Corrosion Protection of Coated Steel Pipeline Structures using CP Technique

Asst. Prof. Dr. Fahim F. Al-Himdani
Mechanical Eng. Dept., College of Engineering
Al-Mustansiriya University, Baghdad, Iraq

Dr. Wathik Issa Mahdi
Control & Computer Engineering Department
University of Technology, Baghdad, Iraq

Asst. Lect. Abdul-Wahab Hassan Khuder
Mechanical Eng. Dept., College of Engineering
Al-Mustansiriya University, Baghdad, Iraq

Abstract

This work is directed toward the development of the corrosion resistance of the steel pipeline structures utilizing concrete coating using the cathodic protection technique to protect the structure of the coated steel pipeline structure. It deals with the matter of steel structures upon the survey periods, electrochemical dormant period because of the continuous cathodic prevention and the activation corrosion upon interruption period of this cathodic prevention and treatment this case of corrosion using the cathodic protection technique. The initial free corrosion potential ($E_{\text{corr}}$) upon intermittently intervals and the corrosion rate measurement of the specimens using full polarization curve (Tafel Method) has been observed.

The results clearly indicated that to achieve efficient design of a cathodic protection, the protected area should be divided into discrete electrochemical areas depending on the electrical resistance and steel potential to prevent the over-protection in the low electrical resistance areas when applying the designing criteria on the high electrical resistance areas. Furthermore, the results indicate that the absolute value of protection potential does not adequately describe the electrochemical changes undergone by the polarized coated steel pipe. Owing to the flowing current between the anode and cathode, the voltage drop is mainly not proportional with the electrical resistance of isolated coating, only when the coating is uniform over the entire area of the steel pipeline.


1. Introduction

Cathodic protection (CP) could be defined as the use of direct electrical current from an external source to oppose the discharge of corrosion current from anodic areas. The national association of corrosion engineers (NACE) defines cathodic protection as a technique for preventing the corrosion of a metallic surface. This is done by making that surface a cathode in an electrochemical cell. It is obvious if the entire area of the exposed metal surface could be made to collect current, it would not corrode because the entire surface would be cathodic. This is what cathodic protection does. Direct current is forced to flow from a source external to the metallic structure into all surfaces of the metallic structure. When the current is properly adjusted, it will overcome the corrosion current flowing from the structure and there will not be a current flow on to the structure surface at all points \(^1,2\).

Although the basic theory of cathodic protection is simple, practical designs for the various applications can differ considerably because they depend upon the structure which is to be protected and the conditions of the environment, which are encountered. This is where the complications arise and where trained corrosion personnel are required. Cathodic protection does not eliminate corrosion, but merely controls where it occurs. For every structure there is a special cathodic protection system dependent on the structure. There are two types of applying cathodic protection systems (CPS) to the metallic structures, these are \(^3,4\):

1. Sacrificial Anode Cathodic Protection.
2. Impressed Current Cathodic Protection.

Current distribution in cathodic protection systems is dependent on several factors, the most important of which are driving potential, anode and cathode geometry, spacing between anode and cathode and the conductivity of the aqueous environment which is favorable towards good distribution of current \(^5\).

2. Sacrificial Anode Cathodic Protection (SACP)

The SACP is designed upon the following general pattern:
(a) The surface area of steelwork submerged in the sea driven/buried in the bottom is calculated and the current for CP is estimated.

(b) The total weight of sacrificial anode material required to provide this necessary current for the required design life is calculated on the basis of the ampere-hour/kilogram capacity of the chosen material (aluminum, zinc and magnesium alloys are available for SACP).

(c) The distribution of this calculated weight of anodes is then assessed by calculation of the ability of anodes of a given anode potential to throw current for a certain distance in given environments.

(d) The final check, which may result obtained from (b) and (c), is to estimate the current requirement of the structure during selected periods of the design life, e.g. initially when the current for polarising an uncoated structure will be at maximum, or during the final year of the design when the anodes will be largely consumed and have their minimum capability to produce current [6,7].

Figure (1) shows steel pipeline bracelet zinc anodes being fitted prior to the application of the concrete based weight coat to the pipeline.

Figure (1) Zinc Bracelet Anode at a Joint in an Offshore Steel Pipeline

3. Impressed Current Cathodic Protection (ICCP)

The design of ICCP for an offshore steel structure follows a similar pattern to that indicated for sacrificial anode design:

(a) The surface area of steelwork requiring protection is calculated and its current demand for cathodic protection is estimated.

(b) The selection of the anode material to be employed, the number of anodes and their distribution over or in relation to the structure and the final allowance of current density are all inter-related decisions.
Having determined the anode requirements and locations then selection of the power source and related cables between it and the structure and it and the anodes is undertaken \cite{6,7}.

The power source will generally be a transformer-rectifier (TR), the function of which is to provide relatively low voltage direct current to flow from the anodes, into the seawater and onto the structure. The transformer-rectifier power source may be manually or automatically controlled. In the case of manually controlled equipment measurements of steel/sea water potentials are made at intervals and the current output from the transformer-rectifier manually adjusted by tap change switches, or similar, in order to maintain or achieve the required steel/sea water potentials. Automatically controlled, or potentiostatic, equipment utilize continuous measurements of steel/sea water potentials from permanently installed reference electrodes and amplify these signals to achieve continuous control within pre-set levels.

4. Cathodic Protection Principle (CPP)

Lowering the potential below the equilibrium potential ($E_{eq}$) given by Nernst law, the metal condition moves into a zone of immunity, the region where electrochemical attack, cannot occur. From Fig.\(\text{(2)}\) under freely corroding conditions the specimen has a mixed corrosion potential ($E$) and is corroding at a rate equivalent to ($i_{corr}$). In cathodic protection an external current ($i_1$) is supplied to the corroding metal by an auxiliary anode, so that the potential of the specimen is lowered to ($E_1$). Then the specimen will be partly protected, since the corrosion rate will have been reduced from ($i_{corr}$) to ($-i_{corr}$) If the externally applied current is increased to ($i_2$), so that the potential is lowered to ($E_2$), the reversible potential of the anodic reaction, anodic dissolution will be stopped. As a result there is no net loss of metal. Essentially the whole surface of the object is then providing sites only for cathodic reaction, which will be oxygen reduction, hydrogen ion reduction or both. The balancing anodic reaction occurs in a connected anode. This is the basis of cathodic protection of metals \cite{8,9}.
5. Materials Selection and Experimental Details

The materials used are the following:

1. Carbon Steel Pipe, (13 mm-diameter x 700 mm-long).
2. Brass Alloy Bar, (3 mm-diameter x 600 mm-long).

The chemical compositions are presented in Tables (1) and (2). With regard to concrete coating work, the following materials are used:

2. Aggregate Natural gravel of 20 mm max. size, sand is 10 mm max. size.
3. Water. Tap water is used for mixing and curing operations.

The chemical compositions are presented in Tables (3), (4), (5) and (6). Moreover, the preparation of concrete coating procedure was accomplished by the mixing proportions by weight of cement; fine and coarse aggregates are 1:2:4. The ingredient proportions are kept constant throughout the experimental work. The cement content is 350 kg/m$^3$, w/c ratio is 0.6 for all the specimens. An electric pan mixer has been used to mix concrete ingredients. Coarse, fine aggregate and cement are first fed into the mixer and mixed in a dry state for approximately two minutes. Having obtained a homogeneous mix, greater part of the designed amount of water is added, the remaining small amount is withheld until visual assessment made as to the required amount of water to achieve the required workability.

Table (1) Chemical Composition of the Steel Pipe used

<table>
<thead>
<tr>
<th>Materials</th>
<th>Composition %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Carbon Steel</td>
<td>.649</td>
</tr>
</tbody>
</table>

Figure (2) Principle of CP Illustrated on a Potential-Current Diagram
Table (2) Chemical Composition of the Brass Bar Alloy used

<table>
<thead>
<tr>
<th>Materials</th>
<th>Composition %</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Zn</td>
</tr>
<tr>
<td>Brass Alloy</td>
<td>30</td>
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Table (3) Percentage Oxide Composition and Main Compounds of Cement

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Content %</th>
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<tbody>
<tr>
<td>SiO₂, Silica</td>
<td>21.6</td>
</tr>
<tr>
<td>CaO, Lime</td>
<td>61.2</td>
</tr>
<tr>
<td>MgO, Magnesium Oxide</td>
<td>3.6</td>
</tr>
<tr>
<td>Fe₂O₃, Ferric Oxide</td>
<td>3.24</td>
</tr>
<tr>
<td>Al₂O₃, Aluminum Oxide</td>
<td>5.36</td>
</tr>
<tr>
<td>SO₃, Sulfur Trioxide</td>
<td>2.5</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>1.5</td>
</tr>
<tr>
<td>Insoluble Residue</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Main compounds</th>
<th>% by wt. of cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S, Tricalcium Silicate</td>
<td>37.88</td>
</tr>
<tr>
<td>C₂S, Dicalcium Silicate</td>
<td>33.35</td>
</tr>
<tr>
<td>C₃A, Tricalcium Aluminate</td>
<td>8.2</td>
</tr>
<tr>
<td>C₄AF, Tetra Aluminoferrite</td>
<td>9.85</td>
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Table (4) Sieve analysis of coarse aggregate

<table>
<thead>
<tr>
<th>Sieve size (mm)</th>
<th>Cumulative percentage passing</th>
<th>Limit of Iraqi Specification No. 45/1984</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.5</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>92.8</td>
<td>95-100</td>
</tr>
<tr>
<td>10</td>
<td>26.3</td>
<td>30-60</td>
</tr>
<tr>
<td>4.75</td>
<td>2</td>
<td>0-10</td>
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</tbody>
</table>

Sulphate content = 0.05% by weight of gravel as SO₃
Table (5) Sieve Analysis of Fine Aggregate

<table>
<thead>
<tr>
<th>Sieve size (mm)</th>
<th>Cumulative percentage passing</th>
<th>Limit of Iraqi Specification No. 45/1984</th>
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</thead>
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<tr>
<td>10</td>
<td>99.3</td>
<td>100</td>
</tr>
<tr>
<td>4.57</td>
<td>91.9</td>
<td>90-100</td>
</tr>
<tr>
<td>2.36</td>
<td>78.96</td>
<td>75-100</td>
</tr>
<tr>
<td>1.18</td>
<td>69.6</td>
<td>55-90</td>
</tr>
<tr>
<td>0.6</td>
<td>55.9</td>
<td>35-59</td>
</tr>
<tr>
<td>0.3</td>
<td>30.6</td>
<td>8-30</td>
</tr>
<tr>
<td>0.15</td>
<td>8.9</td>
<td>0-10</td>
</tr>
</tbody>
</table>

Sulphate content = 0.1% by weight of gravel as SO$_3$

Table (6) Chemical Analysis of Tap Water

<table>
<thead>
<tr>
<th>Ions</th>
<th>Concentration (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>156</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>49</td>
</tr>
<tr>
<td>Ca$^{++}$</td>
<td>68</td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>28</td>
</tr>
<tr>
<td>pH value</td>
<td>7.60</td>
</tr>
</tbody>
</table>

6. Instrumentation & Test Procedure

The following instruments were used:

1. Controllable DC power supply, providing a current of 2A max. at approximately 30V.
2. Digital multimeter type DT-830 BUZ, with DC mode.
3. Reference electrode, Acopper /copper sulphate electrode (CSE).

With regard to test procedure, the polarization of the working electrode (steel pipe) is achieved by the application of a constant current sufficient to produce the level of protection. The electrical circuit and test arrangement used is illustrated in Fig.(3). The supply of the protection current is controlled by the variable resistance.
7. Results and Discussions

The degree of control of the protection potential between different specimens is shown in Fig.(4). This figure shows clearly that the potentials of the specimens are consistently identical and that the potentials have been maintained almost constant throughout the activation period.

Figure (5) presents the variation with time of the nominal potential shift for the same specimens. The nominal potential shift is defined as, the difference between the initial corrosion potential and the newly attained potential during cathodic polarization. It can be seen that the nominal potential shifts have been maintained nearly constant throughout the activation period, which are analogous to the protection potential.

Figure (6) presents the effect of the level of cathodic polarization on the flowing current for the specimens. The results indicate that higher cathodic polarization, which reflects higher potential shift, as shown earlier in Fig.(5), would result in greater flowing current. It should be noted that the increase in current is proportional to the increase in potential.

The variation with activation period of the feeding voltage for test specimens is shown in Fig.(7). The feeding voltage is expressed as the voltage difference between the anode and the cathode. As would be expected, the lower the required protection potential the lower the feeding voltage is applied. Also this figure shows that the feeding voltage is slightly adjusted during the activation period in order to maintain the potential of the coated steel pipe at the...
required level. It is clear that the first hour of system energization requires the maximum feeding voltage.

Figure (4) Change in Protection Potential with Time of the Specimens of Different Protection Potential

Figure (5) Variation with time of the nominal potential shift of the specimens of different protection potential
Figure (6) Change in Current with Time for the Specimens under Three Level of Protection Potential

Figure (7) Change in Feeding Voltage with Activation Period for All Specimens
Figures (8) to (10) present the variation with time of the polarization variables monitored during the activation period for the specimens at the submerged zone. For a given test condition, the results clearly show that in all cases there is a difference between the protection potential and the instant off potential and that this difference is dependent on the potential shift. Accordingly, greater deviation between these potentials is associated with greater protection potential which obviously involves greater potential shift.

Periodic measurements of the 4-hrs and 24-hrs decay potential show that the potential decay is time dependent and tend to stabilize after (24-48) hrs from power switch off. It is interesting to observe that the electrode perturbation, i.e. the difference between the actual corrosion potential 24-hrs after the feeding system has been switched off ($E_{corr.24h}$) and the initial corrosion potential ($E_{corr}$), is also directly proportional with the amount of potential shift.

Figure (11) shows typical potential decay after interruption which indicate that greater proportion of decay is expected during the first 24-hrs regardless of the activation period. This observation is, in fact, suggesting that the actual potential shift ($\Delta E_{act}$) becomes that which is associated with the new stable corrosion potential. The new, i.e. upon system activation, potential shift is clearly lower than that applied initially which can conveniently be termed as the nominal potential shift ($\Delta E_{nom}$).

The instant off potential is theoretically the polarized potential of the steel-electrolyte interface independent of the position of the reference electrode relative to the coated steel pipeline. The difference between the protection potential ($E_{prot}$) and the instant off potential ($E_{IOP}$) presents the IR-drop across the electrolyte due to electrolytic resistance. Consequently, the IR-drop is dependent on the amount of the flowing current (I) and the coating resistance (R). Figure (12) indicates that the difference between ($E_{prot}$) and ($E_{IOP}$) is in fact increased as the potential shift increased. This is clearly expected as greater polarization potential produces greater flowing current for nearly constant coating resistance. The (IR) value will be increased accordingly. The coating resistance cannot, always, be determined from IR-drop value and the corresponding measured external current. Only when the resistance of the coating is uniform over the entire area that the IR-drop is directly proportional with the resistance through Ohm law:

$$\text{IR-drop} = \text{Voltage drop} = I_{\text{measured}} \times R \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1)$$

In the present work, the effect of the corrosion activity on the required protective potential is studied by deliberately increasing the corrosion activity of the coated steel pipe of selective specimens. Corrosion has been activated by polarizing the steel anodically to high positive potential exceeding 2V (CSE). This is achieved upon an application of a maximum of 4V (CSE) external voltage. The effect of prevention, corrosion and protection on the corrosion rate has been examined by an Tafel extrapolation method for specimen AD1. Tafel plots for the three cases are presented in the Fig.(13). Table (7) compares the protection current just
before the termination of the prevention and protection period with the corresponding corrosion rate as determined from Tafel plots.

**Figure (8) Change in Potential Parameters for the Specimen (AD1)**

**Figure (9) Change in Potential Parameters for the Specimen (AD2)**
Figure (10) Change in Potential Parameters for the Specimen (AD3)

Protection Potential = -1250 mV (CSE)

-1450
-1350
-1250
-1150
-1050
-950
-850
-750
-650
-550
-450
-350
-250
-150
0
10
30
50
70
90
110
130
150
170
190
210
Activation period (days)

Figure (11) Potential Decay Curve upon Current Switches off for the Specimen (AD1)

Protection Potential = -650 mV (CSE)

0
-150
-250
-350
-450
-550
-650
-750
Potential mV (CSE)

IR-drop

E_{corr} = -180 mV (CSE)

185 mV (CSE)

Activation period

185 days (activation period)

Time upon current switch off (hrs)
Figure (12) Dependence of IR-Drop Value on the Flowing Current for the Specimen of a Constant Resistance Value
Figure (13) Tafel Plots for the Specimen AD1 after Cathodic Prevention, Corrosion and Cathodic Protection
### Table (7) Protection Current & Corrosion Current

<table>
<thead>
<tr>
<th>Testing</th>
<th>$I_{\text{corr}}$ (mA)</th>
<th>$I_{\text{prot}}$ (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prevention</td>
<td>0.055</td>
<td>0.153</td>
</tr>
<tr>
<td>Corrosion at intermediate period</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>Protection</td>
<td>0.11</td>
<td>0.65</td>
</tr>
</tbody>
</table>

**Figure (14)** indicates that the total current flowing in the three different zones along the specimen of the same protection potential. This observation is of practical significance in that current measurements can not be relied upon to assess the degree of protection or the amount of current received by different parts of the structure unless reasonably accurate distinction between different anodic areas is established. For this reason, it is not possible to determine the current distribution of the specimens having different resistivity zones. If the resistance of different areas is known, the flowing current at each part of the specimens can be determined fairly accurately. The imposed current at different areas would produce an instantaneous potential shift ($\Delta E_{\text{act}}$) equals the difference between the rest potential ($E_{\text{corr}} = E_i$) and the newly attained electrode potential ($E_t$).

\[
I_1 = \frac{E_{\text{corr}} - E_{\text{t1}}}{R_1} = \frac{\Delta E_1}{R_1} \quad \text{................................................. (2)}
\]

and

\[
I_n = \frac{E_{\text{corr}} - E_{\text{tn}}}{R_n} = \frac{\Delta E_n}{R_n} \quad \text{................................................. (3)}
\]

Therefore:

\[
I_{\text{prot}} = \frac{\Delta E_1}{R_1} + \ldots + \frac{\Delta E_n}{R_n} \quad \text{................................................. (4)}
\]

These equations have an extremely significant practical implementation and enable the cathodic protection designer to estimate accurately the current distribution along various electrically connected anodic zones.
8. Conclusions

The following are the most notable conclusions which can be summarized as follows:

1. The mechanism of the polarization behavior of steel pipe structure in aqueous solution is a fundamental different because of the high resistance of concrete coating and the alkali environment in which becomes the dominance factor on the polarization trends and eliminate or confined the effect of polarization type technique of the electrode. Also, the results indicated that the relationship between the steel pipe potential and flowing current in calculation the electrical resistance of concrete coating is extremely important in account of the effect of environment in progressive or repulsion the corrosion processes.

2. The results described that the interpretation of potential and current data is an extremely delicate matter. In this respect, the peculiarities of the environment surrounding the steel pipe need to be fully appreciated including the multi anode effect.

3. The absolute value of the protection potential does not adequately describe the probable electrochemical changes undergone by the polarized steel pipe, unless taken in conjunction with other polarization related current and potential parameters. 4-hrs or 24-hrs decay criteria provide different information when used for system of different corrosion activity. It is, thus, not a reliable basis for performance evaluation.

4. The coating resistance cannot, always, be determined from IR-drop value and the corresponding measured external current. Only when the resistance of the coating is
uniform over the entire area that the IR-drop is directly proportioned with the resistance through Ohm law.

5. The instant off potential \( (E_{\text{IOP}}) \) provides the thermodynamic tendency for corrosion without providing quantitative information. It may lead to wrong conclusion and needs to be seen in conjunction with other electrochemical parameters.

6. An important setback of \( (E_{\text{IOP}}) \) criteria arises when \( (E_{\text{IOP}}) \) approaches \( (E_{\text{prot}}) \). In theory, this case represents the event when the actual polarization, as opposed to the nominal polarization, becomes zero with very small or no current flowing in the outer circuit.

9. References


Notations

CP = Cathodic Protection.
CPS = Cathodic Protection System.
CPP = Cathodic Protection Principles.
SACP = Sacrificial Anode Cathodic Protection.
ICCP = Impressed Current Cathodic Protection.
TR = Transformer Rectifier.
E = Potential.
E_{corr.} = Corrosion Potential.
E_{eq} = Equilibrium Potential.
E_a = Anodic Potential.
E_c = Cathodic Potential.
E_{corr 4} = 4-hrs Potential.
E_{corr 24} = 24-hrs Potential.
E_{prot} = Protection Potential.
E_{IOP} = Instant Off Potential.
E_i = Initial Corrosion Potential.
E_t = Actual Corrosion Potential at time (t).
i = Current Density.
i_a = Anodic Current Density.
i_{app} = Applied Current.
i_c = Cathodic Current Density.
i_{corr} = Corrosion Current.
i_{prot} = Protection Current Density.
I = Current.
R = Coating Resistance.
R_S = Variable Resistance.
CSE = Copper/Copper Sulphate Electrode.
\Delta E_{act} = Actual Potential Shifts.
\Delta E_{nom} = Nominal Potential Shifts.
AD1 = Test Specimen No. 1.
AD2 = Test Specimen No. 2.
AD3 = Test Specimen No. 3.