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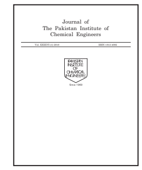

Corrosion Resistance Evaluation of Zinc Coatings on Mild Steel Substrate for Soil Applications

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Abstract

.The underground and over-ground pipelines and structures are extensively used for transporting natural gas and oil are made of expensive steel alloys. They are used in many aggressive media: sea water, soil, marine and industrial environments. Because of the presence of salt content and other atmospheric factors, the pipeline goes under severe corrosion problems. This causes pits and holes in pipe surface making it useless and causing a huge loss of money and time. This study aimed to corrosion resistance evaluation of different zinc coatings (cold galvanized and zinc electroplating) on mild steel substrate for soil applications. Two types of coatings were deposited on mild steel substrate cold galvanized zinc coatings and industrial grade electroplated zinc coating. Cold galvanized zinc coatings were applied on substrate using two methods; brushing and dipping. Corrosion behavior of the zinc coated and uncoated mild steel samples was assessed in prepared soil by open circuit potential (OCP) and Electrochemical impedance spectroscopy (EIS) at 0 and 24hours. The EIS study revealed that all types of zinc coatings have barrier properties in prepared soil. Cyclic polarization revealed that cold galvanized zinc coating produced by brushing was highly susceptibility to pitting. Cold galvanized dipped coating behaved well in the electrochemical testing and proved to be the best coating in prepared soil. The high coating thickness, uniform coating over substrate and low surface roughness were the main factor contributed towards its better corrosion resistance than the other coatings in prepared soil.

***Keywords**: Cold Galvanizing, Epoxy Zinc Coating, Electrochemical Impedance Spectroscopy (EIS), Open* circuit potential (OCP)

1. Introduction:

Mild steel is a major constructional material and extensively used in underground gas and oil pipelines and in chemical as well as allied industries for solution handling [1]. The corrosion of galvanized steel is a very complex process that involves several electrochemical and physical mechanisms [2]. Coatings on its own cannot protect steel as they have pin holes, porosity, defects during application. Zinc rich paints are most effective in corrosion protection of steel and a suitable alternative of these coatings [3]. Soil is a highly inhomogeneous environment which subject the galvanized steel to a lot of corrosion risks which are enhanced by aggressiveness of soil depending upon its pH, resistivity, moisture content, temperature, oxygen availability and soluble salt concentration [4].

In soil environment the corrosion risk to mild steel are reduced and the substrate is protected by the

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application of zinc as sacrificial protective coatings which are produced by several methods like electroplating, hot dipping or spray. These metallic coatings oxidized to a depth of 100 A° forming a layer of zinc oxide and thereby reduced the corrosion rate [5]. These coatings on its own cannot provide full protection as they have defects like porosity and pin holes and upon chemical damage give a direct pathway to corrosion species to reach the substrate and spoil their corrosion resistance properties. On this argument zinc rich paint are the best alternative of these coatings in soil environment as they offer dual protection to substrate [6]. Zinc rich paints offers sacrificial protection at first even after a slight mechanical damage and after that a compact barrier layer of insoluble corrosion product gives barrier protection from corrosion [7]. A general description of zinc rich paints is that zinc dust (spherical, lamellar or combination of both) is dispersed in saponification resistant organic (usually epoxies) or inorganic binder (usually orthosilicates) [8].

Electrochemical impedance spectroscopy (EIS) scans have been used for over 40 years to measure the properties of coated panels and to study the corrosion protection mechanism of organic coatings [9, 10]. In this work zinc rich paint namely cold galvanizing paint is applied on mild steel substrate by different methods. The corrosion behavior of zinc rich cold galvanizing is compared with zinc electroplating in a soil medium. The corrosion protection mechanism is analyzed by EIS and open circuit potential while the susceptibility to pitting corrosion is checked by cyclic polarization test.

2. Experimental Procedure

The substrate material used in this experimental work was cold rolled mild steel (ASTM-1020). The substrate samples having dimension 6in x 3in x 0.12in were prepared for coatings application. The samples were cleaned using bench grinder to remove any loose rust, contaminations and greases. Two kinds of coatings were produced; cold galvanized zinc coating using zinc rich epoxy manufactured by Shanghai Roval Zinc Rich Paint Corporation, China and zinc electroplated coating at a local industry in Lahore. Cold galvanized coating was applied on the substrate by using two methods; brushing and dipping. The thickness of coated samples was measured using Elcometer 3236 instrument and optical microscopy. The roughness values (Ra) for all of the coated samples were measured using contact profilometer.

Corrosion resistance of the coated samples was evaluated using Potentiostate (Gamry instrument IFC100-10181) in prepared soil with composition given in **Table 1.** The comparative corrosion behavior of coated and uncoated mild steel samples was assessed by open circuit potential, electrochemical impedance spectroscopy and cyclic polarization conducted at 0 and 24 hours. A three cell electrode was prepared, coated specimen as a working electrode, $Cu/CuSO_4$ as a reference electrode and graphite cylinder electrode as a counter electrode. Electrochemical impedance spectroscopy measurement was monitored against the exposure time within frequency range of 100 kHz to 0.01 Hz. Open circuit potential was recorded as a function of exposure time being buried in the soil. Cyclic polarization measurements were conducted at a potential range of -0.3 mV to 1 mV.

The abbreviation used to describe different types of coatings in this paper are as follow;

CGD is for cold galvanized dipped coating, CGB is for cold galvanized brushed coating and ZnE for zinc coating by electroplating whereas MS is for mild steel substrate.

Table 1: Composition of prepared soil

Description		Composition
pH of the soil paste		8.0
Sodium Adsorption ratio S.A.R		5.3
Saturation %age		41
Soluble Cations mg/l	Ca + Mg	3.5
	Na	7.0
	K	0
Soluble Anions mg/l	CO_2	-
	HCO_3	2.0
	Cl^-	1.25
	SO_4	7.25
Sand % age 1-2 mm		1.0
Sand % age 0.05-1 mm		5.7
Silt % age		67.3
Clay % age		26.0

3. Results and Discussion

3.1 Coating Characterization

Coating characterization work includes its topography, roughness and thickness evaluation for all samples.

3.1.1 Coating Topography

Optical microscopic images of different zinc coating surfaces produced by electroplating technique and cold galvanize technique (dipped and brushed) are shown in Figure 1.

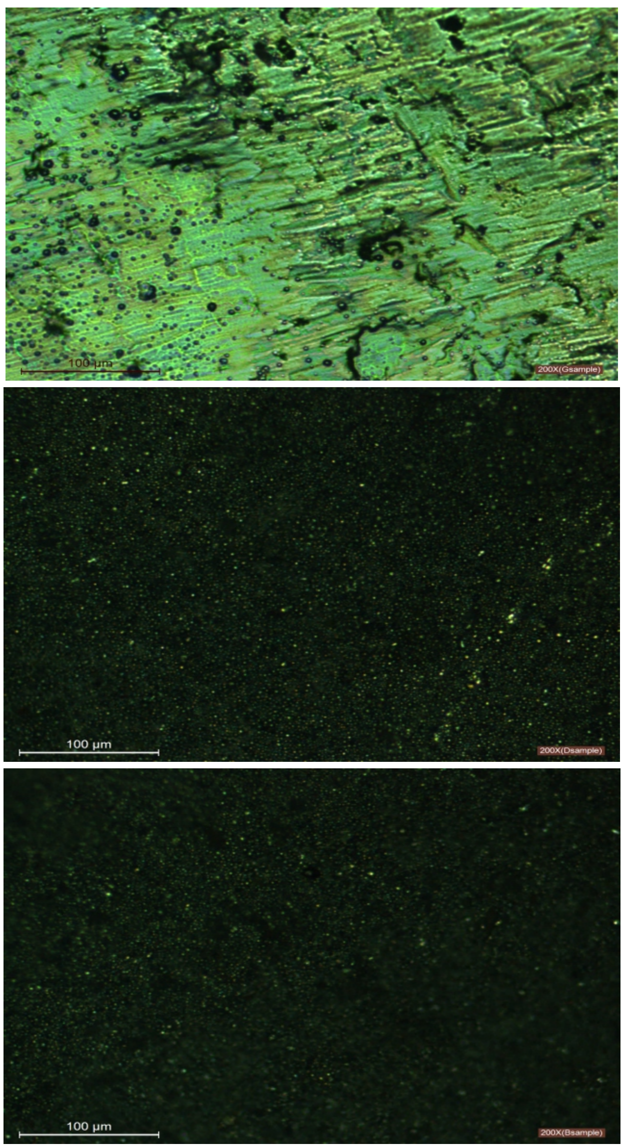

Figure 1: *Optical microscopic images of different zinc coating surfaces (A) Zn electroplated coating sample (B) Cold galvanized brushed sample (C) Cold* galvanized dipped

3.1.2 Coating Roughness

The coating roughness values (Ra) for zinc coating produce by electroplating was measured as 0.45µm whereas for cold galvanized coatings produced by brushing and dipping methods were 1.15 µm and 0.8 µm respectively. The lowest surface roughness of Zn coating produced by electroplating is due to its smoother surface which is also confirmed from the optical microscopic image (Figure 1A).

3.1.3 Coating Thickness

Coating's thickness measurement using Elcometer for Cold galvanized zinc coatings produced by brushing and dipping were measured as 37.3 µm and 171.7 µm respectively.

The average coating thickness measurements using optical microcopy for zinc coating produced by electroplating was 16.2 µm whereas for cold galvanizing zinc coatings produce by brushing and dipping were 49.4 µm , 161 µm respectively.

3.2 Open Circuit Potential (OCP)

Figure 2 shows the OCP of all the coatings and mild steel in prepared soil at 0hr immersion. The open circuit potential of MS substrate was -0.535 V vs $Cu/CuSO_4$ whereas its value for ZnE, CGD and CGB coatings over substrate were -1.061, -0.784 and -0.951 V vs $Cu/CuSO_4$ respectively in prepared soil at 0hr of immersion. In soil, the OCP of all the coatings is on the more active side than MS substrate. Which clearly indicate that all types of coatings will protect MS substrate. This means that coatings will show a sacrificial behavior in soil.

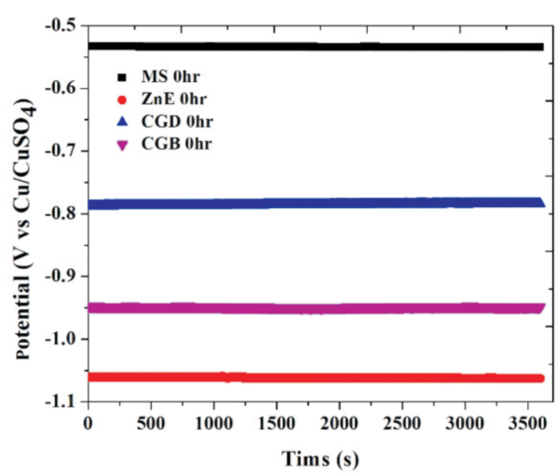

Figure 2: *Open circuit potential of MS, ZnE, CGD and CGB in prepared soil at 0hr*

The ZnE coating has the maximum potential difference of -0.52 V vs $Cu/CuSO_4$ with MS substrate than CGD -0.24 V vs $Cu/CuSO_4$ and CGB 0.41 V vs $Cu/CuSO_4$. This shows that the delamination of ZnE coating will occur more quickly than CGB and CGD coatings. In comparison of CGD and CGB coatings the earlier have potential difference of -0.24 V vs $Cu/CuSO_4$ and later have -0.41 V vs $Cu/CuSO_4$ which is higher than CGD. These results indicate that CGD will protect the MS substrate better than the other coatings and thus sacrifice itself slowly.

Figure 3 shows the OCP of coatings after 24hr of immersion in prepared soil. The OCP of CGD, CGB and ZnE were -0.770, -0.840 and -1.055 volts vs $Cu/CuSO_4$ respectively. It is clear from the results of OCP after 24hr of immersion that the potential have shifted toward noble side for all coatings. This is because after 24hr soil evaporates its moisture and its conductivity decreased. Therefore, coatings still have the same trend as at 0hr. ZnE has maximum potential difference of -0.52 $Cu/CuSO_4$ with mild steel substrate than CGD -0.23 $Cu/CuSO_4$ and CGB -0.30 $Cu/CuSO_4$. After 24hr immersion CGD still have minimum potential difference with MS substrate thus giving a longer sacrificial protection than CGB and CGD.

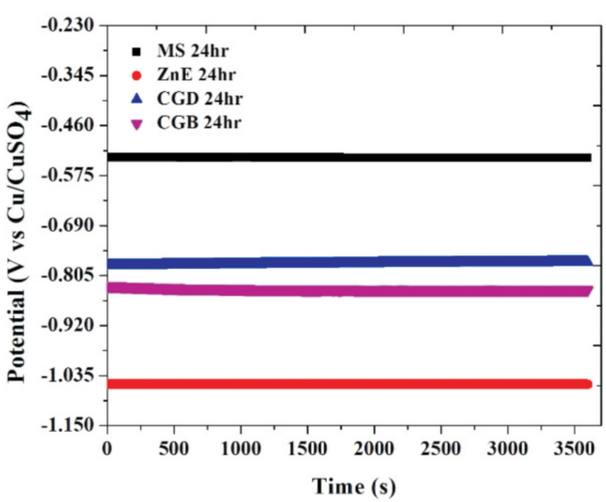

Figure 3: Open circuit potential of MS, ZnE, CGD and CGB in prepared soil at 24hr

3.3 Electrochemical Impedance Spectroscopy:

Figure 4 shows Nyquist diagram of Zn coating by electroplating in prepared soil at 0hr and 24 hr. The coating shows similar trend at 0hr and 24hr of immersion and results in complete semi-circles.

This is showing barrier properties of ZnE coating in prepared soil. Further, these semi-circles indicate the formation of smooth barrier layer on the coating and semi-electrolyte interface. The reason of shifting the semi-circle to the greater corrosion resistance value after 24hr of immersion is its barrier properties has enhanced. It is also clear from the radius of semi-circle that after 24hr of immersion its radius increased which shows the barrier properties has also increased. The enhanced barrier properties are due to the formation of zinc corrosion product likely to be zinc chloride. The results also confirmed the increase in polarization resistance from 455.60 $Ohm.cm^2$ at 0hr of immersion to 522.37 $Ohm.cm^2$ at 24hr of immersion.

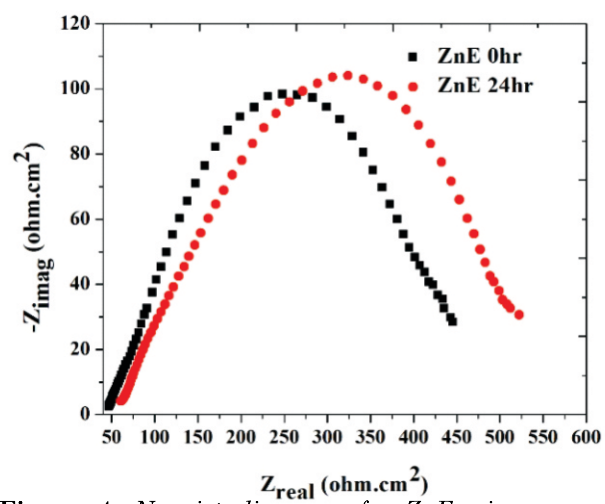

Figure 4: *Nyquist diagrams for ZnE in prepared soil in prepared soil after 0hr & 24hr*

However, The Nyquist diagram of CGB coating at 0hr and 24hr of immersion in prepared soil showed an abrupt behavior and this kind of behavior is usually linked with the high surface roughness and non-uniform thickness of these kind of coatings.

Figure 5 shows the Nyquist diagram of CGD coating at 0hr of immersion and 24hr of immersion in prepared soil. The results indicate complete semi-circles at 0hr and 24hr of immersion in prepared soil. This is due to the formation of a stable barrier layer on the semi-electrolyte and coating interface. Formation of complete semi-circle indicates the capacitive nature of coating at 0hr and 24hr of immersion in prepared soil. It shows that this coating protect the mild steel substrate due to the presence of barrier layer. After 24hr of immersion its barrier properties has enhanced as the radius of semi-circle is large than the radius of semi-circle at 0hr of immersion. The reason of these enhanced properties is the formation of zinc corrosion product. It is also indicated that the polarization resistance value increased from 895.6 $Ohm.cm^2$ at 0hr of immersion to 1039.6 $Ohm.cm^2$ after 24hr of immersion.

Based on EIS results, CGD coating proved to be better coating in prepared soil at 0hr and 24hr immersion due to large semi-circle radii. The large polarization resistance values of this coating compared with other coatings further confirm this. This coating have a good compact barrier layer due to smooth coating surface and uniform coating layer.

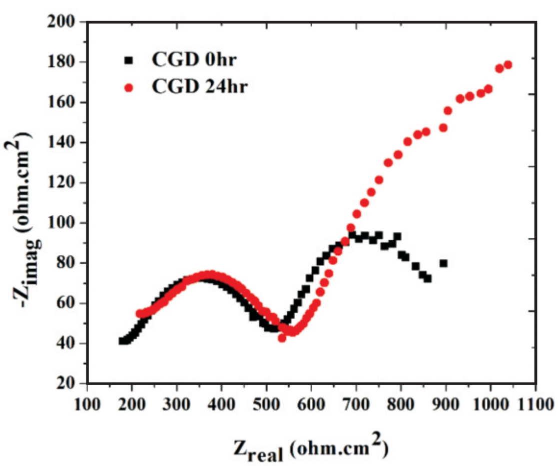

Figure 5: Nyquist diagrams for CGD in prepared soil after 0hr & 24hr

3.4 Cyclic Polarization

Figure 6 shows the comparison of cyclic polarization curves for MS substrate and all the coatings in prepared soil after 24hr of immersion. The cyclic polarization curve for MS substrate shows a large positive loop in soil and thus highly suspected to pitting. Breakdown potential (E_b) is -0.542 V vs $Cu/CuSO_4$ and corrosion potential -0.550 V vs $Cu/CuSO_4$ values are almost same. It means that immediately after the corrosion potential (E_{corr}) the pits will be initiated. Reverse scan cut the forward scan at a potential of -0.484 V vs $Cu/CuSO_4$ which is the re-passivation potential E_{rp}. In case of CGD and ZnE cyclic polarization curves, the current density decreased in reverse scan and moved from the left side of forward scan making a negative loop. So these coatings are not suspected to pitting corrosion after 24hr of immersion in prepared soil.

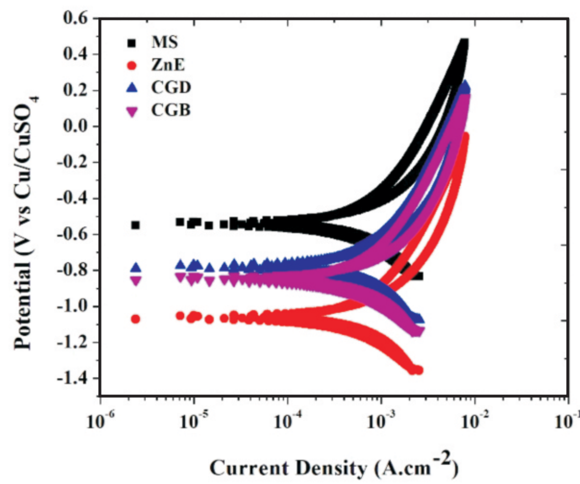

Figure 6: Comparison of Cyclic polarization curves in prepared soil

In case of CGB cyclic polarization curves, the current density is increased in reverse scan and moved from the right side of the forward scan making a positive loop and hence suspected to pitting corrosion. The reason of the pitting corrosion susceptibility in CGB was due to high surface roughness and non-uniform coating thickness of the coating. Open circuit potential and EIS also confirmed the results obtained from cyclic polarization curves.

4. Conclusions

Open circuit potential (OCP) of all the coatings are on more active side than the mild steel substrate indicating sacrificial behavior of these coatings. Dipped cold galvanized coating behaves well because of its less potential difference with mild steel substrate,. Electrochemical impedance spectroscopy results showed better barrier properties of dipped cold galvanized coating than the other types of coatings. Cyclic Polarization curves indicate that cold galvanized coating produce by brushing is highly susceptibility to pitting. The high coating thickness, uniform coating over substrate and low surface roughness are the main factor contributing towards the better corrosion resistance of dipped galvanized coating in prepared soil.

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