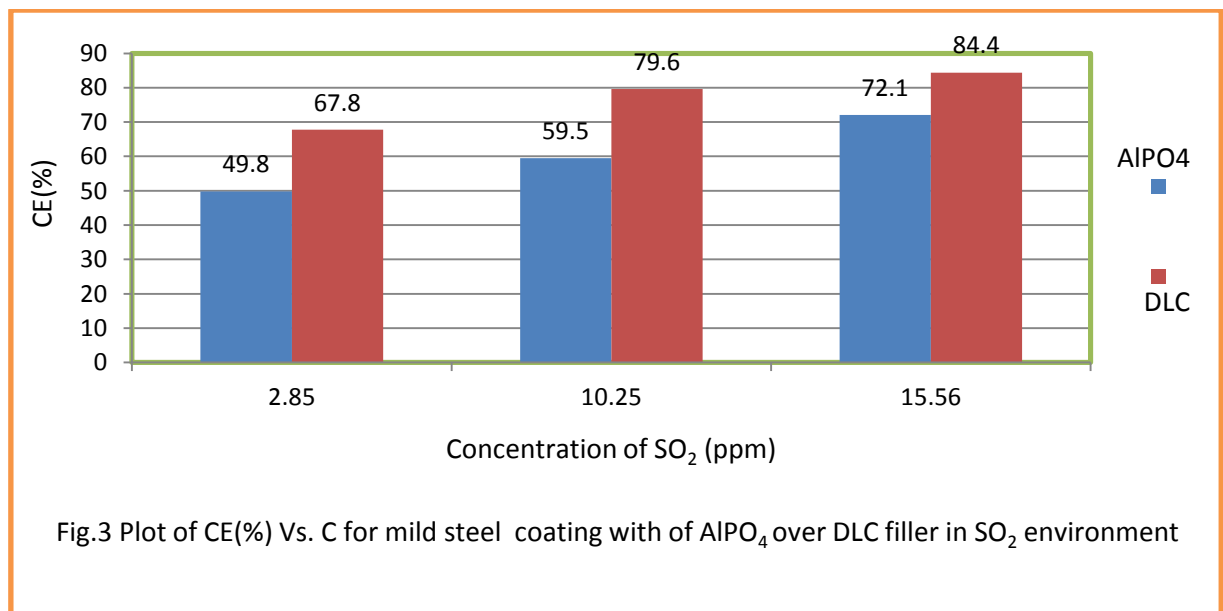

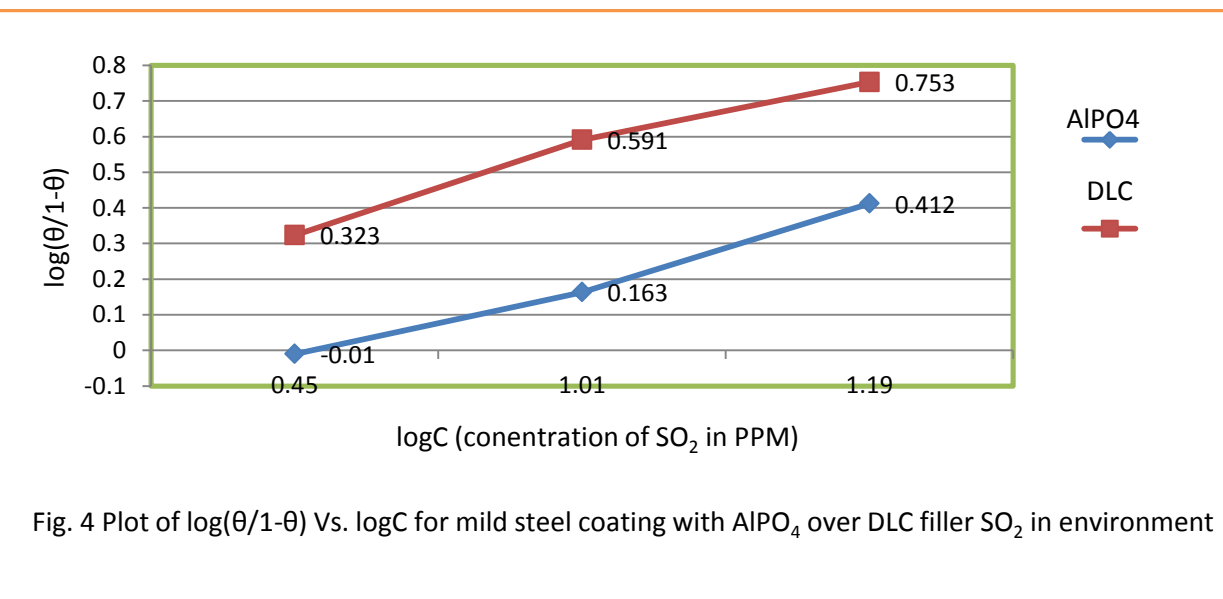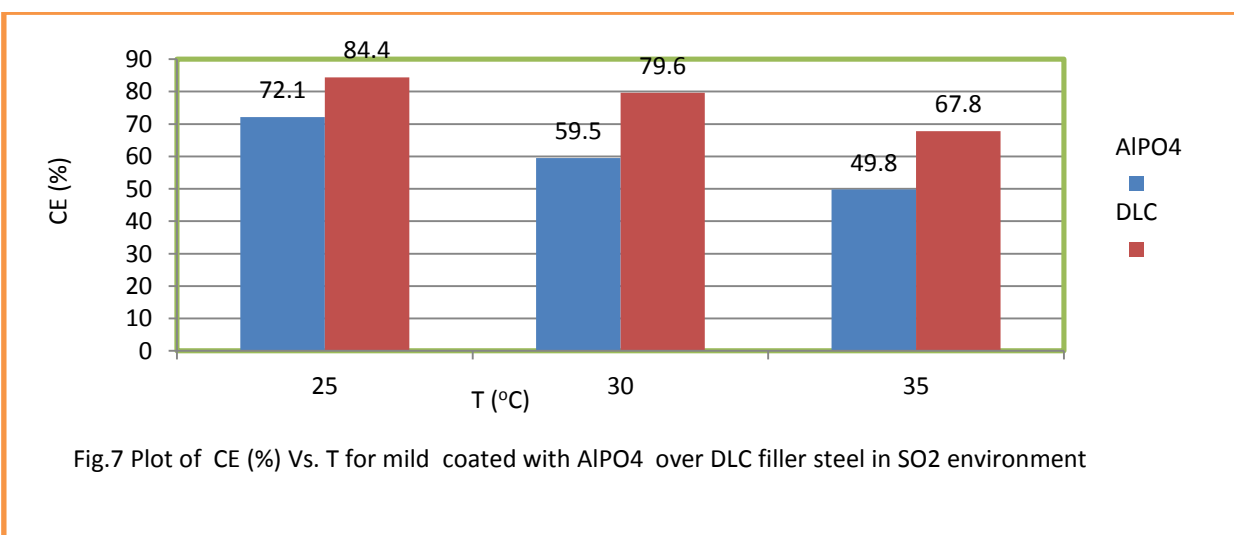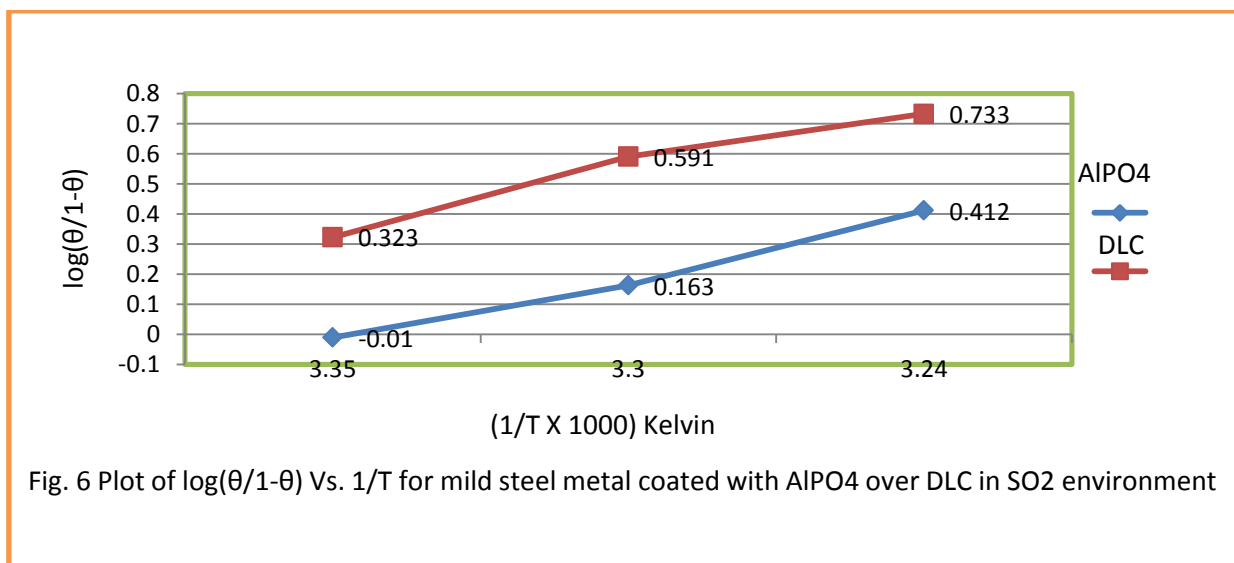Fig.3 Plot of CE(%) Vs. C for mild steel coating with of $AlPO_4$ over DLC filler in SO_2 environment

Fig. 4 Plot of log(θ/1-θ) Vs. logC for mild steel coating with $AlPO_4$ over DLC filler SO_2 in environment

SO2 concentration varies from winter to summer because atmospheric temperature will be changed. The corrosion rate, surface coverage area and coating efficiencies values were expressed in Table1 and Table2 in absence and presence of AlPO4 and DLC in different temperatures. The Table 1 and Table2 results noticed that coating and filler materials developed passive layer against SO2. The plot corrosion rate logK vs. 1/T, log (θ/1- θ) vs. 1/T and CE vs. T ware depicted in Fig.5, Fig.6 and Fig.7. The analysis of these figures exhibited that AlPO4 and DLC have good adherence properties in SO_2 environment.

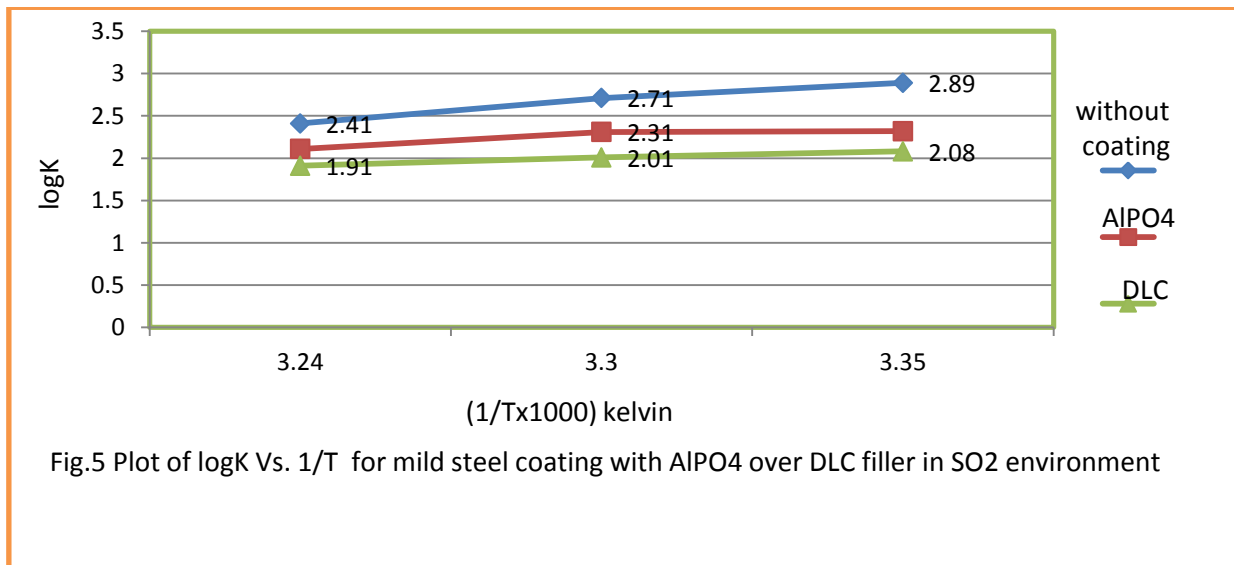Fig.5 Plot of logK Vs. 1/T for mild steel coating with AlPO4 over DLC filler in SO2 environment

Fig. 6 Plot of log(θ/1-θ) Vs. 1/T for mild steel metal coated with AlPO4 over DLC in SO2 environment

Fig.7 Plot of CE (%) Vs. T for mild coated with AlPO4 over DLC filler steel in SO2 environment

The activation energy, heat of adsorption, free energy, enthalpy and entropy were calculated by equation4, equation5, equation6 and equation7 for $AlPO_4$ and DLC in summer, rainy and winter seasons and its values were recorded in Table3 and Table4. The activation energy increased before coating and its values decreased after coating so it indicated that coating materials were effective in SO_2 environment. Heat of adsorption, free energy, enthalpy and entropy values were observed negative with $AlPO_4$ and DLC filler hence these coating and filler materials were strongly bonded with mild steel. Thermodynamical results of $AlPO_4$ and DLC were concerned 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

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

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

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

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.

Table 3: Thermodynamical values of coated $AlPO_4$ on the surface of mild steel in SO_2 environment

Seasons	Summer	Rainy	Winter
$E_a(o)(kJmol^{-1})$	179.12	170.76	154.18
$E_a(kJmol^{-1})$	144.29	145.89	135.02
$Q_{ads.} (kJmol^{-1})$	-25.53	-10.29	-0.512
$\Delta G(kJmol^{-1})$	-238.62	-241.78	-231.92
$\Delta H(kJmol^{-1})$	-101.25	-113.20	-112.18
$\Delta S(JK^{-1})$	-268.01	-276.05	-274.64

Table 4: Thermodynamical values of DLC filler on $AlPO_4$ on the surface of mild steel in SO_2 environment

Seasons	Summer	Rainy	Winter
$E_a(o)(kJmol^{-1})$	179.12	170.76	154.18
$E_a(kJmol^{-1})$	129.04	127.01	122.59
$Q_{ads.} (kJmol^{-1})$	-45.43	-37.30	-20.69
$\Delta G(kJmol^{-1})$	-223.45	-223.17	-220.21
$\Delta H(kJmol^{-1})$	-97.44	-94.33	-97.44
$\Delta S(JK^{-1})$	-416.95	-454.87	-259.45

The corrosion current density determined in the absence and presence of $AlPO_4$ and DLC with the help of equation 8 and their values are recorded in Table5.

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

where $\Delta E/\Delta I$ 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 $AlPO_4$ 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 indicated that corrosion current increased without coating and it reduced after coating and its values more decreased with DLC filler. Tafel graph was plotted in Figure8 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 and coating efficiency increased. The gravimetric results and potentiostat results were shown equality hence these coating materials were effective in SO_2 environment.

Table 5: Potentiostatic polarization of coated $AlPO_4$ and DLC filler on the surface of mild steel in SO_2 environment

$\Delta E(mV)$	ΔI	β_a	β_c	$I_{corr.}$	K	$AlPO_4(gm)$	DLC(gm)
-850	425	350	225	29.73	230	0.00	0.00
-750	275	150	250	14.90	115	25	10
-650	175	100	285	8.65	67		

Fig.8 Plot of E(mV) Vs Icorr. (mA/cm^2) for mild steel coated with $AlPO_4$ and DLC filler in SO_2 environment
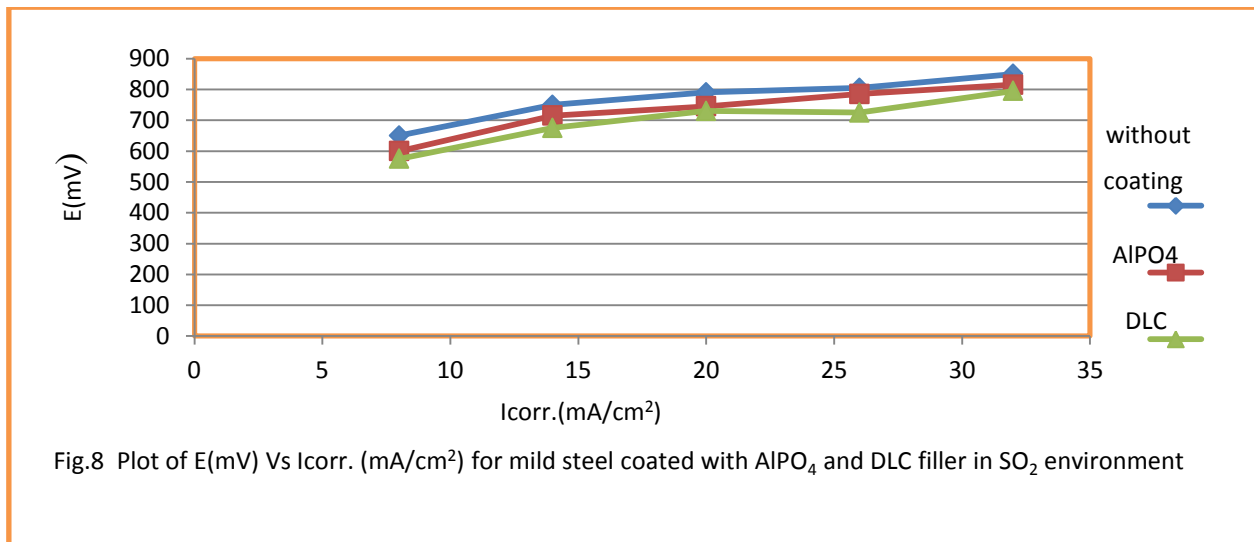
CONCLUSION

Corrosion is one of the major problems among the materials. It is impossible to fully control but it can be minimized with the application of suitable coating materials with application of filler. Mild steel is an important engineering metal which is used in different appliances of our purposes. It gets corroded badly in SO_2 environment. The corrosion protection of mild steel by nanocoating of $AlPO_4$ and DLC as a filler can be used in SO_2 corrosive environment which have highly effective anticorrosive properties. The coated metal coupons by these materials were kept into winter, rainy and summer seasons in SO_2 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 SO_2 medium.

ACKNOWLEDGEMENT

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