Predicting the Corrosion Rate of Steel in Cathodically Protected Concrete Using Potential Shift

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Abstract
The commonly accepted Cathodic Protection (CP) criterion i.e. 100mV decay evolves from experimental investigations and may not always be accurate. Alternatively, corrosion rate monitoring can assess the adequacy of CP. This work examines the possibility of predicting the corrosion rate of steel in concrete using polarization data induced by known applied current density using Butler Volmer equation. For this, the value of cathodic Tafel slope ($\beta_c$) plays an important role; decreasing $\beta_c$ from 210 to 60mV, decreases the corrosion rate by 92% at 20mA/m$^2$ current density.

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The adequacy of the proposed method is evaluated by applying Impressed Current Cathodic Protection (ICCP) to concrete specimens which have a zinc rich paint (ZRP) as an external anode for a short duration of time. Results showed that to achieve at least 100mV of depolarization, the applied current density should be at least 7 times the corrosion rate for the ZRP anode. However, this holds true, considering the short duration of the tests. Prediction of the corrosion rate of steel from potential shift forms the basis for the improved CP performance criterion for reinforced concrete structures.

**Keywords:** Corrosion; Reinforced Concrete; Cathodic Protection; Potential Shift; Butler Volmer Equation, Corrosion Rate

1. Introduction

Cathodic protection (CP) is an electrochemical technique used for halting or reducing the rate of corrosion in reinforced concrete structures without having to remove chloride-contaminated concrete [1–6]. In 1982, the U.S. Federal Highway Administration memorandum stated that ‘the only rehabilitation technique that has been proven to stop corrosion in salt-contaminated bridge decks regardless of the chloride content of the concrete is cathodic protection’[7]. It is cost effective in the long run compared to other electrochemical techniques. It can treat a larger area simultaneously and most importantly does not give rise to incipient anode problems. Therefore, it is the most suited repair technique to be employed in chloride contaminated structures [8].

The principle of CP is to deliver an appropriate cathodic polarization current to the protected structure so that the potential of the protected structure is negatively shifted such that the corrosion rate is either reduced or the steel reaches its passivation [2,9]. The suitability of CP can be assessed on two bases: 1) it involves thermodynamic considerations which include moving steel potential to the immune zone of Pourbaix diagram, 2) It involves examining the
kinetics of the involved reactions based on experimental measurements of current to potential relationships of both cathodic reactions and metal dissolutions [10]. Some of the methods used for monitoring are: Absolute Potential, Polarization curves, Depolarization method and AC impedance response. The most commonly used method for CP monitoring for atmospherically exposed structures is based on BS EN ISO 12696 criteria i.e. a) Instantaneous OFF potential more negative than -720 mV vs Ag/AgCl/0.5MKCl (silver-silver chloride) or b) 100 mV decay criterion [11]. However, the adequacy of 100 mV criterion has been challenged by some researchers and the theoretical basis for its use is still subject to investigation [12]. Moreover, 100 mV decay measurement alone might not be enough to accurately predict corrosion state of rebar. Therefore, for more accurate determination of corrosion state and to assess future corrosion risk, it is necessary to determine the corrosion rate of steel in concrete.

Corrosion rates are related to potential shifts and applied current density [13]. Stern and Geary, developed an experimental procedure for measuring corrosion rates known as Linear Polarization Resistance technique (LPR) [14]. The LPR method provides quantitative information on corrosion rates; however, the value obtained is an instantaneous value and is largely influenced by climatic changes such as temperature and humidity [15,16]. In this paper, an alternative approach is suggested to monitor the corrosion rate of steel in concrete after the application of cathodic protection, using the polarization data.

This work examines the adequacy of cathodic protection through the Butler Volmer equation and tests its validity when applied to reinforced concrete. The adequacy is tested by applying Impressed Current Cathodic Protection (ICCP) to concrete specimens having Zinc Rich Paint (ZRP) as an anode system. Zinc-rich paints (ZRPs) are efficiently used as an anticorrosion
paint on ferrous metals and as a substitute to hot-dip galvanizing [17]. They are used as a conductive coating anode for ICCP system in the present study.

2. Theoretical Basis

Considering equilibrium at any given point on the metal surface, the rate of forward and backward reactions is equal. In concrete, at equilibrium conditions, reactions given by Eq. 1 and 2 are equal at steel surface. However, when cathodic and anodic half cells are ionically (through concrete pore solution) and metallically (through reinforcement) connected, a net current flows between them and equilibrium potential shifts through polarization [18].

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \tag{1}
\]

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

If the concentrations of the reactants and products at the electrode surface are the same as in the bulk solution, the difference in potential from the reversible potential for a given reaction is called activation overvoltage or charge transfer overvoltage [19]. For such reactions, the relationship between the rate of reaction, which can be expressed by a current density \(i\), and the driving force for the reaction, or potential \(E\), is given by the Butler-Volmer equation (Eq. 3) [19,20]:

\[
i = i_c - i_\alpha = i_0 \left[ \exp \left( \frac{\eta - \varphi}{RT} \right) - \exp \left( \frac{\alpha_c \varphi}{RT} \right) \right] \tag{3}
\]

Where \(\eta = E - \varphi\) i.e. the difference between the potential, \(E\), when a net current flows through electrochemical cell and reversible half-cell potential, \(\varphi\); \(i_0\) (A/m²) is exchange current density; R is Gas Constant; F is Faraday’s Constant; \(T\) is Absolute Temperature and \(\alpha_c\) is the
fraction of total energy that decreases the energy barrier for cathodic reactions and $\alpha_a$ is the fraction of total energy that increases the energy barrier for anodic reactions.

At large over potential ($\eta$) and anodic partial current, the cathodic term becomes negligible and above equation is simplified to:

$$i = -i_a = \frac{1}{i}$$ (4)

$$i_a = i^0 \exp \left( \frac{-\alpha_a F \eta}{RT} \right)$$ (5)

Anodic sites on a steel surface are mainly polarized through the activation polarization [18]. Rearranging the above equation gives,

$$\eta_a = E_a - E_{Fe} = \beta_a \log \frac{i_a}{i^0}$$ (6)

Where, $E_a$ (V) is polarized anodic potential, $E_{Fe}$ as is given in Eq. 7, $\beta_a$ (V/dec) is anode Tafel slope given by $\beta_a = (2.3RT/\alpha_a F)$, $i^0$(A/m$^2$) is anodic exchange current density and $i_a$ (A/m$^2$) is anodic current density.

$$E_{Fe} = 0.440 - 0.0295 \log [Fe^{2+}]$$ (7)

On the other hand, cathodic sites on a steel surface can be polarized through both activation and concentration polarization, given by:

$$\eta_c = E_c - E_{O_2} = \beta_c \log \frac{i_c}{i^0} - \frac{2.303RT}{nF} \log \frac{i_c}{i_L + i_c}$$ (8)

\[ \text{Activation} \quad \text{Concentration Polarization} \]
Where, $E_c$ (V) is polarized cathodic potential, $E_{O2}$ as given in Eq. 9, $\beta_c$ (V/dec) is cathode Tafel slope given by $\beta_c = (-2.3RT/\alpha_c F)$, $i^0$ (A/m$^2$) is cathodic exchange current density, $i_c$ (A/m$^2$) is cathodic current density, $n$ is no. of electrons and $i_L$ is limiting current density (Eq. 10):

$$E_{O2} = 1.229 + 0.0148\log[O_2] - 0.0591pH$$  \hspace{1cm} (9)

$$i_L = \frac{DnFC_{O2}}{d}$$  \hspace{1cm} (10)

Where $d$ (m) is diffusion layer thickness, $D$ (m$^2$/s) is oxygen diffusion coefficient, $C_{O2}$ (mol/m$^3$ pore solution) is the concentration of dissolved oxygen on the concrete surface. The concentration polarization occurs only when oxygen availability at the cathodic site is not enough to sustain the oxygen reduction process [18].

In the 1950s, the Butler Volmer equation was simplified by assuming that the potential shift was small (10-20 mV). The relationship between current and potential was approximated to be linear rather than exponential when measured close to equilibrium potential and the linear polarization method was developed. Thus, approximating the exponential terms of the above B-V equation (Equation 3) based on ($e^x = 1 + x$):

$$\exp\left(\frac{-\alpha_nF\eta}{RT}\right) = 1 + \left(\frac{-\alpha_nF\eta}{RT}\right)$$  and  $$\exp\left(\frac{(1-\alpha)F\eta}{RT}\right) = 1 + \left(\frac{(1-\alpha)F\eta}{RT}\right)$$  \hspace{1cm} (11)

$$i = -i^0\frac{\eta F\eta}{RT} = \frac{B}{R_P}$$  \hspace{1cm} (12)
Where \( R_p = \frac{R_T}{nF} \) is polarization resistance and \( B \) is Stern Geary constant. The value of
Stern Geary Constant i.e. \( B = \frac{\beta_a - \beta_c}{2.303(\beta_a + \beta_c)} \) is typically used as 26 mV for an active steel
and 52 mV for a passive steel [21,22].

The LPR method is most widely used to measure corrosion rates. However, the value
obtained through LPR is approximated, instantaneous and largely influenced by climatic
changes such as temperature and humidity [15,16]. This may lead to over or underestimation
of corrosion rates. However, the LPR method cannot be used at potential shifts above 20mV,
thus limiting its use for corrosion rate estimation for monitoring cathodic protection.

Alternatively, for Cathodic Protection, using the polarization data, corrosion rate can be
predicted using the Butler Volmer Equation. Modifying equation 3 and substituting
\( \beta_c = (-2.3RT/\alpha_c F), \beta_a = (2.3RT/\alpha_a F), i = i_{app}, i^0 = i_{corr}, \eta = \Delta E \)

\[
i = i^0 \{\exp \left( \frac{2.3\eta}{\beta_c} \right) - \exp \left( \frac{-2.3\eta}{\beta_a} \right) \}
\]

\[
i_{app} = i_{corr} \left( \exp \left( \frac{2.3\Delta E}{\beta_c} \right) - \exp \left( \frac{-2.3\Delta E}{\beta_a} \right) \right)
\]

Where \( i_{app} \) is the applied current density, \( i_{corr} \) is the corrosion rate, \( \Delta E \) is the potential shift
and \( \beta_a \) and \( \beta_c \) are constants. This will give a better and more accurate prediction of the
corrosion rate in comparison to LPR.

In the present paper, this method is used to predict corrosion rate after cathodic protection of
steel.
3. Experimental Method

3.1 Specimens

Three reinforced concrete slab specimens of size 200×200×70 mm were made of C32/40 grade concrete with a water-cement ratio of 0.5. The details of the concrete mix proportions are presented in Table 1. Each specimen contained two 10 mm diameter ribbed steel bars with an exposed length of 100 mm and a silver/silver chloride (Ag/AgCl/0.5M KCl) reference electrode. 3% NaCl solution was used for both curing and mixing to investigate the performance of cathodic protection and its equivalent percentage by weight of cement was deliberately added to the mixing water during casting. Specimens were demoulded after 24 hours and cured in potable water for a total period of 28 days.

<table>
<thead>
<tr>
<th>Mix</th>
<th>w/c Ratio</th>
<th>Water (kg/m³)</th>
<th>Ordinary Portland Cement (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Gravel (kg/m³)</th>
<th>Chloride (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3% Chloride</td>
<td>0.5</td>
<td>180</td>
<td>360</td>
<td>640.5</td>
<td>1189.5</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Table 1. Mix proportioning of concrete specimens

The surface of the specimens was prepared by wire brushing so that it attains medium roughness. Then primary anode conductor (Anomet Cu/Nb/Pt wire of 2mm diameter) was fixed on the top surface of concrete slab using epoxy resin. Then, the top face of each slab specimen was painted with three layers of Zinc Rich Paint (ZRP), making sure that the primary anode conductor is covered with the ZRP (Fig. 1) [23]. ZRP was used as an anode material to provide an impressed current cathodic protection to steel in concrete. Because of the pending patent and commercial confidentiality, it is not possible to disclose the full chemical composition of the ZRP. The specimens were then kept in the curing tank containing 3% NaCl water so that the samples were partially submerged in the salt solution. The environmental temperature conditions were kept constant at 23±1°C.
The cathodic polarization test was carried out on the specimens at five levels of current densities, i.e., 10, 20, 30, 40 and 50 mA/m$^2$ of steel surface area, which were approximately 3.12, 6.25, 9.37, 12.5 and 15.62 mA/m$^2$ of the anode surface area. Each sample was polarized five times for different level of current densities. The constant current output was supplied for 3 days at each current level as steel/concrete potential shift became negligible after 3 days, and the polarization characteristics were recorded every minute using a computerized data logger. After 3 days, the ICCP system was switched off and instant-off potentials were recorded. The depolarization was continuously monitored using the computerized data logging for a 24-hour period, at a 1-minute interval. The polarization and depolarization data obtained from the application of various current densities in the experiment mentioned above were used to assess the corrosion rate using the Butler Volmer equation (Eq. 14).

The LPR test was performed to determine the initial corrosion rate of the specimen before the application of CP by applying a small perturbation using a Potentiostat (make: Digi-Ivy, model DY 2300) to the slab specimens. In this method, reinforcements were polarized at a sweep rate of 0.01V/min within the range of potential change from -20 mV to +20 mV.
4. Experimental Results and Discussion

4.1 Cathodic Polarization of Steel in Concrete using ZRP Anode

The polarization and depolarization behavior evaluation of the ZRP anode with five different current densities (10, 20, 30, 40 and 50 mA/m² per steel surface area) respectively are shown in Fig. 2. Some spikes were observed in the graph due to the fluctuation in the power supply to maintain a constant current.

![Graph](image)

Fig. 2. (a) Polarization and (b) Depolarization behaviour of specimens at five different current densities w.r.t Ag/AgCl/0.5MKCl reference electrode

The steel/concrete potential shift and potential decay for each current density is shown in Table 2. Potential shift is used to describe the difference between pre-energization potential and instant off potential, whereas potential decay is used to describe the extent of depolarization from instant off potentials. It can be observed that the higher the applied current density, the higher the steel/concrete potential shift. Moreover, the 100 mV decay
criterion was met at 40 and 50 mA/m² of current density per steel surface area. The instant off potentials are IR free potentials.

<table>
<thead>
<tr>
<th>Current density/steel area (mA/m²)</th>
<th>Current density/anode area (mA/m²)</th>
<th>Pre energization Potential (mV)</th>
<th>Instant Off Potential (mV)</th>
<th>Steel/Concrete Potential Shift (mV) vs Ag/AgCl/0.5MKCl</th>
<th>24 hr Decay (mV) vs Ag/AgCl/0.5MKCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>3.12</td>
<td>-393</td>
<td>-411</td>
<td>-18</td>
<td>16</td>
</tr>
<tr>
<td>20</td>
<td>6.25</td>
<td>-320</td>
<td>-376</td>
<td>-56</td>
<td>48</td>
</tr>
<tr>
<td>30</td>
<td>9.37</td>
<td>-318</td>
<td>-383</td>
<td>-65</td>
<td>80</td>
</tr>
<tr>
<td>40</td>
<td>12.50</td>
<td>-300</td>
<td>-486</td>
<td>-186</td>
<td>180</td>
</tr>
<tr>
<td>50</td>
<td>15.62</td>
<td>-342</td>
<td>-498</td>
<td>-156.0</td>
<td>153</td>
</tr>
</tbody>
</table>

**Table 2. Summary of polarization test results**

Further, corrosion rate was determined from the modified BV equation (Eq. 14) using the potential shift and the applied current density data and assuming an anodic and cathodic Tafel slope of 120 mV. The relationship between potential shift and corrosion rate is shown in **Fig. 3**. The negative shift in steel/concrete/electrode corrosion potential is accompanied by a logarithmic decrease in the corrosion rate i.e. the higher the potential shift during polarization, the lesser the corrosion rate.

![Fig. 3. Relationship between potential shift and corrosion rate](image-url)
As per BS EN ISO 12696: 2016 [11], the boundary between steel in a passive state and low corrosion risk is at an average of 2 mA/m\(^2\) corrosion rate. From Fig. 3, it can be seen that in order to move steel/concrete/electrode potential to the passive zone, a minimum of 150 mV potential shift is required during ICCP using a ZRP anode system. However, this criterion holds true only considering the short period of testing. For a longer period of polarization, the potential shift required might be different.

Table 3 shows the corrosion rate measured using the LPR and BV methods before and after the polarization respectively. A decrease in corrosion rate is observed after the application of CP. Corrosion rate could not be determined from the LPR after polarization as it is limited for potential shifts less than 20 mV.

<table>
<thead>
<tr>
<th>Applied Current Density (mA/m(^2))</th>
<th>Corrosion Rate before CP: LPR (mA/m(^2))</th>
<th>Corrosion Rate after CP: BV (mA/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>19.1</td>
<td>18.0</td>
</tr>
<tr>
<td>20</td>
<td>19.6</td>
<td>14.0</td>
</tr>
<tr>
<td>30</td>
<td>11.7</td>
<td>10.6</td>
</tr>
<tr>
<td>40</td>
<td>16.5</td>
<td>1.2</td>
</tr>
<tr>
<td>50</td>
<td>9.4</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 3: Corrosion rate before and after polarization

4.2 Effect of Tafel slope on Corrosion Rate Estimation

For on-site measurement, to predict the corrosion rate from linear polarization resistance method, \(\beta_a = \beta_c = 120\) mV, which gives B=26 mV is recommended [16]. Fig. 4. shows the effect of cathodic and anodic Tafel slopes on the corrosion rate estimation at different current densities. The values are obtained by changing \(\beta_c\) and \(\beta_a\) value from 30 to 210 mV and using potential shift data from the polarization results.
Fig. 4. Effect of (a) Cathodic and (b) Anodic Tafel slope on corrosion rate estimation at different current densities

It can be observed that the effect of the anodic Tafel slope is small when compared to the cathodic Tafel slope. An increase of $\beta_c$ value from 60 to 210 mV, increased the corrosion rate from 0.4 to 5.7 mA/m² at 20 mA/m² current density. On the other hand, a change in $\beta_a$ from 60 to 210 mV increased corrosion rate slightly from 2.07 to 2.13 mA/m² at 20 mA/m². Hence, corrosion rate estimation is more sensitive to the $\beta_c$ value, and considering it as a constant value may result in errors in corrosion rate prediction.

Thus, for further analysis, $\beta_c$ is predicted by plotting the change in steel/concrete/electrode potential against the logarithm of the applied current after each polarization. The slope of the curve will give an indication of the cathodic Tafel slope (Fig. 5).

Fig. 5. Prediction of cathodic Tafel slope from a potential-current graph
The tafel slopes obtained were 147 mV, 173 mv and 219 mV for 10, 20 and 30 mA/m² of current density respectively. In all the cases, the estimated cathodic Tafel slope is more than 120 mV. Thus a Tafel slope of 120 mV used to evaluate the protection level will result in underestimation of the corrosion rate. This will risk suggesting a low corrosion that may not be the case in practice.

4.4 Protection Criteria

The steel/concrete potential shift vs Ag/AgCl/0.5MKCl is plotted against the ratio of the applied current density to corrosion rate from Butler Volmer (calculated from Eq. 14) in Fig. 6. It can be observed that a higher ratio of applied current density to corrosion rate is accompanied by a higher potential shift.

As mentioned above, the most commonly used and recommended cathodic protection monitoring criterion is to measure 100 mV potential decay following the interruption of the polarization current [11,24]. This implies that in order to achieve this criterion, at least 100 mV of potential shift is required. Thus, from Fig. 6, it can be estimated that when the ZRP is used as the primary anode for cathodic protection of steel in concrete, to achieve this criterion, the applied current density should be at least 7 times the corrosion rate. This was in close agreement with the ratio suggested by Glass et al. [12]. As in all the specimens, steel was in a highly chloride contaminated environment before application of ICCP, thus the steel
was in a moderate to high corrosion risk state. Considering the boundary between moderate and high corrosion risk, as recommended by the Concrete Society Technical Report No. 60 [25] to be average 5 mA/m² corrosion rate, the required current density to satisfy ICCP protection criterion is minimum 7 times the corrosion rate i.e. 35 mA/m² per steel surface area.

This confirmed the previous postulate where 40 mA/m² per steel surface area equivalent to 12.5 mA/m² per anode surface area was obtained as an optimum current density required for cathodic polarization of steel in concrete using ZRP anode to satisfy 100 mV decay criterion. Moreover, it was observed in Fig. 3 that to move steel/concrete potential to a passive zone in the case of using the ZRP anode system for cathodic protection, at least 150 mV potential shift is required. Thus from Fig. 6, it is estimated that the applied current density should be at least 15 times the corrosion rate to achieve 150 mV potential shift. Since the optimum applied current density is 40 mA/m² per steel surface area (i.e. 12.5 m² per anode surface area), the achievement of this implies that steel is in near passive state.

However, this postulate holds true considering the short duration of the test, as a result BS EN ISO 12696 criteria (a) [11] was not achieved for lower applied current densities. Hence a higher current density was applied. Moreover, samples were polarized in partially saturated conditions, thus requiring a higher potential shift to satisfy the BS EN ISO 12696 criterion (b) [11]. For atmospherically exposed concrete specimens polarized for longer durations, criterion (b) could be met with a smaller current density.

5. Conclusion

Potential shift data obtained from polarization results by applying a known current density may be used to successfully estimate the corrosion rate of steel in concrete using the Butler Volmer equation.
Moreover, it was observed that the cathodic Tafel slope ($\beta_c$) plays an important role in corrosion rate estimation. Keeping this value constant, as in the case of LPR, results in an underestimation of corrosion rate. Moreover, results showed that to achieve at least 100 mV of depolarization, the applied current density should be at least 7 times the corrosion rate, which is true considering the short duration of the test. For atmospherically exposed concrete that is polarized for a longer period of time, CP performance criteria could be achieved for lower current density. Hence, predicting corrosion rates from the BV equation using potential shift forms the basis for an improved cathodic protection performance criterion for atmospherically exposed reinforced concrete.

6. References


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**Declaration of Interest**

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.