ASSESSMENT OF THE EFFECTIVENESS OF BUTLER-VOLMER EQUATION TO PREDICT CORROSION RATE IN CATHODICALLY PROTECTED STRUCTURES

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ABSTRACT

Various reinforced concrete structure around the world, such as bridges are exposed to aggressive chloride environment, hence, start to corrode after short service period. The main reason for the deterioration of these structures is corrosion of steel reinforcement due to chlorides. Poor quality concrete and low cover are contributory factors. The cost of repairing or replacing the deteriorated structure has become the major concern for the asset owners. One of the most successful and substantiated techniques of protecting structure from corrosion is cathodic protection (CP). The BS EN ISO 12696 performance criteria followed for monitoring CP efficiency is evolved from the experimental analysis and may not be always correct. This paper suggests an improved method for monitoring corrosion rate through Butler Volmer equation using the polarization data. This method has been applied to one year CP monitoring data from a viaduct site. It was observed that corrosion rate was reducing with time, showing the effectiveness of CP to protect the steel in structure. Prediction of corrosion rate of the steel from potential shift forms the basis for the improved CP performance criterion for reinforced concrete structures. Information about the actual corrosion rate would be beneficial to predict the true state of steel reinforcement and accordingly apply a suitable repair technique to extend the service life of RC structures.

Keywords: Corrosion, Cathodic Protection, Potential Shift, Butler Volmer equation, Corrosion Rate

INTRODUCTION

Corrosion of steel bars is one of the biggest durability issue for reinforced concrete structures. Out of various preventive techniques, cathodic protection (CP) technique has been shown to be highly effective to prevent corrosion of steel in chloride contaminated concrete (Goyal et al., 2018). The technique is based upon delivering required DC current to the steel to be protected to shift its potential to negative direction such that corrosion rate is either significantly reduced or steel reaches its passivation (Goyal et al., 2019; Marcassoli et al., 2015).

The most common protection criteria used to monitor the performance of CP system is to check 100 mV potential decay following interruption of the potential current (Atkins and Macdonald, 2010.; Eichler et al., 2009; Funahashi and Bushman, 1991; Glass, 1999; Gummow, 2007). The magnitude of the potential decay required is usually 100 mV. This is referred to as 100 mV decay criteria. This method is recommended by BS EN ISO 12696:2016 (British Standards Institution, 2016).

Most of the structures in natural environment, cannot achieve thermodynamic reversibility and immunity (Barlo, 2001). Thus, corrosion control is achieved by reducing the corrosion process kinetics (i.e. corrosion rate) to sufficiently low levels that corrosion appears to be stopped. 100 mV polarization criteria achieves corrosion control in this way (Barlo, 2001). However, this method was evolved mainly from experimental basis. The disadvantage of this method is that it cannot be used with mixed metal structures (Barlo, 2001; Gummow, 2007). Moreover, it is not considered valid when elevated temperature or sulphate reducing bacteria are present (Khosravi and Ghafourian, 2013, 2012). Furthermore, some researchers has challenged the adequacy of 100 mV criterion and the theoretical basis for its use is still subject to investigation (Glass et al., 1997).

This paper suggests an improved method for monitoring corrosion rate through Butler Volmer equation using the polarization data, which forms the basis for monitoring efficacy of CP structure. The modified method was used to evaluate one year monitoring data collected from a cathodically protected 20-span viaduct in Peterborough.

NEW APPROACH FOR CP PERFORMANCE ASSESSMENT

In 1950, the Butler Volmner equation, given in eq (1), was simplified by assuming potential shift was small (10-20mV) and forms the basis of most widely used linear polarization resistance (LPR) method used to measure corrosion rate of steel. The simplified butler Volmer equation is given in eq (2).

$$i = i^o\{exp\left(\frac{-\alpha_c F\eta}{RT}\right) - exp\left(\frac{\alpha_a F\eta}{RT}\right)\}$$
(1)

Where $\eta = E - e_e$ i.e. the difference between the potential, E, when a net current flows through electrochemical cell and reversible half-cell potential, e_e; i^o (A/m^2) is exchange current density; i is current density; R is Gas Constant; F is Faraday's Constant; T is Absolute Temperature and α_c is the fraction of total energy that decreases the energy barrier for cathodic reactions and α_a is the fraction of total energy that increases the energy barrier for anodic reactions (Popov, 2015).

$$i = -i^o \frac{nF\eta}{RT} = \frac{B}{R_p} \tag{2}$$

Where $R_p = \frac{RT}{nFi^o}$, is polarization resistance and B is Stern Geary constant. The value of Stern Geary Constant i.e. B ($B = \frac{\beta a * \beta c}{2.303(\beta a + \beta c)}$) is typically used as 26 mV for an active steel and 52 mV for a passive steel (Song and Saraswathy, 2007).

Since, this method is only limited to 10-20 mV shift, it's not applicable for monitoring CP performance. Hence, Butler Volmer equation was improved as given in eq (3), which can be used for CP performance assessment. The detailed analysis of the method is given in author's previous work (Goyal et al., 2019).

$$i_{\text{app}} = i_{\text{corr}}\{exp\left(\frac{2.3\Delta E}{\beta_c}\right) - exp\left(\frac{-2.3\Delta E}{\beta_a}\right)\} \tag{3}$$

Where i_{app} is the applied current density, i_{corr} is the corrosion rate, ΔE is the potential shift and β_a and β_c are constants.

The method uses polarization results from CP monitoring data, in which the steel/concrete/electrode potential shift, and applied current density are the major parameters. Moreover, value of cathodic tafel slope (β_c) plays a major role. The tafel slopes are obtained 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 (β_c). Anodic tafel slope (β_a) has minimal effect on the corrosion rate prediction and thus taken as constant of 120 mV, which is used while LPR monitoring.

BRIEF DESCRIPTION OF THE STRUCTURE AND ANODE SYSTEMS

The structure selected for monitoring was 20-span viaduct in Peterborough. Each span was approximately 16m. The structure comprises 6 leaf piers and 14 T shape piers. Cathodic protection was applied to the structure in 2008 as part a major refurbishment scheme to prevent RC elements from further deterioration and reinforcement corrosion. For the present analysis, 3 no. piers were selected.

The Anode System

Three types of anodes were used for installation of CP to the piers i.e. (a) De Nora LIDA 19mm diameter MMO/Ti based discrete anodes, (b) Elgard 150 mesh anodes, and (c) Elgard 100 ribbon mesh anode. Pier 1 and 2 have similar geometry and are protected by installing rows of ribbon anodes on all four sides of a column at a spacing of 300mm (Figure 1 (a) and (b)). The bearing shelf is protected by discrete anodes with ribbon anodes on soffit and sides (Figure1 (c)). Each pier is divided to a number of zones as shown in Figures 1. For present analysis 4 ribbon anode zones (two from column and 2 from crossbeam) and 1 discrete anode zone were selected for pier 1 and 2. Data were collected remotely using a dedicated software and downloaded to an off-site computer in an Excel file format.

Pier 3 is leaf pier and has discrete anode zone at the top and mesh anode zone on the side (Figure 2). For analysis, one discrete anode zone and one mesh anode zone were selected. Details of all the CP zones and anode system are given in Table 1.

(a) North Elevation Column: Zone 1 (North and South combine)

(b) West Elevation Column: Zone 2 (West and East combine)

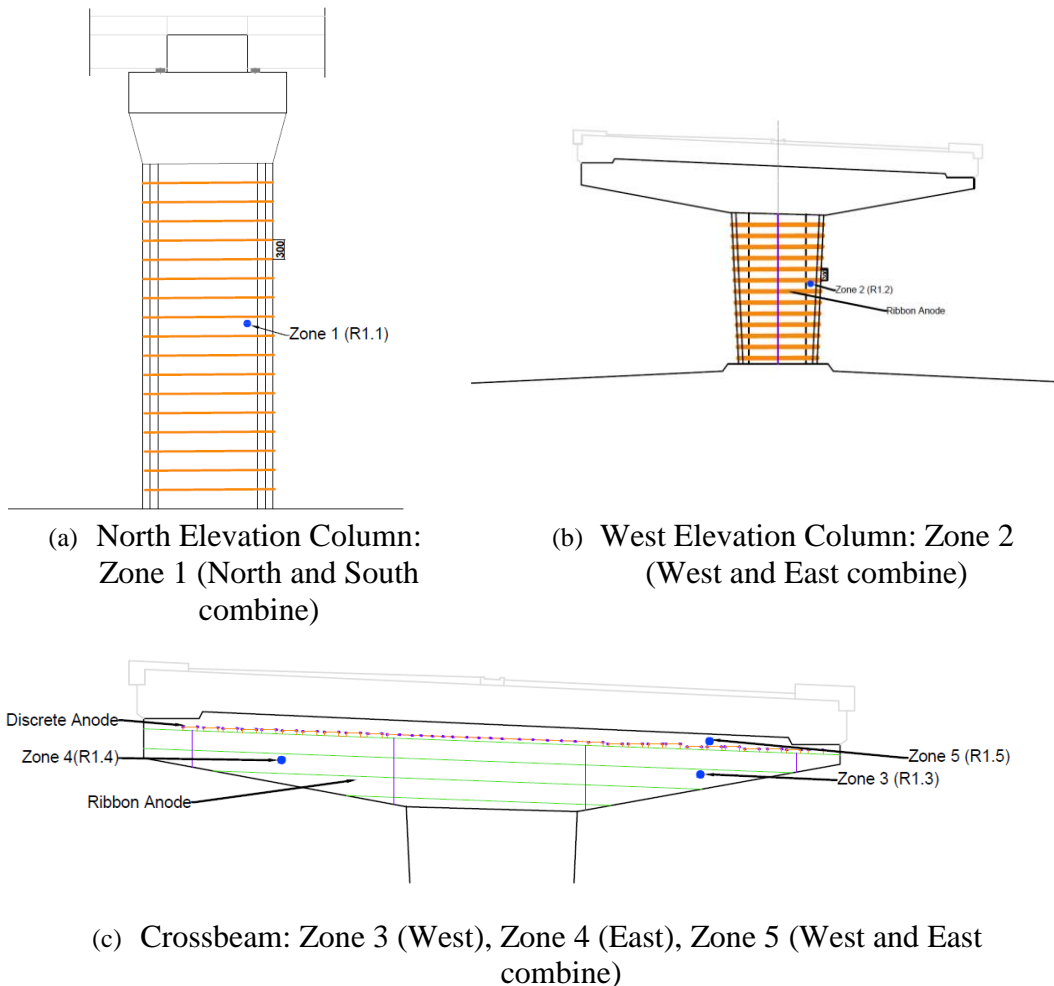(c) Crossbeam: Zone 3 (West), Zone 4 (East), Zone 5 (West and East combine)

Figure 1: Pier 1 showing anode placement (a) North elevation (b) West elevation (c) Crossbeam
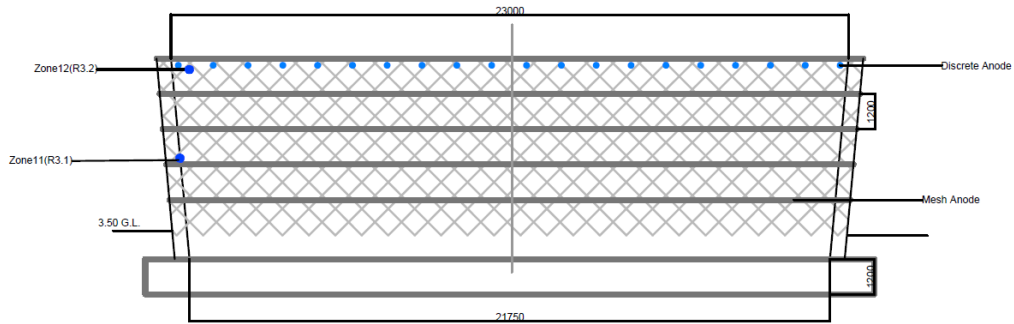

Figure 2: Pier 3 showing anode placement: Zone 11 and 12 (West and east side combine)

Table 1: Details of the selected anodes

Pier	Zone	Reference Electrode	Anode
Pier 1	1	R1.1	Ribbon
	2	R1.2	Ribbon
	3	R1.3	Ribbon
	4	R1.4	Ribbon
	5	R1.5	Discrete anode
Pier 2	6	R2.1	Ribbon
	7	R2.2	Ribbon
	8	R2.3	Ribbon
	9	R2.4	Ribbon
	10	R2.5	Discrete anode
Pier 3	11	R3.1	Mesh anode
	12	R3.2	Discrete anode

The site images of the installed or during installation of various anodes are shown in Figure 3.

Figure 3: Site images showing anode installation (a) Pier 3 (b) Pier 1and 2

ANALYSIS AND DISCUSSION

CP Monitoring Using 100 mV Decay Criterion

Individual CP Zones were energised at initial 25% of their design current density of $15mA/m^2$ and then adjusted over time The polarization behaviour of the anodes zones were observed and analysed after period of 1 month and 1year by automatic pre-programmed switching off the power supply and monitoring steel/concrete 24 hours potential decay. All decay values were measured from instant off potentials with respect to silver/silver chloride reference electrodes. Results are shown in Table 2. All the zones showed at least 100m V decay after both 1 month and 1 year of polarization, thus satisfies the BS EN 12696: 2016 criterion (British Standards Institution, 2016). However, this method only satisfied the standard requirement for performance of the CP technique and do not provide any information with which or the remaining service life of the structure can be estimated.

Table 2: Polarization results for various zones after 1 month and 1 year

Zone	Reference Electrode	Potential shift (mV):1 month	Potential shift (mV):1 year	24 h decay (mV): 1 month	24 h decay (mV): 1 year
1	R1.1	-145	-128	160	143
2	R1.2	-166	-166	198	196
3	R1.3	-319	-290	301	262
4	R1.4	-200	-178	254	234
5	R1.5	-214	-155	235	188
6	R2.1	-155	-179	159	161
7	R2.2	-325	-300	215	280
8	R2.3	-265	-171	282	235
9	R2.4	-374	-333	274	242
10	R2.5	-293	-242	268	241

| 11 | R3.1 | -217 | -224 | 149 | 156 |
| 12 | R3.2 | -186 | -163 | 192 | 180 |

Corrosion Rate Determination from Improved Monitoring Method

The cathodic tafel slope (β_c) is obtained by plotting the change in steel/concrete/electrode potential against the logarithm of the applied current density, as shown in Figure 4. It can be observed that β_c changes for different zones and is not constant (120 mV) as considered while measuring corrosion rate using LPR on site.
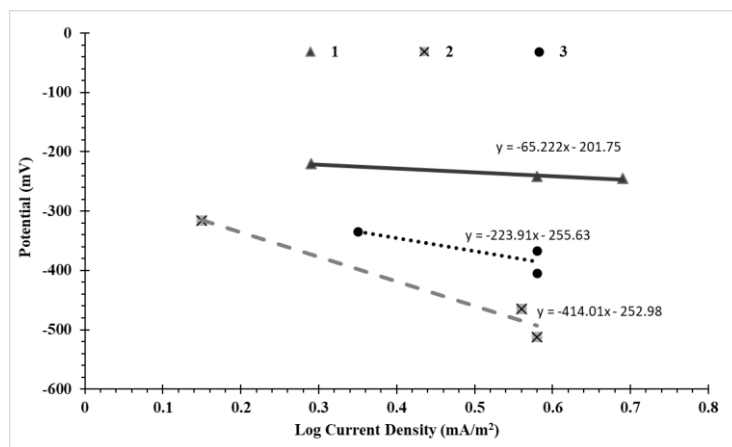

Figure 4: Cathodic Slope prediction from potential current graph

Figure 5 shows corrosion rate calculated using modified Butler Volmer equation (Equation 3) with an assumption of β_c to be 120 mV (Figure 5(a)) and β_c obtained from Figure 4 (Figure 5(b)). It can be observed that assuming β_c to be 120 mV constant gives an underestimation of the corrosion rate.
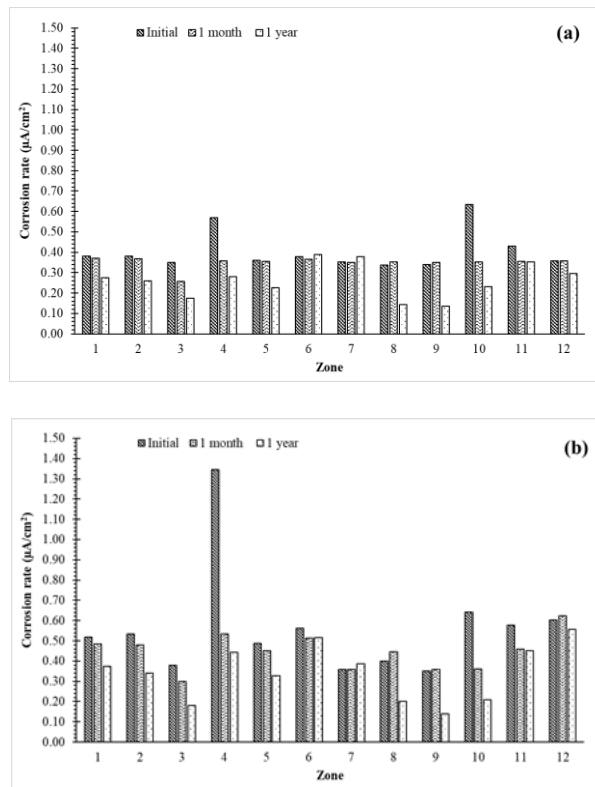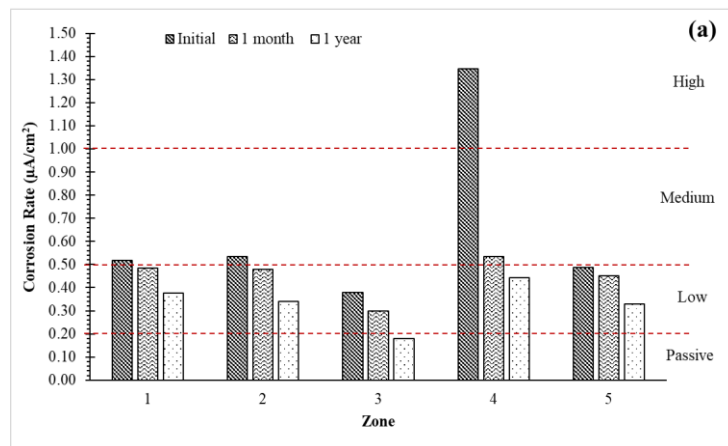
Figure 5: Corrosion rate for different zones considering cathodic tafel slope of (a)
120 mV (b) obtained from cathodic slope prediction (Figure 4)

Performance of individual CP zones are also shown in Figure 6 against published
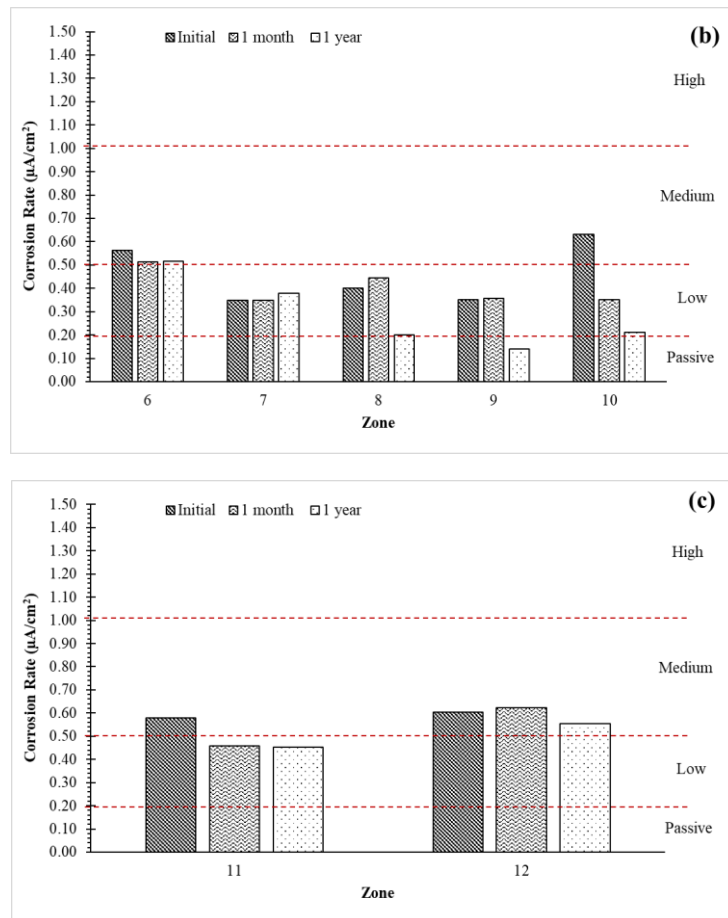corrosion state as suggested by concrete society (Report, 2004) given in Table 3

Figure 6: Corrosion rate using suggested method of monitoring for different zones
(a) Pier 1 (b) Pier 2 and (c) Pier 3

Table 3: Corrosion current vs. condition of the rebar (Report, 2004)

Corrosion current (I_{corr}), $\mu A/cm^2$	Condition of the rebar/ corrosion rate
< 0.1-0.2	Passive
0.2 – 0.5	Low to moderate corrosion
0.5 – 1.0	Moderate to high corrosion
>1.0	High corrosion

It can be observed from Figure 6 that corrosion rate decreases with time for all the zones and piers. Cathodic protection is observed to be highly effective for zones shown in figure 6. For zone 3, 8, 9 and 10 steel moves to passive zone after 1 year of CP application. The largest drop in corrosion rate was observed for zone 8, where corrosion rate dropped by 67% moving steel from highly corrosive to low corrosion state. This shows the effectiveness of CP for pier 1 and 2.

Moreover, for pier 3, steel does not show a much drop in corrosion rate and steel remains in its initial corrosion state. Thus, requires longer protection or increased current output for the zones.

Comparing the results from two different analysing methods, it can be clearly observed that suggested improved method gives the better indication of the efficacy of the preventive technique. 100 mV decay criterion shows that for each zone prevention has been achieved, however that is not true seeing the corrosion rate of steel from the modified method.

CONCLUSION

The commonly used 100 mV decay criteria is evolved from experimental investigation and may not always be accurate. Suggested method of monitoring by using potential shift data obtained from polarization results by applying a known current density can be used to get an estimation of the corrosion state of steel and the efficiency of the CP using Butler Volmer equation. A decrease in the corrosion rate also indicates that CP is providing effective protection.

Moreover, corrosion rate estimation is highly sensitive to value of cathodic tafel slope. Corrosion rate estimated from analysing the field data assuming cathodic tafel slope to be 120 mV constant gives an underestimation of the corrosion rate. Data obtained from suggested method will be beneficial to structural engineer for structural assessment. Corrosion rate obtained can be used to estimate the capacity of the structure in the long run and estimate the remaining service life.

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