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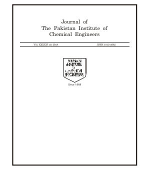

Corrosion Resistance Evaluation of Zinc Coatings on Mild Steel Substrate for Marine Applications

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Abstract

Steels are the most important structural materials and their corrosion problems must be considered during industrial and marine applications. Corrosion protection of over-ground and underground structures by protective coatings is one of the most proven methods. Zinc rich coatings are being used by many industries for the corrosion protection of steel substrates. This study looked at corrosion resistance evaluation of different zinc coatings (cold galvanized and zinc electroplating) on mild steel substrates for marine applications. Cold galvanized zinc coating was applied by two methods; brushing and dipping. Electrochemical techniques were utilized to assess the corrosion resistance of different zinc rich coatings in medium of 3.5%w/v NaCl solution. The tests were done at 0 hour exposure and 24 hours exposure in 3.5% NaCl solution as a corrosive medium. Salt spray test was also employed to get the corrosion resistance comparison of the coatings carried out for 500 hours. Open circuit potential revealed that all the zinc rich coatings were sacrificial in nature. Electrochemical impedance spectroscopy also revealed that their corrosion resistance increased after 24 hours of exposure in 3.5% NaCl solution due to the formation of corrosion product. Pitting susceptibility of coatings was also evaluated by cyclic polarization. The visual inspection of salt spray samples clarify the results of electrochemical testing by showing most of the white rust as corrosion product. The results of both electrochemical and salt spray testing indicated, cold galvanized zinc coating applied by dipping as the best coating for marine applications.

***Keywords**: Cold Galvanizing, Epoxy Zinc Coating, Electrochemical Impedance Spectroscopy, Marine Applications, Open circuit potential*

1. Introduction:

Steels are the most important and major structural material in the world, extensively used in construction, automobile, chemical and allied industries for solution handling. Application of coatings and paints for corrosion protection are most widely used methods [1, 2].

Subsea pipelines are one of the most economic and reliable means of transporting hydrocarbons. However, in remote areas, they may be susceptible to leakage and rupture due to unavoidable factors [3]. Corrosion threat to the Pakistan's industrial infrastructure is an economic and engineering problem, while the cost of the coatings is a small fraction of the entire cost of the project. All the paints and coatings protect the substrate by different manners influenced by several factors and can be summarized in three ways; physical barrier (hindering diffusion pathways of water and oxygen

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to the substrate), chemical inhibition and electric resistance. Zinc is a typical metal pigment which was first demonstrated for steel protection in 1742 and now widely used in anti-corrosion coatings [4, 5]. Zinc is more electronegative than the steel thus when in contact with steel in the presence of electrolyte, it interrupts the normal corrosion process of steel by donating its electrons to prevent steel from losing its electrons. Thus, zinc sacrifices itself in order to protect steel from corroding. [6] The corrosion of galvanized steel is a very complex process that involves several electrochemical and physical mechanisms. Coatings on its own cannot protect steel as they have pin holes, porosity, defects during application. Zinc rich coatings are being used by many industries for the corrosion protection of steel substrates. Zinc rich paints are most effective in corrosion protection of steel and a suitable alternative of these coatings. [7]. These zinc rich paints are used in different corrosive environment like seawater, marine and industrial atmosphere as they protect the steel substrate when it is mechanically damaged. At the beginning of immersion the zinc rich paints give sacrificial cathodic protection to steel due to the high zinc content in dry film which is electrically connected to the substrate. For this protection to occur zinc particles must touch each other and the steel substrate providing electrical contact; as particles are consumed the protection is reduced until all the zinc is consumed or electrical continuity is lost. After the sacrificial galvanic protection the zinc rich paints offers a long term barrier protection due to the formation of zinc corrosion product. [8,9]. Recent research in zinc coatings for marine applications is more focused towards using thermally sprayed zinc coatings and alloys. This is because thermally sprayed zinc coatings offer both barrier and sacrificial corrosion protection mechanisms. [10]. Thus resulted in extended service life of components as compared with organic coatings. Zn, Al and Zn-Al thermally sprayed coatings for protection of mild steel were studied by a number of researcher for marine applications [11, 12].

Study of corrosion mechanism and the evaluation of protective properties of organic coatings is done by electrochemical impedance spectroscopy [2]. Using electrochemical impedance spectroscopy, one can measure the impedance of a system as a function of frequency due to applied A.C wave. The data is represented either as Nyquist plot or bode plot. In Nyquist plot the real impedance on x-axis is plotted against imaginary impedance on y-axis and pure capacitance coating gives a single complete semicircle. While in bode plot modulus of impedance and phase angle are plotted as a function of frequency and a straight line with unit negative slope is shown for a highly barrier coating indicating capacitive behavior. Cyclic polarization tells about the susceptibility to pitting corrosion [13]. Salt spray test is carried out to visually inspect the effect of corrosion on coated samples. [14]

2. Experimental Procedure

2.1 Material and Sample Preparation

The substrate material used in this this study was cold rolled mild steel (ASTM 1020) that was cut into panels of dimension 6in x 3in x 0.12in. Prior to coating application, the substrate surface was cleaned from greases, oil and loose rust using bench top wheel. Two types of zinc coatings; cold galvanized and electroplated zinc were deposited on the mild substrate. The cold galvanized zinc coatings were produced by using commercial zinc epoxy resin (with 96% Zinc content in epoxy) manufactured by Shanghai Roval Zinc Rich Paint Corporation, China. Cold galvanized zinc coating was applied on the substrate using brushing and dipping techniques. The industrial grade zinc electroplated coated were deposited at a local industry in Lahore. The cold galvanized zinc coated samples were kept in a dust free room for 15-20 minutes at ambient temperature to dry. The coating thickness was measured using Elcometer 3236 instrument and optical microscopy. The surface roughness was measured using Profilometer Mitutoyo SJ-201

2.2 Electrochemical Testing in sea water and Salt Spray Test

Electrochemical measurements were carried out for coated and uncoated samples using a potentiostat (Gamry instrument IFC100-10181) in sea water (3.5% NaCl solution). 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. This consisted of a coated specimen as a working electrode, Ag/AgCl as a reference electrode and graphite cylinder electrode as a counter electrode. The Ag/AgCl reference electrode was used in 3.5% NaCl solution. Electrochemical impedance spectroscopy measurement was monitored against the exposure time in frequency range of 100 kHz to 0.01 Hz. Open circuit potential was recorded as a function of exposure time while immersing in 3.5% NaCl. Cyclic polarization measurements were taken at a potential range of -0.3 mV to 1 mV. Salt spray testing was carried out as per ASTM B-117 standard test protocol using SF-100 salt spray apparatus. Specimens were placed in salt spray chamber at an angle of 30° parallel to the flow of fog throw in the chamber. The test solution was 5 ± 1 parts by mass of sodium chloride (NaCl) and 95 parts of water. The pH of the solution was 6.85 at temperature of 35°C. Specimens were exposed in salt spray chamber for 500 hours. After the test, all of the coated samples were inspected visually and their images were taken using digital camera.

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.

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 coating surface of samples produced by electroplating technique and cold galvanize technique (dipped and brushed) are shown in Figure1.

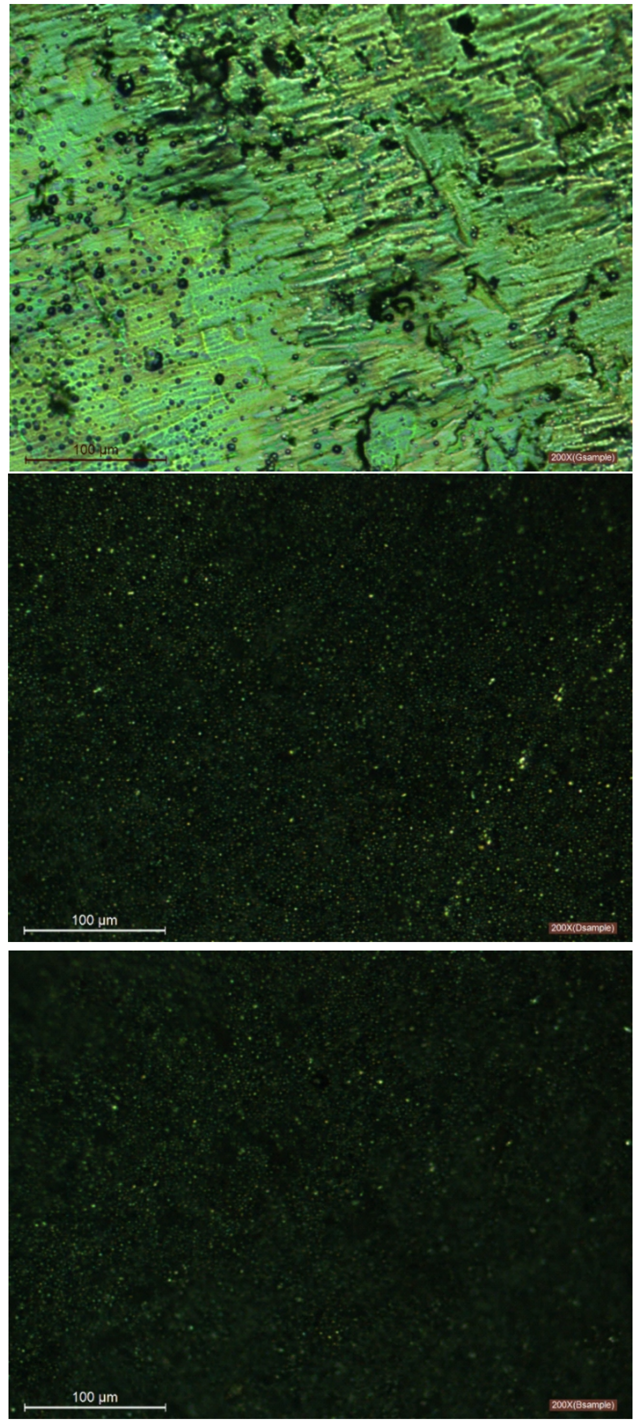


Figure 1: Optical microscopic images of different zinc coating surfaces (A) Zn electroplated coating sample (B) Cold galvanized brushed sample (C) Cold galvanized dipped.

3.1.2 Coating Roughness

The coating roughness values (Ra) for zinc coating produced 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 measurement using optical microcopy for zinc coating produced by electroplating was 16.2 μm. Whereas, for cold galvanizing zinc coatings produced by brushing and dipping had an average measurement of 49.4 μm, 161 μm respectively.

4. Electrochemical Testing

4.1 Open Circuit Potential

Open circuit potential is used to describe the electrochemical properties of coatings in contact with the substrate. Figure 2 shows the open circuit potential (OCP) of all coatings in comparison with mild steel substrate in 3.5% NaCl solutions at 0hr of immersion. The coatings offer sacrificial cathodic protection until their open circuit potential remains lower than the OCP of the mild steel substrate and thus protect mild steel substrate. The OCP of mild steel substrate is -0.693 V vs Ag/AgCl whereas its values for ZnE, CGD and CGB coated samples are -1.009 V, -0.961 V and -0.989 V vs Ag/AgCl respectively in 3.5% NaCl solution at 0hrs of immersion. It is clearly presenting that the potential of coatings is on the more active side than MS substrate and coatings and that their behavior is sacrificial in nature. In case of any mechanical damage and exposure of substrate to seawater the coating will sacrifice itself first. For good sacrificial coatings the potential difference between the MS substrate and coating should be small. When the potential difference is large the coating will sacrifice quickly and tend to delaminate.

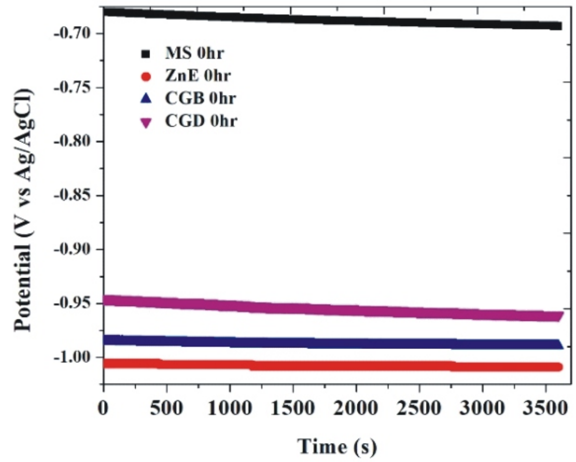


Figure 2: *Open circuit potential of MS, ZnE, CGD and CGB in 3.5% NaCl solution at 0hr.*

Figure 2 shows maximum potential difference of -0.316 V vs Ag/AgCl between MS substrate and ZnE coating and hence it will delaminate and sacrifice more quickly than CGD and CGB coatings in sea water. CGD is a better coating than CGB in sea water because of less potential difference of -0.268 V vs Ag/AgCl than CGB of -0.296 V vs Ag/AgCl.

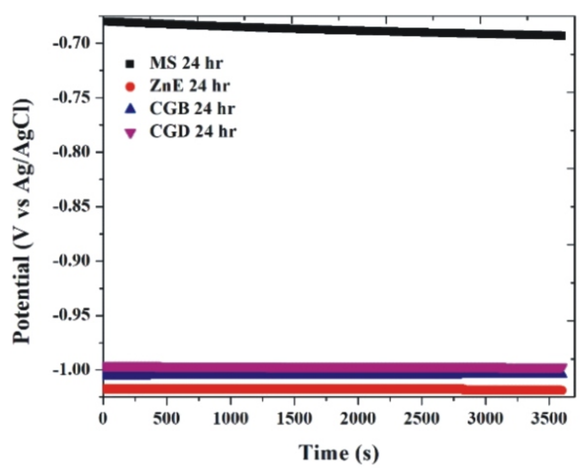


Figure 3: *Open circuit potential of MS, ZnE, CGD and CGB in 3.5% NaCl solution at 24hrs.*

Figure 3 shows the open circuit potential of MS substrate as well as ZnE, CGD, and CGB coatings in 3.5% NaCl solution (sea water) after 24hrs of immersion. After 24hrs, the potential of all coatings has shifted towards the more active side. The OCP of CGD, CGB and ZnE is -0.364, -0.015, and -0.010 volts vs Ag/AgCl respectively. All coatings after 24hrs are sacrificing quickly and tend to delaminate. ZnE has maximum potential difference of -0.326 V vs Ag/AgCl with MS substrate than the CGB -0.321 V vs Ag/AgCl and CGD -0.304 V vs Ag/AgCl. After 24hrs of immersion in the sea CGD still has minimum potential difference with MS substrate thus giving a longer sacrificial protection than CGB and CGD.

4.2 Electrochemical Impedance Spectroscopy

Figure 4 and Figure 5 shows the Nyquist plot of EIS for all the coatings in 3.5% NaCl solution at 0hr and 24 hours of immersion. A half semi-circle within the Nyquist diagram indicates dissolution of the metal whereas the radius of the semi-circle shows its corrosion resistance. Figure 4 shows a larger radius of half semi-circle of bare MS substrate than all of the coatings indicating that it will corrode faster and has no corrosion resistance in 3.5% NaCl solution even at 0hrs of immersion. A protective coating which forms a complete semi-circle shows pure capacitive behavior due to the formation of a good Helmoltz double layer on the coating electrolyte interface. Figure 4 shows barrier properties of ZnE coating in prepared sea water at 0hrs and thus it will protect MS substrate. The value of polarization resistance ZnE coating at 0hrs of immersion is 433.9 $Ohm.m^{-2}$. Figure 5 shows the semi-circle of ZnE at 24hrs of immersion. It can be clearly seen that the radius of semi-circle after 24hrs of immersion is decreased as compared to its radius at 0hrs of immersion. This indicates that the coating shows sacrificial behavior to protect MS substrate at 24hrs. It is clear from the Figure 5 that the semi-circle is not perfect after 24hrs of immersion unlike at 0hrs of immersion. This is because the electrolyte is trying to ingress inside the coating and coating is being sacrificed. The value of polarization resistance of the ZnE coating at 24hrs of immersion is 200.5 $Ohm.m^{-2}$ which is half of its value at 0hrs of immersion. It means after 24hrs of immersion the ZnE coating has less corrosion resistance and is thus protecting the substrate by sacrificing itself.

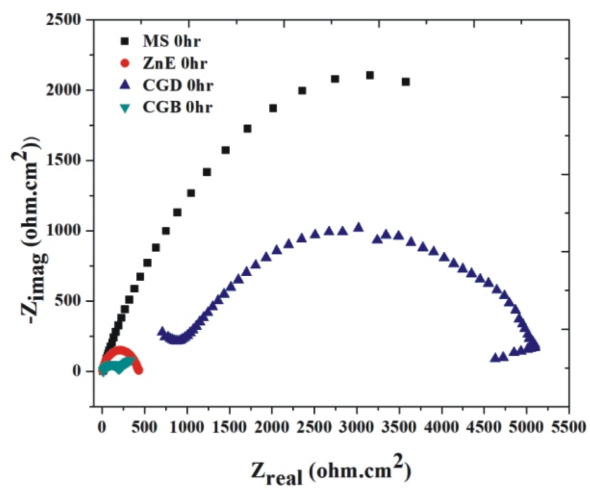


Figure 4: *Nyquist diagrams for MS.SW, ZnE.SW, CGD.SW, and CGB.SW while immersing in 3.5% NaCl Solution after 0hrs*

CGB coating at 0hr of immersion in seawater in Figure 4 shows two times constant in its EIS and there are two capacitive semi-circles are to be found in the same test condition. The EIS interpretation of zinc rich paints may have two or three times constant which indicate there sacrificial behavior [15]. The high frequency range present on the right side of in Nyquist diagram shows the barrier layer properties of the coating while the low frequency range on the right side of Nyquist diagram shows the corrosion reaction of the metal coating system. The straight line going up shows that the coating is dissoluting itself and protecting the substrate and the polarization resistance value at 0hr of immersion is 335 $Ohm.cm^2$. This polarization resistance value is less than mild steel and as it is clear from the graph that this lies below the half semi-circle of mild steel. Figure 5 shows CGB coating after 24hr of immersion and still it forms two times constant and there are two semi-circle. After 24hrs of immersion the CGB coating shows that the first semi-circle present on the high frequency range of Nyquist diagram indicating barrier properties of the coating, has increased its radius than the semi-circle on the high frequency side at 0hr of immersion. This is also clear from the polarization resistance value at 24hr of immersion (381.1 $Ohm.cm^2$), which is increased and the reason is the formation of a little corrosion product.

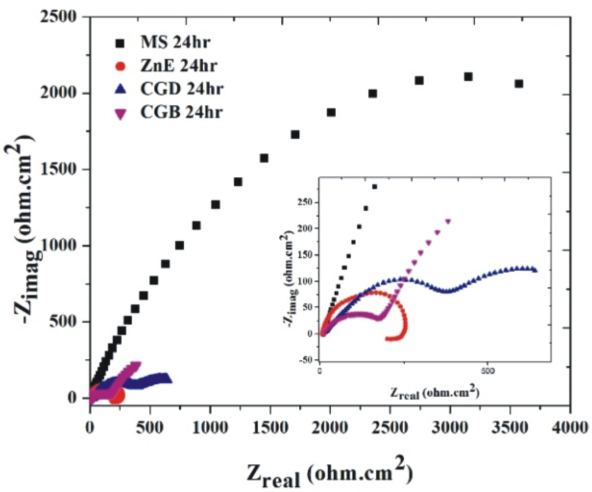


Figure 5: *Nyquist diagrams for MS., ZnE, CGD and CGB while immersing in 3.5% NaCl Solution after 24hrs*

Figure 4 shows CGD coatings at 0hrs of immersion in 3.5% NaCl solution. The EIS curve for CGD starts at large resistance values than ZnE and CGB. This is also evident from the graph that CGD has larger radius than the combined radius of ZnE and CGB and more polarization resistance than mild steel substrate. The reason is that CGD has more thickness and did not allow electrolyte to ingress in it and to reach the substrate at 0hr of immersion, however some imperfections at start and last of semi-circle show disturbed and broken Helmholtz double layer.

CGD coating at 24hr of immersion in 3.5% NaCl solution clearly shows the formation of two time constant which indicates the sacrifice behavior of this coating. The combined radius for CGD is larger than the ZnE and CGB describes that it will not delaminate and gives long term sacrificial protection as it evident from OCP results of small potential difference with the mild steel substrate than others.

CGD coatings in comparison with Zn electroplated coatings and CGB coatings, are more corrosion resistant and have good sacrificial properties at 0hrs of immersion. After 24hrs of immersion, dipped coatings are till a better sacrificial coating with good corrosion resistance as clear from Figure 5.

These results are also proved from the open circuit potential which shows that dipped coatings are sacrificial in nature but have less potential difference than MS substrate giving them long term sacrificial protection.

Cyclic Polarization

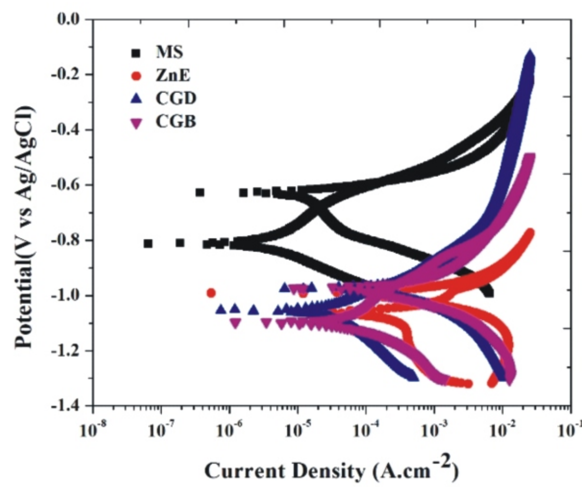
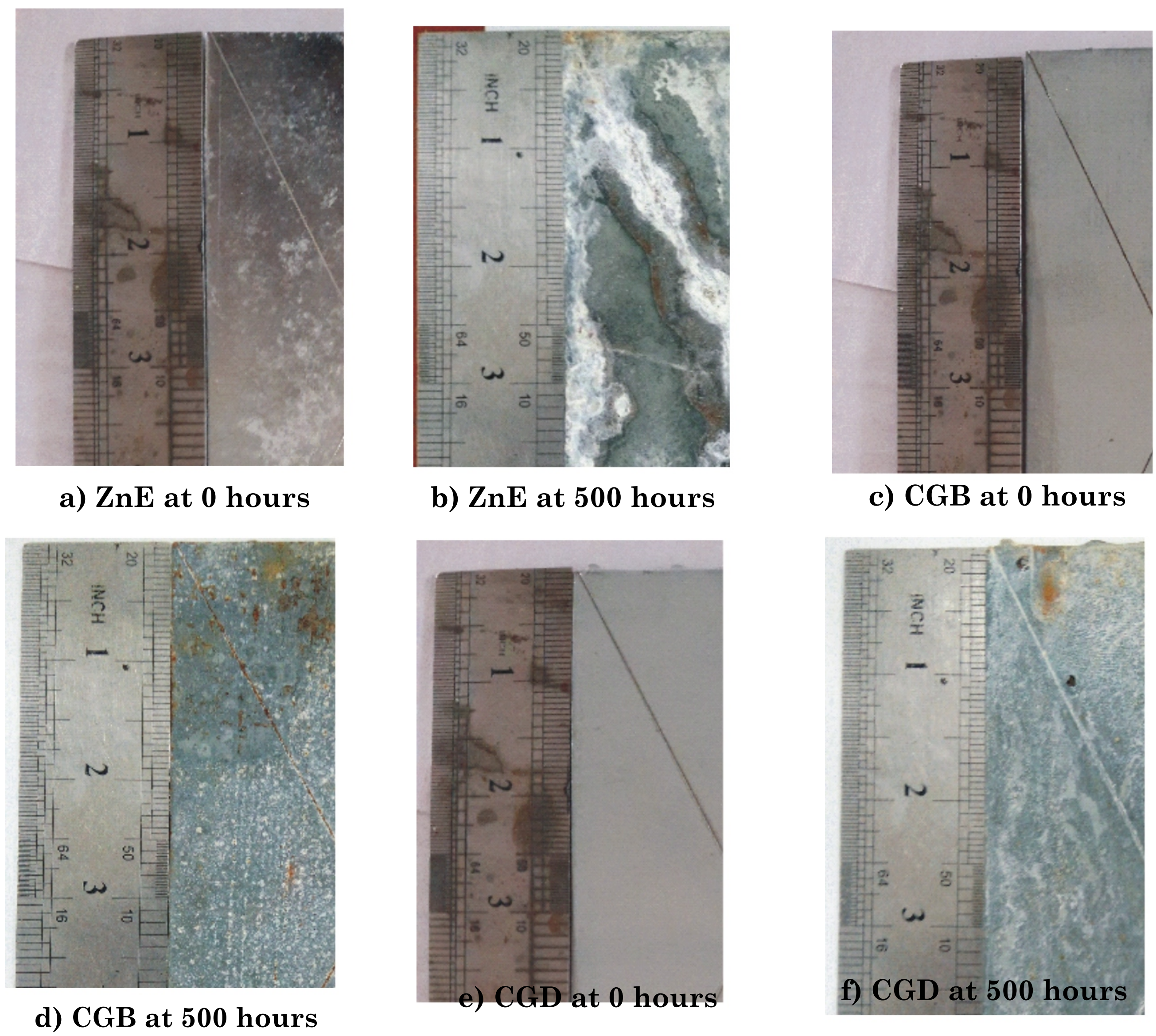


Figure 6: *Comparison of Cyclic polarization curves in 3.5% NaCl*

Figure 6 shows the comparison of cyclic polarization curves for MS substrate and all the coatings in 3.5% NaCl solution after 24hrs of immersion. The Cyclic polarization curve for MS substrate shows a positive loop as the current density is moving on the higher values in reverse scan as compared to current density in forward scan. The potential at which pits starts to initiate is the breakdown potential (E_b) and the value of E_b for MS substrate is -0.653 V vs Ag/AgCl. The area of the loop is directly proportional to corrosion rate and in that area of loop no further pits are produced that only present pits propagate. The potential at which the forward scan cut reverse scan is the re-passivation potential, the E_{rp} and the E_{rp} value for MS substrate is -0.589 V vs Ag/AgCl. At this potential all the pits will be re-passivated and below this potential there will be no pits. It is clear from the Figure 6 that the cyclic polarization curve of all coatings shows no pitting as reverse scan essentially retraced the forward scan.

5. Salt Spray

Figure 7 shows coated samples before and after 500 hours of exposure in salt spray chamber (Model SF/1000). All the coatings have white rust on their surface which is the corrosion product of zinc. This means that coating behavior is sacrificial in nature to protect MS substrate by sacrificing zinc as zinc chloride (white rust). ZnE coating has more white rust which means that it delaminates quicker than CGB and CGD coatings. CGD coatings produce good results because of having least white rust. ZnE and CGB coatings showed brown rust which is the corrosion product of iron and this indicates that these coatings do not protect mild steel substrate by sacrificial protection efficiently because of their lower coating thickness CGD coatings showed good results with minimum ground rust. Salt spray test shows the similar trend after 500 hours of exposure as predicted by electrochemical impedance spectroscopy and open circuit potential.



a) ZnE at 0 hours **b) ZnE at 500 hours** **c) CGB at 0 hours**

d) CGB at 500 hours **e) CGD at 0 hours** **f) CGD at 500 hours**

Figure 7: *Photographic images Zinc Electroplated (ZnE), Cold Galvanized Brushed (CGB) and Cold Galvanized Dipped (CGD) at 0 & 500hrs.*

6. Conclusions:

Dipped cold galvanized coating got the better coating thickness and surface topography properties than the cold galvanized coating produced by brushing method and zinc electroplating. Open circuit potential (OCP) of all the coatings is on the more active side than the mild steel substrate, indicating sacrificial behavior of the coatings. In 3.5% NaCl solution, dipped cold galvanized coating behaves well as there is less potential difference with mild steel substrate. Non uniform semi-circle of electrochemical impedance spectroscopy in 3.5% NaCl solution showed that the dipped cold galvanized sample sacrificed in a better way than brushed cold galvanized sample and Zn electroplated sample. Cyclic Polarization in 3.5% NaCl solution indicates no pitting and susceptibility for all the coatings. Visual inspection of salt spray reveal that dipped cold galvanized sample is best as it only has a zinc corrosion product while other samples have red rust (iron corrosion product).

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