ABSTRACT

This thesis proposes a methodology for predicting the corrosion behaviour of uncoated steel & different polymer-organic coated steel (coal tar enamel, coal tar epoxy and coal tar tape) in Tap and Saline water. Corrosion properties were measured by Gamry Instrument. The I_{CORR} & E_{CORR} values are calculated by using Gamry Echem Software. The experimental measurement value used the Linear Polarization and Tofel Extrapolation curve techniques for determining the corrosion rate. Comparison of corrosion resistance among the coated samples reveal a few interesting observations. Coal tar epoxy coated sample shows better corrosion resistance than the other different coated sample in different environment. From LPR test Rp values were also obtained. Higher Rp values indicate good coating property.

Keywords: coal tar epoxy, corrosion rate, polarization resistance, tafel curve.
1. INTRODUCTION

Corrosion of steel in different environment leads to the premature failure of many structures. Rust products form on the steel, expanding its volume and creating stress in the surrounding structure. This leads to cracking and spalling, both of which can severely reduce the service life and strength of a member [6]. Corrosion of steel structures is one of the most expensive problems facing engineers in present world. The structural integrity of many bridges overpasses, parking garages, and other steel based structures has been impaired by corrosion, and repairs are urgently required to ensure public safety. As structures approach the end of their design life, new and improved methods for repair and rehabilitation of corroded members must be developed. To prevent and arrest corrosion activity at an early stage, accurate detection techniques are necessary. Because of the increasing number of corrosion related problems in the field of structural design, research is continuously being conducted to evaluate and implement efficient repair strategies.

Polymer coated, inorganic or organic materials have been used for years as a method of providing added strength and ductility to steel structures. In recent years, Polymer & organic coating has been considered and implemented for corrosion protection [12,13]. Corrosion due to chloride ingress is purportedly arrested by the prevention of further chloride contamination and penetration by the oxygen and water needed to continue a corrosion process that has begun or has caused damage [2,3]. Many factors influence the durability of a steel structure. It is possible to greatly reduce the risk of corrosion by proper material selection and by implementing suitable design and maintenance principles.

Stainless Steel is more resistant to chloride penetration and carbonation but has high cost of implement. Low permeability is crucial in defining durability [5]. It is important to protect the steel from rain and chemicals that might cause it to corrode before placement. A harsh environment will cause corrosion even in the highest quality steel. Alternating wet/dry cycles are very detrimental to steel structures. Marine exposure is one of the most severe environments in nature accelerating the corrosion process. Deicing salts and other chemicals facilitate the penetration of chlorides and increase the likelihood of corrosion [8]. High temperatures, contaminated soils, industrial and polluted air are other factors that increase the rate of corrosion. Increasing the resistance of the concrete cover to the penetration of chlorides is the primary measure used in increasing the service life of marine structures [1].

As an electrochemical process, corrosion involves the transfer of electrons as a result of chemical reactions. This requires an anode and a cathode. The anode is the site of the oxidation of the steel. The reaction at the anode is expressed as:

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-
\]

The liberated electrons are used at the cathode – the site of the reduction reaction:

\[
2\text{e}^- + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow 2\text{OH}^-
\]

With the corrosion process underway, the bare steel oxidizes to form ferric oxide (Fe$_2$O$_3$) or rust [7].
The process is expressed by the following equations:

\[
\begin{align*}
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 \\
4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 4\text{Fe(OH)}_3 \\
2\text{Fe(OH)}_3 & \rightarrow \text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]

The formation of rust is the most tangible evidence of corrosion and causes many of the problems associated with corrosion damage in steel based structure [5,8].

1.1 CORROSION PROTECTION PROVIDED BY VARIOUS COATING SYSTEMS

Coating systems have been used extensively in seismic retrofits and for structural maintenance. Many of the maintenance applications depend on the external wrap to prevent further chloride ingress and therefore halt the corrosion process inside the structure.

The results of past research have raised questions regarding the effectiveness of Polymer wrap and jacket systems to prevent ongoing corrosion. The laboratory research involves repaired structures that have undergone some corrosion. The corrosion behaviour of previously unexposed (new) structures treated with an Polymer wrapping system has not been thoroughly evaluated and is an integral portion of the laboratory program described herein [12,13].

Much of today’s research to improve the durability of steel based structures focuses on the use of polymer coating in large-scale infrastructure projects. Polymer Coating exhibit excellent corrosion resistance comparable to bare steel. Reduced maintenance and repair expenses justify their higher initial cost. This section will define key terms related to different type of coating and focus on different type of polymer -organic coating as a protective barrier against corrosion.

The Corrosion experiment is carried out with three different coating steel and with bare steel. The name of different coating is as following:

a) Coal Tar Enamel Coating.

b) Coal Tar Epoxy Coating.
This report represents an initial account of laboratory studies. The report will provide information on material selection and different coating system practices. The specimen variables chosen for analysis are defined, and a detailed monitoring program data collection is furnished. In addition to presenting laboratory work, a review of existing corrosion detection and repair methods is presented. In the following chapter, corrosion attack, different type of coating, and experimental method is described. The information will be helpful in identifying other engineering and government groups conducting re-search on coating or having completed successful infrastructure projects.

2. EXPERIMENTAL PROCEDURE

The mild steel and the coated steel samples were supplied from industry in a form of cold rolled, annealed condition. The sample is to be coated is properly polished. Then the sample is used as anode & graphite plate is used as cathode. Then several experiments is done by varying the current & potential [15]. Standard Corrosion Cell has been used to perform the electrochemical potentiodynamic polarization tests on standard flat metal specimens. Polarization experiments have been carried out as per ASTM ST72 using Gamry Potentiostat. The software used is Gamry Echem Analyst. First the potentiodynamic experiment is done with the as received sample with the scan rate of 1mV/sec and the $I_{\text{CORR}} - E_{\text{CORR}}$ value is obtained by Tafel’s extrapolation and Linear Polarization Resistance method [14]. The experiment is done in tap and salt water solution. The experiment Set up of the polarization testing is shown in fig.

2.1 TEST PROCEDURE

- A particular steel specimen was selected to be the working electrode.
- The tip of the working electrode was ground off, if it was a coated steel, to facilitate proper electrical connections.
- The tip was well polished.
- The working area (the portion of the steel sample to be exposed to the electrolyte) of the steel was cleaned and degreased.
- The surface area of the sample portion to be exposed was measured (in square cm).
- Polymer-Coated steel with Their Tips Polished to Ensure Good Electrical Contact during Polarization Resistance Test.

Table 2.5.1: Density and Equivalent Weight of iron / steel

<table>
<thead>
<tr>
<th>Metal / Alloy</th>
<th>Density (g/cc)</th>
<th>Equivalent Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron/Steel</td>
<td>7.87</td>
<td>27.92</td>
</tr>
</tbody>
</table>

3. RESULT

While all of the types of samples were immersed in the two different corrosive environments (Tap water and saline water), PR tests were carried out for mild steel, mild steel with coal tar enamel coating, M.S. with coal tar epoxy coating and M.S. with coal tar tape coating. The results are discussed below and shown in figure 3.1 through 3.16.

Tafel Extrapolation Curves (Tap Water)

![Tafel curve for Mild Steel –tap water.](image_url)
Figure: 3.2 Tafel curve for Coal Tar Enamel Coating –tap water.

Figure: 3.3 Tafel curve for Coal Tar Epoxy Coating –tap water.

Figure: 3.4 Tafel curve for Coal Tar Tape Coating –tap water.

Figure: 3.5 Tafel curve for Mild Steel –Sea water.
The linear polarization method takes its name from the apparent linearity of polarization curves near their origin. This is the region of low applied current and subsequently low over voltages (voltages differing from the determined corrosion potential, $E_{corr}$). Note that the region of curve linearity is limited to points near the origin.
Figure: 3.9  LP curve (mild steel-tap water)

Figure: 3.10  LP curve (coal tar enamel Coating -tap water).

Figure: 3.11  LP curve (coal tar epoxy Coating -tap water).

Figure: 3.12  LP curve (coal tar tape Coating -tap water).
Linear Polarization Curve (Sea Water)

Figure: 3.13 LP curve (mild steel -sea water)

Figure: 3.14 LP curve (coal tar enamel Coating -sea water)

Figure: 3.15 LP curve (coal tar epoxy Coating -sea water)

Figure: 3.16 LP curve (coal tar tape Coating -sea water)
4. DISCUSSION

The corrosion data of different coated samples were derived from figures 3.1 to 3.16 by using Gamry Echem software and Tafel Extrapolation method.

**Table 4.1 Corrosion data of as received sample**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\beta_a$ mV (anodic tafel constant)</th>
<th>$\beta_c$ mV (cathodic tafel constant)</th>
<th>$R_p$ (k-ohm-cm$^2$)</th>
<th>$I_{corr} = \frac{\beta_a \cdot \beta_b}{2.3 \cdot R_p \cdot (\beta_a + \beta_b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild steel in tap water</td>
<td>99.55</td>
<td>215.9</td>
<td>0.973</td>
<td>30.40 $\mu$A/cm$^2$</td>
</tr>
<tr>
<td>Mild steel in sea water</td>
<td>50.8</td>
<td>96.06</td>
<td>0.197</td>
<td>73.33 $\mu$A/cm$^2$</td>
</tr>
</tbody>
</table>

**Table 4.2 Corrosion data & $R_p$ of different coated samples**

<table>
<thead>
<tr>
<th>NOMENCLATURE (sample in tap water)</th>
<th>$\beta_a$ mV (anodic tafel constant)</th>
<th>$\beta_c$ mV (cathodic tafel constant)</th>
<th>$R_p$ (k-ohm-cm$^2$)</th>
<th>$I_{corr} = \frac{\beta_a \cdot \beta_b}{2.3 \cdot R_p \cdot (\beta_a + \beta_b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal tar enamel coating</td>
<td>95.20</td>
<td>164.1</td>
<td>107.18</td>
<td>244.4 nA/cm$^2$</td>
</tr>
<tr>
<td>Coal tar epoxy coating</td>
<td>112.1</td>
<td>142.8</td>
<td>320.68</td>
<td>85.14 nA/cm$^2$</td>
</tr>
<tr>
<td>Coal tar tape coating</td>
<td>118.9</td>
<td>129.0</td>
<td>45.57</td>
<td>590.3 nA/cm$^2$</td>
</tr>
</tbody>
</table>

Corrosion rates of the coal tar tape coating sample in tap water were found to be on the higher sides, but corrosion rate of coal tar epoxy coating sample were found to be on the lower side of entire corrosive (Tap water) environment.

On the other hand similar effect were found for coal tar tape coating in saline water environment and as well as for coal tar epoxy coating in same environment. It is notice that presence of organic materials on the sample, when tested always shows the corrosion rate higher than the different types polymer coated samples in both the environment i.e, tap & saline water.
Table 4.2 Corrosion data & $R_p$ of different coated samples

<table>
<thead>
<tr>
<th>NOMENCLATURE (sample in sea water)</th>
<th>$\beta_a$ mV (anodic tafel constant)</th>
<th>$\beta_c$ mV (cathodic tafel constant)</th>
<th>$R_p$ (k-ohm-cm$^2$)</th>
<th>$\text{I}_{\text{corr}} = \frac{\beta_a \times \beta_b}{2.3 \times R_p \times (\beta_a + \beta_b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal tar enamel coating</td>
<td>91.83</td>
<td>63.66</td>
<td>27.75</td>
<td>589.0 nA/cm$^2$</td>
</tr>
<tr>
<td>Coal tar epoxy coating</td>
<td>43.89</td>
<td>115.5</td>
<td>205.38</td>
<td>67.32 nA/cm$^2$</td>
</tr>
<tr>
<td>Coal tar tape coating</td>
<td>77.84</td>
<td>60.52</td>
<td>11.95</td>
<td>1.238 $\mu$A/cm$^2$</td>
</tr>
</tbody>
</table>

The corrosion properties of coal tar epoxy and were found to be far superior as reported in the literature. The corrosion properties of coated samples are much superior than the bare received sample. Among the coated sample coal tar epoxy has best corrosion resistance. Its $E_{\text{CORR}}$ value is also much nobler.

From PR test we get the $R_p$ value, which is known as polarization resistance. Using the Stern and Geary relationship, corrosion rates can be calculated from the polarization resistance ($R_p$) as per the relation $\text{I}_{\text{corr}} = K/R_p$. Where K is a constant. However K also includes the Tafel slope values. Knowing Tafel slopes corrosion rates can be calculated. The stability of the coating depends on the $R_p$ value. Higher the $R_p$ higher is the stability. The $R_p$ values of the samples are given in table 5.1. From this it can say that the coating of epoxy is far better than the other samples.

The corrosion graphs (between corrosion rate and polarization resistance versus salt concentration) for different coated samples were shown in figure 4.1 to 4.4 and which are derived from figures 3.1 to 3.16 by using Gamry Echem software and Tafel Extrapolation method.

![Figure: 4.1 Corr. Rate and PR versus Salt Concentration for Mild Steel.](image-url)
5. COMPARISON OF ALL COATING SYSTEMS

A comparison of all the different type of polymer-organic coating is given in Table 5.1 and Figure 5.1- 5.6. It is evident that coal tar epoxy performed quite well (Figure 5.3 – 5.4) in all corrosive environments. It had extremely low corrosion rates and should be an excellent material in the form of a pure rebar or a clad bar (which would be more economical). Coal Tar Tape, had the highest corrosion rate Its corrosion rate increased in the presence of salt. Coal tar Epoxy performed better than Coal Tar Enamel in tap water as well as in the presence of 3.5% NaCl solution.
NOMENCLATURE

<table>
<thead>
<tr>
<th>Corrosion Rate (mpy)</th>
<th>Polarization Resistance (k-ohm-cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In Tap water</td>
</tr>
<tr>
<td>Mild Steel</td>
<td>13.86</td>
</tr>
<tr>
<td>Coal tar enamel coating</td>
<td>0.1114</td>
</tr>
<tr>
<td>Coal tar epoxy coating</td>
<td>0.0306</td>
</tr>
<tr>
<td>Coal tar tape coating</td>
<td>0.269</td>
</tr>
</tbody>
</table>

Figure: 5.1  Comparison of Tafel curve of Various Coating – Tap Water.

Figure: 5.1  Comparison of Tafel curve of Various Coating – Tap Water.
Figure: 5.2 Comparison of Tafel curve of Various Coating - Sea Water.

However, in the presence of 3.5% NaCl, Coal Tar Tape performed worse. This means that there is a greater chance of damage to Coal tar Tape Coated steel. The coal tar Epoxy Coating shows superior corrosion resistance in both the corrosive environment where as coal Tar Tape shows worse from all three different coating systems.

In general, an open water mild steel corrosion rate of 1 MPY or below is considered excellent, 2-3 MPY is considered good, and a rate of 4 MPY is borderline acceptable. Corrosion rates at or exceeding 5 MPY warrant immediate investigation. Rates of 10 MPY and greater signal a serious threat to system safety, reliability, and building or plant operations.

Any corrosion rate above 15 MPY generally indicates a severe pitting condition, an under deposit or cell corrosion condition, or possibly MIC. In most cases, such high corrosion rates dramatically reduce service life, and strongly raise the probability of a premature failure. Corrosion rates above 25 MPY are not uncommon where under deposit corrosion and MIC are involved.
6. CONCLUSIONS

In this project, two types of testing approaches have been made to determine the corrosion evaluation of various coating systems. These include polarization resistance (PR) and tafel extrapolation tests.

Corrosion tests were carried out for all different types of coating in Tap water and solution with 3.5% amounts of sodium chloride. These tests give valuable qualitative information on the nature of corrosion on polymer-organic coating. Two cycles were completed at the time of writing this report. The following conclusions have been drawn:

- Mild steel showed considerable corrosion product formation at the solution-sample Interface in both the environment (Pitting Corrosion). However, no other coating showed corrosion product formation. As demonstrated coal tar epoxy performs excellently in all two corrosive environment. It has extremely low corrosion rates and high polarization resistance, should be an excellent and more economical material in the clad form.

- In the presence of 3.5% NaCl, Coal Tar Tape performs worse. This means that there is a greater chance of damage to Coal tar Tape Coated steel and has lower polarization resistance. The coal tar Epoxy Coating shows superior corrosion resistance in both the corrosive environment where as coal Tar Tape shows worse when compare to all three different coating.

7. ACKNOWLEDGEMENTS

The authors would like to thank Mr.B. Dewari at Rusttech, Inc.Kolkata, provided proprietary different coating steel samples for use in this research work.

8. REFERENCES


APPENDIX

a) EVALUATION OF THE I_{CORR}

Assuming mixed potential theory for activation polarization, the cathodic & anodic overvoltages are given respectively,

\[ \varepsilon_c = \beta_c \log \frac{ic}{icorr} , \]
\[ \varepsilon_a = \beta_a \log \frac{ia}{icorr} \]

Polarization resistance, R_p, is determined by the relationship in Equation:

\[ R_p = \left[ \frac{\Delta e}{\Delta i_{app}} \right] e \to 0 = \frac{B}{icorr} \] ..........2

B is the proportionality constant, as defined in Equation 2, which is also known as the Stern-Geary Equation:

\[ B = \frac{\beta_a \beta_c}{2.3 \left( \beta_a + \beta_c \right)} \] ..........3

From eq.2
\[ R_p \times I_{corr} = B \]

Then eq. 3 becomes,

\[ I_{corr} = \frac{\beta_a \beta_b}{2.3 \cdot R_p \left( \beta_a + \beta_b \right)} \]

\( \beta_a \) anodic tafel constant in mV
\( \beta_b \) cathodic tafel constant in mV
\( R_p \) polarization resistance in k-ohm-cm
\( I_{corr} \) in \( \mu \text{A/cm} \) & in nA/cm
b) CORROSION CONVERSION FACTORS

<table>
<thead>
<tr>
<th>mA cm⁻²</th>
<th>mm year⁻¹</th>
<th>mpy</th>
<th>g m⁻² day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA cm⁻²</td>
<td>1</td>
<td>3.28 M/nd</td>
<td>129 M/nd</td>
</tr>
<tr>
<td>mm year⁻¹</td>
<td>0.306 nd/M</td>
<td>1</td>
<td>39.4</td>
</tr>
<tr>
<td>mpy</td>
<td>0.00777 nd/M</td>
<td>0.0254</td>
<td>1</td>
</tr>
<tr>
<td>g m⁻² day⁻¹</td>
<td>0.112 n/M</td>
<td>0.365 /d</td>
<td>14.4 /d</td>
</tr>
</tbody>
</table>

For example, if the metal is steel or iron (Fe), \( n = 2 \), \( M = 55.85 \text{ g} \) and \( d = 7.88 \text{ g cm}^{-3} \) and the Table of conversion become:

<table>
<thead>
<tr>
<th>mA cm⁻²</th>
<th>mm year⁻¹</th>
<th>mpy</th>
<th>g m⁻² day⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>mA cm⁻²</td>
<td>1</td>
<td>11.6</td>
<td>456</td>
</tr>
<tr>
<td>mm year⁻¹</td>
<td>0.0863</td>
<td>1</td>
<td>39.4</td>
</tr>
<tr>
<td>mpy</td>
<td>0.00219</td>
<td>0.0254</td>
<td>1</td>
</tr>
<tr>
<td>g m⁻² day⁻¹</td>
<td>0.00401</td>
<td>0.0463</td>
<td>1.83</td>
</tr>
</tbody>
</table>

Note: you should read the Table from left to right, i.e.

\[ 1 \text{ mA cm}^{-2} = 11.6 \text{ mm y}^{-1} = 456 \text{ mpy} = 249 \text{ g m}^{-2} \text{ day}^{-1} \]