Corrosion Protection Evaluation of Mild Steel Painted Surface by Electrochemical Impedance Spectroscopy

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Abstract
This study focuses on the evaluation of corrosion protection performance of zinc based epoxy paint on the chemically treated mild steel surface in artificial sea water by Electrochemical Impedance Spectroscopy (EIS). EIS and Open Circuit Potential (O.C.P) measurements of the rusted surface prior to chemical treatment were also studied to make a comparison with the corrosion behavior of the applied paint film. The electrochemical behavior of painted surface was estimated by EIS parameters that contained paint film resistance, paint film capacitance and double layer capacitance. On the basis of calculation using EIS spectrums it was observed that pore resistance (R_{pore}) decreased with the appearance of doubled layer capacitance (C_{dl}) due to the electrolyte penetration through the film. This was further confirmed by the decrease of polarization resistance (R_p) and OCP towards more negative value was also the indicator of the deterioration of paint film protectiveness.
Key words: Mild Steel, EIS, Paint Coatings, Rust, Polarization

Introduction

The long-term performance of a coating is significantly influenced by its ability to adhere properly to the material to which it is applied. This is not simply because the coating might flake away or detach from the surface but because poor adhesion will allow moisture or corrosion products to undercut the coating film from areas of damage. Coating experts often say that surface preparation is the most important factor in determining the success of any protective coating system. By this, it is meant that surface preparation affects the performance of the coating more than any other variable.

Many factors in surface preparation affect the integrity of coating which includes residues of oil grease, rust on the surface and mill scale which can decrease adhesion or mechanical bonding of coating to the surface *(Bayliss and Deacon, 2002).*

For an organic coating to serve its intended purpose, surface pre-treatment of the steel substrate is extremely important. This pre-treatment could be either mechanical or chemical in nature. The chemical pre-treatment comprises of use of primers or coupling agents, solvent degreasing and acid pickling etc which will form a chemical bridge between the steel substrate and the organic coating *(Hare, 1986).*

Whatever the pre-treatment is, an accurate characterization of the steel surface is of great importance towards the durability of the coating bond. Numerous techniques exist for characterization of the coating-substrate interface as well as performance & adhesion of organic coatings. EIS (Electrochemical Impedance Spectroscopy) has been used extensively as a laboratory-based research tool for studying the performance and deterioration of polymeric protective coatings. The EIS data can be

used to predict corrosion protection, film porosity, solution absorption into the coatings and film delamination properties. EIS also provides a technique to optimize coatings while reducing the time of coating evaluation and gives insight into the physical and chemical properties of the coatings *(Mansfeld et al., Scully, 1989, Jhon and Pham, 1996).*

Experimental Methodology

Duplicate mild steel rusted panels were selected as substrate for the present study. These were brushed cleaned to remove loose rust particles. The panels had the following composition (AISI 1020) C = 0.188%, Mn = 0.5%, S = 0.035%, Fe = Balance.

1   Chemical Treatment

One of the panels was chemically treated with 5% H_2SO_4 at room temperature in order to remove corrosion products or any mill scale, and then thoroughly rinsed in water. It was washed with acetone to remove any oil, grease and other organic contaminants before the application of paint. The other panel was only cleaned manually to remove any loss corrosion product by simple brushing. The panels were designated as CTP (Chemically Treated & Painted) and RP (Rusted Panel).

2   Paint Application

The CTP panel was painted with Zinc based Epoxy paint. Firstly, Zinc based epoxy primer (Resin: Hardener = 3:1) was applied on the surface under controlled conditions via paint spraying practice and then applied a Zinc based epoxy top coat (Resin: Hardener = 3:1) to primed coated surface. It was then placed in a close chamber for 48 hours at 38ºC and for 200 hours in a desiccator at room temperature for curing.

3   Electrochemical Impedance Spectroscopy (EIS)

The EIS cell was built by Polycarbonate (PC) tube of 4 inches height and cross sectional area of 6.28 cm^2. Graphite electrode was used as counter electrode and Ag – AgCl electrode as reference electrode, while as received rusted panel (RP) and chemically treated painted (CTP) panel served as working electrodes. A representative cell for EIS measurement was similar, as shown in Fig. 1. EIS measurement was carried out with the help of Gamry EIS 300 Potentiostat (PC/750) for both panels.

Figure 1: A representative EIS Cell
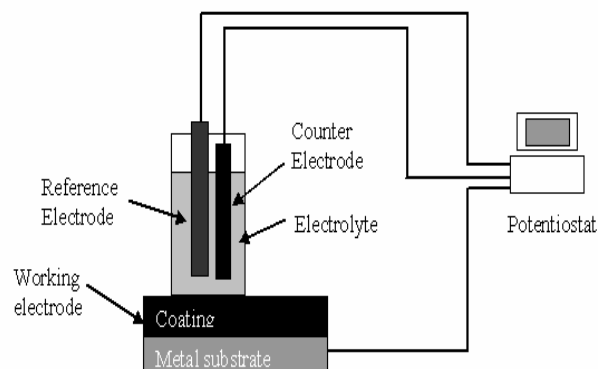
The open circuit potential (OCP) was measured between Ag –AgCl reference electrode and working electrode in artificial sea water (3.5% w/v NaCl) before each scan within a 50 seconds initial delay. The impedance measurements were performed at the OCP using a sine wave of 10mV amplitude peak to peak for each panel. The impedance spectrum was analyzed with Echem Analyst version 5.30 to determine the operating parameters of the system.

4   Experimental Conditions
A 10 mV AC perturbation was employed in the frequency range of 100 kHz to 0.01 Hz. the exposed area of the electrode was 6.28 cm^2 with 3.5% NaCl solution used as an accelerating environment. The RP and CTP panels were exposed for 10 and 40 hours respectively and EIS scans were obtained at a regular interval of 10 minutes excluding 30 minutes testing time.

Results and Discussion
1   Open Circuit Potential Measurements
The OCP measurement is a simple additional tool that provides complementary information to EIS results regarding the corrosion undergone by the steel substrate after exposure to aggressive solutions (*Ramirez et al., 2005)*. The variation of OCP over time for RP and CTP panels are shown in Fig**.** 2 & 3 respectively. The comparison of OCP for both panels is also represented in Fig. 4. The evolution of the curves is clearly related to differences in the surface characteristics.

Figure 2: Variation of OCP with Time in artificial sea water for RP
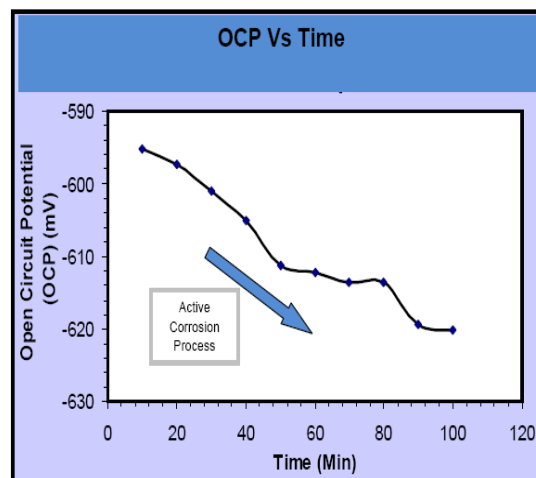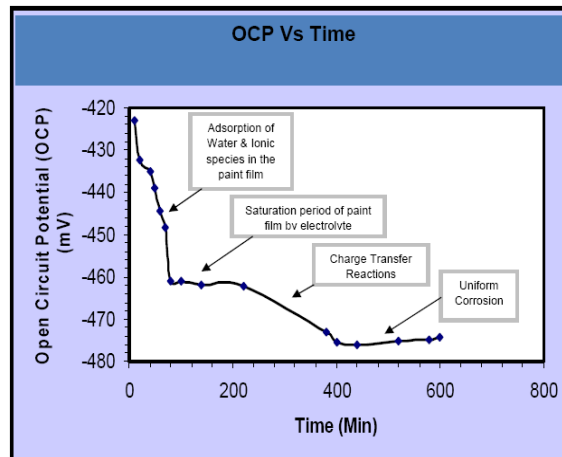
Figure 3: Variation of OCP with time in artificial sea water for CTP

The more noble values for CTP than RP were due to the barrier properties of the paint films. During exposure time, the OCP values varied between -595 to -620mV for RP with a continuous decreasing trend toward more –ve potential which was the direct indication of active corrosion process. While the OCP values for CTP panel were varying between -420 to -480mv with a decreasing trend. The rapid decrease in OCP from -422.9 to -461.0mV in first 70min may be due to the adsorption of water in the paint film.

The OCP behavior remained constant for next 150 min until the saturation limit of the film. The gradual decrease in OCP after 220 min may be produced by the diffusion of water and ionic species such as OH^- and Cl^- etc at the paint/metal interface.

Figure 4: Comparison of OCP between CTP and RP
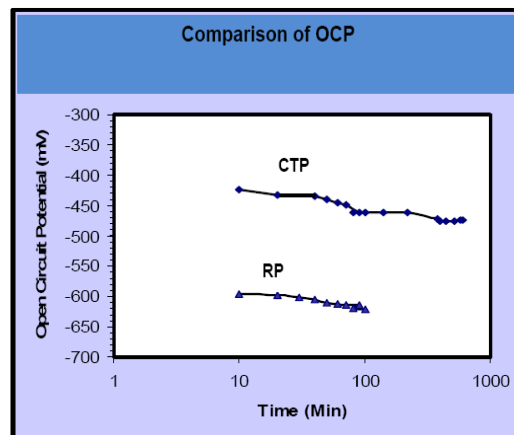
This led to increase in the anodic reaction rate thereby OCP became more negative (Naderi *et al., 2004).* Further constant behavior beyond 400 min may be due to the uniform corrosion reactions at the metal surface after failure of paint film.

2   EIS Measurements

In many papers the corrosion performance of many paint systems applied on carbon steel substrates during their exposure to aqueous solution at ambient temperature has been successfully investigated by EIS. **[8-13]**

In EIS, the results for the RP and CTP panels are expressed by Impedance modulus, Z_{mod} (Ohm) Vs Frequency (Hz), and by the magnitude of the real and imaginary components of impedance Z_{real} (Ohm) Vs $-Z_{imag}$ (Ohm).

In the case of a metal/paint system where R_s is the solution resistance, R_{pore} the pore resistance, C_c the capacitance of protective coating, R_p the polarization resistance and C_{dl} is the double layer capacitance (Chico, 2007).

In EIS bode plot high values of the impedance modulus in the low frequency limit, the phase angle remained close to $0°$ which initially indicated the R_{pore} resistance but after deterioration of paint film this impedance modulus was replaced by R_p. One time constant in Nyquist plot accounts for the barrier properties of the paint film, but with the exposure time the appearance of second time constant indicates the damage of barrier properties of paint film by the formation of double layer capacitance C_{dl} (David, 2004).

The RP panel as it had hydrated oxide layer at the surface, in EIS spectrum this oxide film behaved as a very weak capacitor in initial 70 min which may be due to non uniformity of the surface layer or porous nature of oxide film. But this behavior was changed with increase in capacitance due to corrosion reactions at the surface and formed oxide layer as it may be evaluated from the depressed semicircles in the Nyquist plot of RP with exposure as shown in Fig.5.

**Figure 5: Nyquist Plot of RP panel as a function of time**
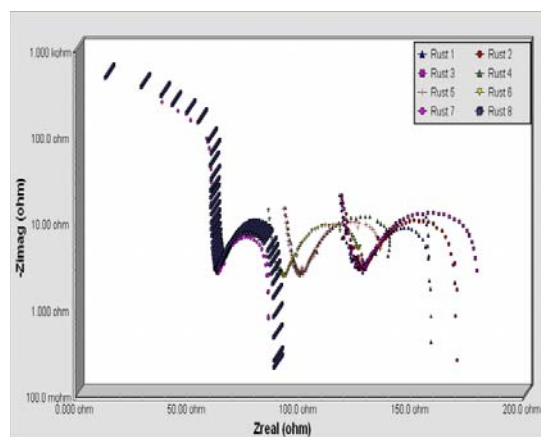
3   Coating Capacitance (C_c)

The capacitance of paint film is an important parameter to measure its integrity. While an ideal film acts like a perfect capacitor, a purely capacitive behavior is characteristic of an effective barrier paint films. Upon initial exposure to an electrolyte paint film with excellent barrier properties acted as an almost perfect capacitor. The capacitance value is dependant on the thickness and its dielectric constant. (David et al., 2004)

$$Coating\ Capacitance\ (C_c) = \varepsilon\varepsilon_0\left(\frac{A}{t}\right) \qquad \text{......... 1}$$

As shown in Fig.6 the rapid decrease of coating capacitance from 0.105nF to 0.0903nF in first 70 min of exposure was a result of water adsorption hence the swelling of paint film which resulted in the increase of film thickness.

Figure 6: Variation of Coating capacitance for CTP panel
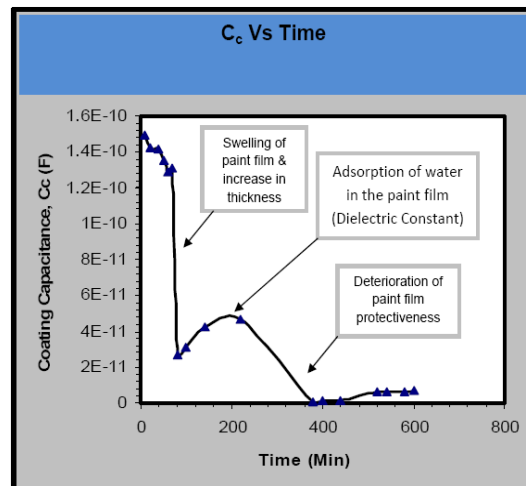
In next 150 min the slight increase in coating capacitance was due to the fact that water has higher dielectric constant ($\epsilon_w = 80$) and at saturation point of water absorption within the film, the coating capacitance was the function of water dielectric constant (ϵ_w) and became independent to paint film thickness. This may be verified from Eq. 1.

Coating capacitance measurements can be used to estimate the relative water uptake rates by the coatings. At saturation limit (after 220 min) the volume fraction of water was 0.34 which may be calculated by Brasher-Kingsbury equation (Brasher et al., 1954).

$$\text{.... 2}$$

$$Volume\ fraction\ of\ Water = (log\frac{C_t}{C_0})/(log\,\varepsilon_w)$$

After 220 min the gradual decrease in capacitance may be correlated with the deterioration of paint film protectiveness and formation of free passage of electrolyte to approach at the interface. Minor increase in the coating capacitance was observed after 400min which may be due to decrease in impedance at high frequency.

4   Pore Resistance (R_{pore})

A coating systems electrical resistance is a general indicator of its performance. The coating resistance degrades with time. This degradation is associated with ions and water penetration into the coating and subsequent electrochemical reactions at the paint/metal interface. The results of CTP panel for coating resistance degradation can easily be interpreted from the EIS, Bode plot Fig. 7, the increase in pore resistance was observed from 905 to 1000 ohms in first 70 min, this increase was attributed to delay in the formation of pores within the film, decreased to 572.6 Ohms, again raised to 647.4 Ohms which may be due to swelling of paint film caused by the penetration of electrolyte and further gradual decrease to almost constant value at about 213.5 Ohms this may be correlated with the complete failure of paint film protectiveness as illustrated in Fig. 8 and 9. The pore resistance is assumed to be essentially constant during the delimitation process (*Jhon and Pham, 1996*).

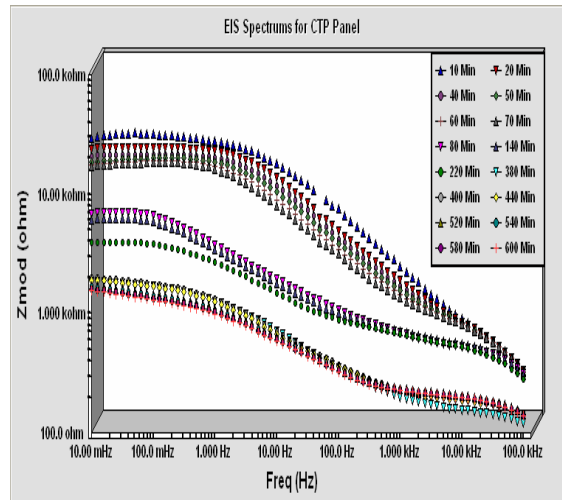**Figure 7: Bode Plot; Decrease of pore resistance (R_{pore}) at low frequency for CTP panel**
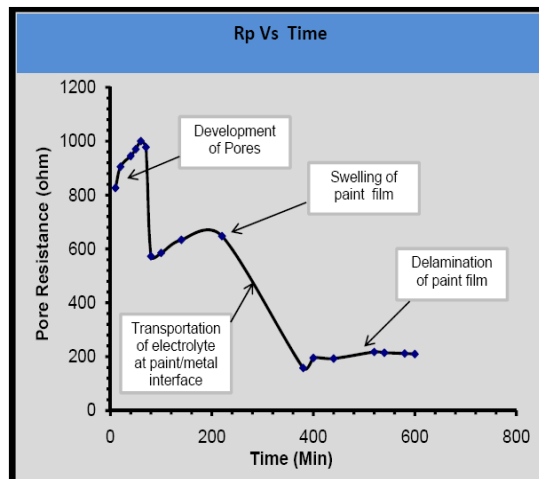

Figure 8: Variation of Pore Resistance for CTP panel

**Figure 9: Complete failure of paint film after 40Hrs of exposure**

5   Polarization Resistance (R_p)

The values of the polarization resistance can be determined using the equivalent circuit model or graphically from the Bode plots by subtracting the pore resistance and solution resistance from total coating resistance.

For a CTP panel as in Fig. 10, the decline of impedance values in the lower frequency region can be interpreted as the delaminating of the coating, although the film was not physically detached from substrate metal surface in the microscopic sense (Yasuda et al., 2001). The clear result of paint film failure may be visualized from Fig. 9.

**Figure 10: Variation of Polarization resistance for CTP panel**
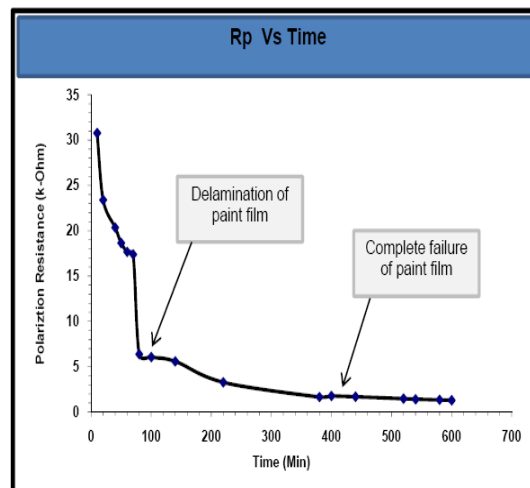
The decrease in polarization resistance may be evaluated from Nyquist plot in low frequency region as shown in Fig. 11. The formation of pores in the paint film may also be estimated from reverse impedance values in low frequency region of Nyquist plot.

Figure 11: Nyquist plot; decrease in Polarization Resistance for CTP panel
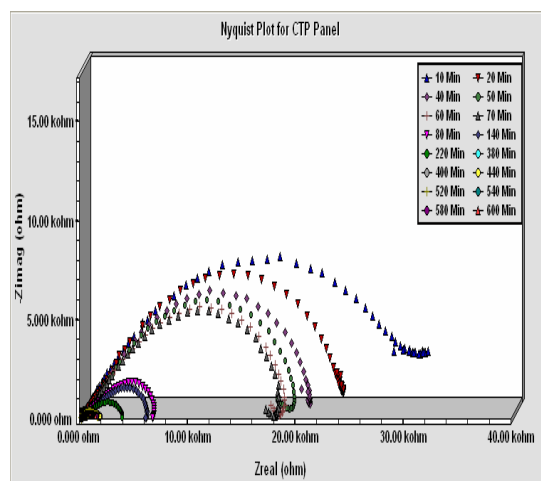
The variation in polarization resistance for rusted panel is shown in Fig. 12 the decrease in polarization resistance was the representation of corrosion kinetic reactions at the surface.

Figure 12: Decrease in the Polarization resistance of RP panel
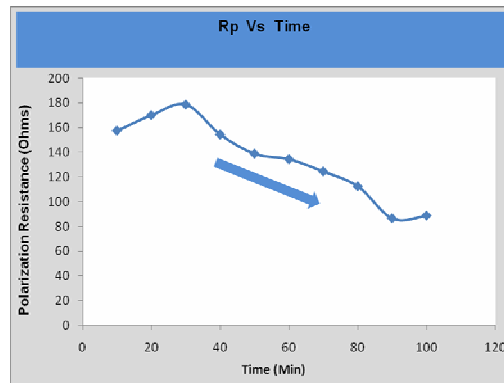
6.   Double Layer capacitance (C_{dl})

The double layer capacitance is proportional to the area of the substrate exposed to the electrolyte, the delaminated area. This occurs after the electrolyte has penetrated through the coating to the substrate. The area exposed through the pores of the coating is considered negligible when compared to disbanded area. In CTP panel it was assumed that the double layer capacitance remained constant throughout the study and it may be approximated by double layer capacitance of an uncoated substrate. The Nyquist plot usually exhibits two time constants on the appearance of double layer capacitance. The first time constant in high frequency region gives the representation of coating characteristics while in low frequency region the second time constant demonstrates kinetics of corrosion. In our case due to complete failure of the paint film protectiveness the second time constant was invisible as shown in the Nyquist plot of CTP panel.

Conclusion

EIS is a good tool which relates to the quality of a coating on a metal substrate. By this analytical technique some pitfalls of the actual measurement were noted and the degradation of paint film has described. Open Circuit Potential (OCP) of paint film was observed less negative than rusted one, the evolution of these values were clearly related to differences in the surface characteristics. The adhesion of a paint film to the substrate is a key measure of its integrity. Adhesion has both chemical and physical aspects. In this research the EIS has provided information on the loss of adhesion, specially the polarization resistance R_p, and coating capacitance C_c which directly correlated with adhesion of the paint film to the surface. R_p and double layer capacitance C_{dl} are the characteristics of the bare metal which do not appear in EIS spectrum until the electrolyte traversed the paint and contacted at the paint/metal interface. In this study at initial stage of the paint film, the damage was observed as characterized by decreasing trend in the coating capacitance due to absorption of electrolyte (swelling). The fall of polarization resistance R_p was the rate determining factors for the paint film failure by its delamination with the formation of uniform double layer at the interface. The resulting under film corrosion caused the loss of adhesion of paint film from the substrate.

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