

Assessment of cathodic protection applied to above ground reinforced concrete

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Standard practice allows the use of developing expertise in the assessment of cathodic protection of steel in concrete. This work sets out a theoretical and empirical basis for such an assessment. Assessment may be based on the observation that, at protection current densities typically used in reinforced concrete, the degree of polarization provides an indication of steel corrosion risk. An example is, a steel polarization of 55 mV or more achieved by a protection current of 5 mA m⁻² or less is indicative of passive steel reinforcement. Such risk assessment criteria are supported by both theory and practice. Polarization is generally a consequence, not a cause, of steel passivity in concrete. The removal of chloride from, or the generation of hydroxide at the steel surface dominate the restoration of steel passivity. Flexibility over the degree of polarization required in cathodic protection systems may be used to address adverse effects associated with the delivery of protection current.

KEYWORDS

cathodic protection, corrosion, electrochemical calculation, passivity, polarization, steel reinforced concrete

1 | INTRODUCTION

Widely accepted standard practice for the cathodic protection of above ground (atmospherically exposed) reinforced concrete justifiably allows for developing expertise in respect of criteria of protection for steel in concrete to accommodate innovation (BS EN ISO 12696:2016, section 8.6).^[1] This option has occasionally been exercised. Examples include the assessment of applications of sacrificial and hybrid corrosion protection systems^[2,3] and the assessment of an interrupted impressed current cathodic protection trial.^[4] However, the use of alternative assessment criteria to those specifically listed in the standard (albeit in a non exhaustive list) has been the source of some debate.^[5] This work considers the theoretical and empirical basis for acceptance criteria applicable to both impressed current and sacrificial cathodic protection systems in above ground reinforced concrete that are allowed in current standard practice.

2 | BACKGROUND THEORY

2.1 | Electrochemical polarization

The main reactions which characterize the corrosion of steel are the anodic dissolution of iron and the cathodic reduction of oxygen. These are dependent on electrode potential and current. The relationship between potential shift and applied current is termed polarization behavior. Polarization (potential shift) arises from activation and mass transfer (diffusional) processes, as well as the resistance of a connecting electrolyte. The well-known textbook theory describing the polarization behavior of these processes is briefly summarized below.^[6]

An applied cathodic current density (i_{appl}) is given by the difference between the cathodic and anodic reaction rates (i_{cath} and i_{an}):

$$i_{\text{appl}} = i_{\text{cath}} - i_{\text{an}} \quad (1)$$

$$\eta = \eta_a + \eta_m \quad (6)$$

This polarizes the steel potential to more negative values. The activation contribution to cathodic and anodic reaction polarization is described by the equations:

$$i_{\text{cath}} = i_{\text{corr}} \exp\left(\frac{2.3\eta_a}{\beta_c}\right) \quad (2)$$

$$i_{\text{an}} = i_{\text{corr}} \exp\left(-\frac{2.3\eta_a}{\beta_a}\right) \quad (3)$$

where i_{corr} , η_a , β_c , and β_a are the corrosion rate in the absence of applied current (open circuit rate), activation polarization, cathodic, and anodic Tafel constants respectively.

The applied current and activation polarization (activation controlled potential shift) are related to the corrosion rate. In 1957 the above equations were simplified based on the assumption that at small potential shifts, the exponential function can be linearized.^[7] While this approximation is still widely used today, it is worth noting that it was only generally required at that time because of the difficulties associated with calculating the output of an exponential function. The analytical solution to the above equations is:

$$i_{\text{corr}} = i_{\text{appl}} / \left(\exp\left(\frac{2.3\eta_a}{\beta_c}\right) - \exp\left(-\frac{2.3\eta_a}{\beta_a}\right) \right) \quad (4)$$

Previously reported corrosion rates determined using the small potential shift method of Stern and Geary and those determined using a sizable cathodic shift in potential have suggested that the size of the perturbation has little effect on the results if the analytical solution (Equation [4]) is used.^[8]

As the cathodic reaction rate approaches the limiting current for oxygen reduction (i_L), mass transfer adds a further component (η_m) to a polarized potential.^[6] One form of this is:

$$\eta_m = \frac{RT}{zF} \ln\left(1 - \frac{i_c}{i_L}\right) \quad (5)$$

where R , T , z , and F are the gas constant, absolute temperature, valence number, and Faraday constant, respectively.

The contribution of electrolyte resistance to polarization may be largely eliminated at the time of measurement. In practice, the potential decay determined relative to the instant off potential, a potential that is largely free of the effects of the electrolyte resistance, provides a conservative estimate of the polarization achieved by the applied current.^[1]

The polarization or potential shift (η) at a cathode that excludes the effects of electrolyte resistance is given by the sum of the activation (η_a) and mass transfer (η_m) potentials:

The inclusion of the effects of mass transfer kinetics introduces complexities that include the absence of an analytical solution to the above equations. Numerical methods are required.^[9]

2.2 | Sensitivity analysis

The constants in the above equations are the anodic and cathodic Tafel constants and the limiting current. Concerns have been raised as to their effect on the calculated corrosion rate.^[5] To assess the sensitivity to changes in these constants, the calculated corrosion rate is plotted as a function of each constant in Figure 1. In these calculations, 50 mV of polarization ($\eta = 50$ mV) was delivered by an applied current of 5 mA m⁻² ($i_{\text{appl}} = 5$ mA m⁻²).

In Figure 1a, the effect of mass transfer is represented by a cathodic limiting current that reduces from 120 mA m⁻² ($\beta_a = \beta_c = 120$ mV). Its effect on the corrosion rate becomes significant as it approaches the applied current when it starts to dominate the level of polarization delivered by the applied current. The calculated open circuit corrosion rate rises at this point because the activation control polarization falls as a proportion of the total polarization (50 mV in this example). The sum of the applied current (5 mA m⁻² in this case) and the corrosion rate of the polarized steel is constrained to be less than or equal to the limiting current. It should be noted that, when the corrosion rate is controlled by a limiting current, steel passivity is not a usual consequence of cathodic protection.^[9]

The limiting current is a measured constant dependant on the environment. Tafel constants on the other hand are substantially based on theory and are governed by the equation:

$$\beta = \frac{2.3RT}{\alpha zF} \quad (7)$$

where z is the number of electrons transferred in the rate controlling step of the electrochemical reaction sequence and α (sometimes $1-\alpha$) is a symmetry factor with a value between 0 and 1.^[6] For $\alpha = 0.5$ and $z = 1$, the Tafel constant has a value of approximately 120 mV. This is the value widely used in determining corrosion rates.^[10] It may vary by a small amount depending on the symmetry factor. In Figure 1b,c, it was assumed to vary between 60 and 180 mV.

The effect of changes in the anodic Tafel constant (Figure 1b) is small. A reduction in sensitivity arises because the steel is cathodically polarized by the current. In the above example, increasing the anodic Tafel constant to infinity would increase the calculated open circuit corrosion rate from about 2 mA m⁻² to about 3 mA m⁻². For smaller levels of polarization, the sensitivity would increase, but not

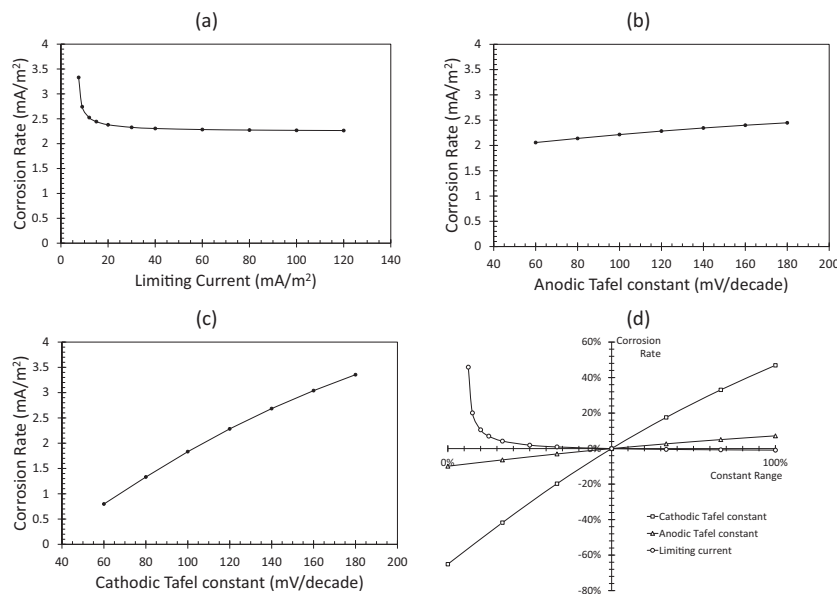


FIGURE 1 Sensitivity of the calculated open circuit corrosion rate to changes in the limiting current and anodic and cathodic Tafel constants

significantly. For example, if 0.8 mA m^{-2} gave rise to 10 mV of polarization, the calculated open circuit corrosion rate would vary from about 2 mA m^{-2} to about 4 mA m^{-2} if the Tafel constant increased from 120 mV to infinity. Hence, the basic assumption for such non-destructive corrosion rate determination is that at least one of the anodic or cathodic kinetics are under activation control.^[11]

The effect of changes in the cathodic Tafel constant (Figure 1c) is more substantial. An increase in sensitivity arises because the steel is cathodically polarized by the current. In this case, a change in Tafel constant from 120 to 180 mV results in the calculated open circuit corrosion rate changing from about 2 to 3.4 mA m^{-2} while decreasing the Tafel constant to 60 mV decreases the calculated corrosion rate to 0.8 mA m^{-2} . The effect of changing the size of the perturbation is to change the sensitivity to errors in the Tafel constants. This sensitivity is low for small polarization levels and higher for larger polarization levels.

For comparison, Figure 1d plots the change in corrosion rate, expressed as a percentage of its value at $\beta_a = 120 \text{ mV}$, $\beta_c = 120 \text{ mV}$, and $i_L = 60 \text{ mA m}^{-2}$, as a function of the percentage of the range of each constant (60 to 180 mV for the Tafel constants and 0 to 120 mA m^{-2} for the limiting current). The most significant effect arises from the cathodic Tafel constant.

3 | EMPIRICAL AND THEORETICAL DATA

3.1 | Cathodic polarization in concrete structures

The widespread use of a cathodic Tafel constant of 120 mV in the determination of corrosion rates in concrete is supported

by the demonstrated success of this non-destructive method when using this value.^[10,12] Indeed $\beta_a = \beta_c = 120 \text{ mV}$ is recommended for onsite measurements.^[10] However, the evidence for the use of this value is limited to laboratory specimens and there have been no reported attempts to determine this parameter in concrete structures.

The applied currents and corrosion potentials measured in cathodic protection systems provides data which gives an indication of this parameter. One set of data obtained during the sacrificial cathodic protection phase of a hybrid corrosion protection system is provided in Figure 2. Long term data for this system (labeled as Whiteadder) has previously been published.^[13,14] The structure was subject to corrosion induced concrete repair in 2006. A temporary impressed current treatment was applied to restore steel passivity by removing chloride from, and generating hydroxide at the steel just prior to the delivery of sacrificial cathodic protection. Recent independent assessment has suggested there is no further significant corrosion.^[15]

Intermittent wetting of the concrete bridge supports resulted in an increase in measured current accompanied by a shift in measured potential. This detail, recorded at 6 h intervals, is expanded in Figure 2. Figure 2a,c,e show the recorded potential of three reference electrodes within a protected zone, together with the current delivered in that zone during current surges after 5, 9, and 10 years of galvanic protection. In context, the protection current was much lower for most of the service life of the system.^[14]

Figure 2b,d,f provide the respective analysis in which the decaying potential at each electrode following the current surge is plotted against the logarithm of the zone current. Included in Figure 2b are three measured potentials at each electrode recorded just before the bridge substructure was

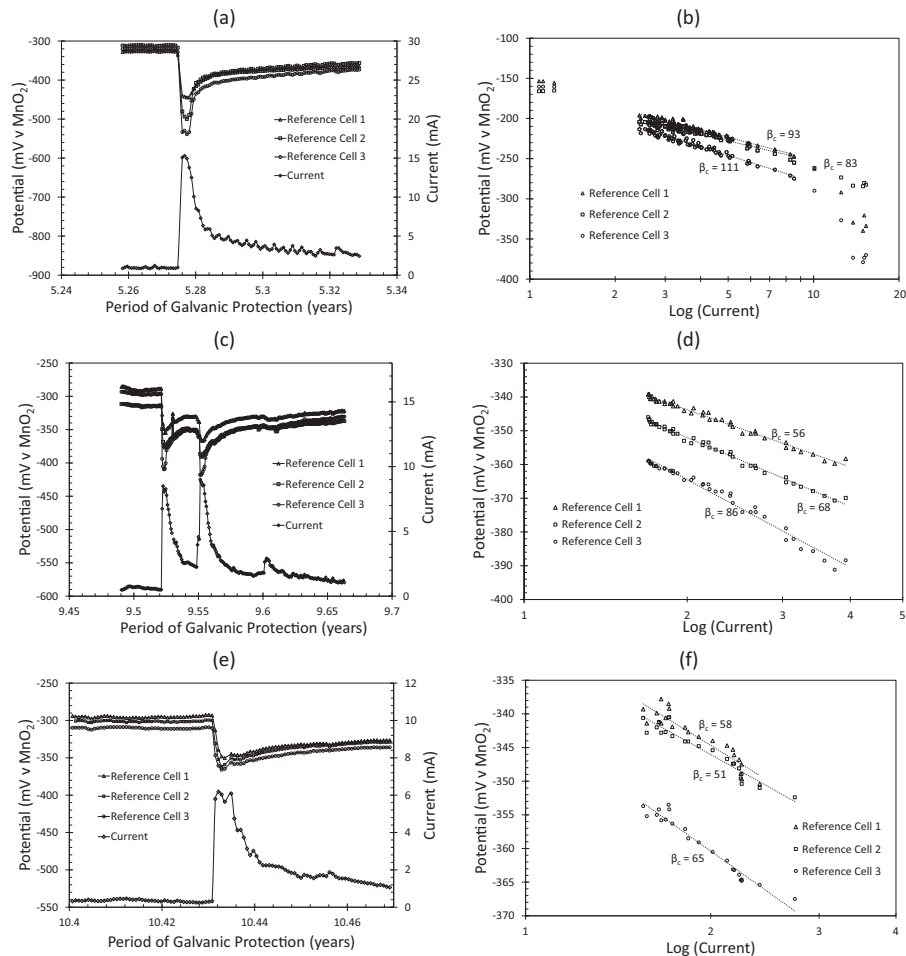


FIGURE 2 Current surges and potential response recorded on a bridge substructure at the location of embedded reference electrodes together with the potential-current analysis

wetted to produce the current surge, together with the measured potentials at the peak of the current surge. These are points in which the environment in which the measurements were made was either changing rapidly or was very different to that encountered in the subsequent decay and they were therefore discounted from the analysis.

The slope of the lines in Figure 2b,d,f provide an indication of the cathodic Tafel constant. The output of this analysis is provided in Table 1.

In all cases the estimated cathodic Tafel constant was less than 120 mV. The effect of this as indicated by Figure 1c is that the use of 120 mV as the cathodic Tafel slope will result in an overestimation of the corrosion rate. Further, the effects of mass transfer on this polarization behavior are negligible.

3.2 | Corrosion risk classification

The above analysis sets out the theoretical link between polarization and corrosion rate (corrosion current density). To convert corrosion current to corrosion current density, the area of corroding steel surface is required. It is possible to

limit this area to a known value by confining the applied current to a specific zone or segment of a zone of a protection system. This provides a measure of the average corrosion current density. However localized corrosion rates may be substantially higher.

Various interested parties have taken average corrosion rate data and converted the numbers into a corrosion risk classification.^[10,16] The classification adapted from a Concrete Society Report^[16] is provided in Table 2.

In Table 2, the boundary between passive steel and a low corrosion risk is set at a steel section loss of 1 mm after 400 to 500 years. The lower boundary of a high corrosion risk is set at a steel section loss of 1 mm after 80 to 90 years. Both of these rates are low, but the risk classification relates to the likelihood of the corrosion being localized to a small percentage of the steel surface area and therefore a locally higher corrosion rate (macrocell corrosion activity).^[5,10]

The percentage of the steel surface in concrete that is actively corroding is the biggest factor affecting the relationship between polarization and corrosion risk. Errors in other parameters will be small by comparison. Further,

TABLE 1 Cathodic slopes measured after 5, 9, and 10 years of galvanic protection

Period (years)	Cathodic slope			β_c
	Cell 1 (mV)	Cell 2 (mV)	Cell 3 (mV)	Average (mV)
5.28	93	83	111	96
9.55	56	68	86	70
10.43	58	51	65	58

while there may be other factors that complicate the theoretical presentation above, such errors introduced often cancel each other.^[17]

3.3 | Polarization as a function of corrosion rate

In Figure 3 the calculated potential shift (level of polarization) at a given applied current is plotted as a function of the open circuit corrosion rate. It is clear from this data that higher levels of polarization are associated with lower open circuit corrosion rates. Further significant levels of polarization would not be achieved by low protection current densities if the steel was not already passive.

4 | DISCUSSION

4.1 | Interpretation of polarization in terms of corrosion risk

The interpretation of the data in Figure 3 in the context of the risk classification in Table 2 is provided in Figure 4. Figure 4 shows the potential shift as a function of the open circuit corrosion rate at an applied current density of 5 mA m^{-2} . The boundary between passive steel and a low corrosion risk is added as a vertical line that intercepts the x-axis at 2 mA m^{-2} . At this corrosion rate, about 55 mV of potential shift is required at a protection current of 5 mA m^{-2} . Thus achieving 55 mV or more with an applied current of 5 mA m^{-2} or less is indicative of passive steel. This represents a new protection criterion.

Concrete is unique in that it sustains a high pH that supports steel passivity (steel is naturally passive in atmospherically exposed concrete). Passive film breakdown

is typically caused by contamination of the concrete.^[18] A protection current may reverse the effects of concrete contamination at the steel, thereby restoring steel passivity. As noted in the introduction, the list of criteria for cathodic protection of reinforced concrete may be supplemented with a criterion like that set out above which shows that the steel is passive.

There are an infinite number of similar criteria to that described above. Such criteria are based on the observation that, at protection current densities typically used in reinforced concrete, the degree of polarization provides an indication of the steel corrosion risk in an unprotected condition.

4.2 | Empirical support for corrosion risk based criteria

In the system that provided the data for Figure 3 above, the current output was low and the polarization was minimal for most of the time.^[13] Substantial polarization was only delivered to the steel in response to environmental effects. Nevertheless, both corrosion rate data and visual assessment of the structure have suggested that the steel remains passive in this and other similarly treated structures.^[14,15] In such examples, corrosion risk assessment was low and sustained polarization was not required for periods exceeding 10 years.

In an independent study on several aged impressed current systems on UK highways agency structures, the protection current was interrupted for a period of at least 3 years on the basis that the steel was, and remained passive during this period on these structures.^[4,19] Passivity was assessed using corrosion rate, corrosion potential and visual data. Thus for a period of about 3 years, no protection current and no polarization were required because the corrosion risk

TABLE 2 Corrosion risk classification

Average corrosion current density (mA m^{-2})	Average rate of steel section loss ($\mu\text{m year}^{-1}$)	Risk classification
Up to 1-2	Up to 1-2	Very low or passive
2 to 5	2 to 6	Low to moderate
5 to 10	6 to 12	Moderate to high
>10	>12	High

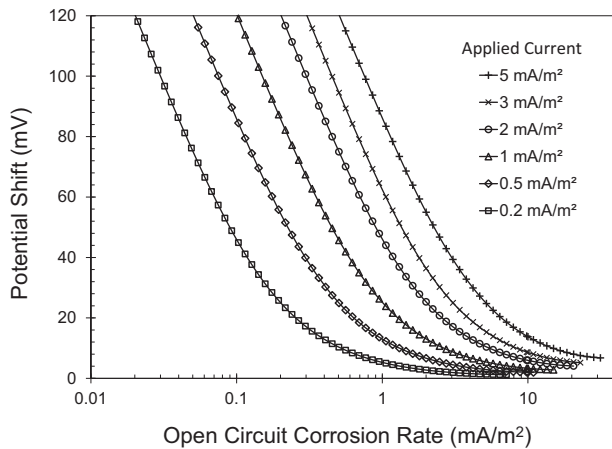


FIGURE 3 Theoretical potential shift as a function of open circuit corrosion rate at various applied current densities

assessment showed the steel was already passive in these examples.

At the other end of the scale the adequacy of 100 mV of polarization in very aggressive environments has been challenged.^[20] The applied currents in this laboratory study were about 100 mA m^{-2} . Inserting this current density and potential shift (100 mA m^{-2} and 100 mV) into equation (4) above suggests that the open circuit corrosion rate is 15 mA m^{-2} . As set out in Table 3 this represents a high corrosion risk. In this example, even 100 mV of polarization may represent a corrosion risk.

These examples show that, in addition to the theoretical basis presented above, there is empirical support for the use of corrosion risk based criteria for steel in concrete.

4.3 | Adequate polarization

In the 1950's, a cathodic protection trial was applied to reinforced concrete bridge beams.^[21] It was the first recorded

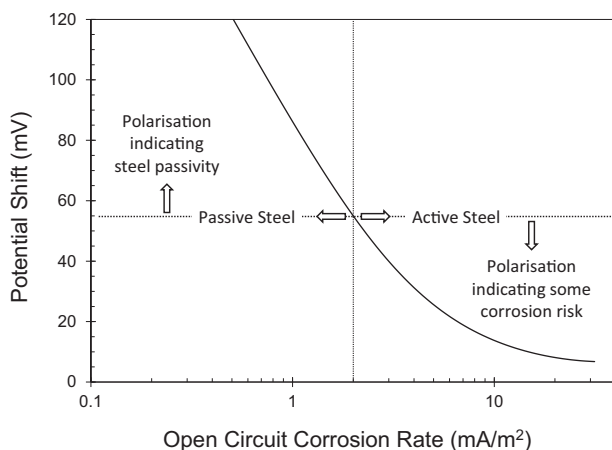


FIGURE 4 Interpretation of potential shift in terms of corrosion risk

trial applied to above ground (atmospherically exposed) reinforced concrete. The existing criterion was to achieve an absolute polarized steel potential of about -800 mV (Cu/CuSO₄ saturated). At or below this potential steel is immune to corrosion. Such negative potentials are readily achieved when the cathodic reaction kinetics are easily polarized (the cathodic polarization resistance is high), such as in submerged conditions when oxygen reduction is limited by diffusion.

The recorded currents required to achieve such a criterion on a concrete bridge beam were in excess of 100 mA m^{-2} .^[21] The sustained delivery of such a protection current density to a concrete surface was impractical. Historically, cathodic protection was generally not considered to be a realistic option when the cathodic reaction is difficult to polarize (the cathodic polarization resistance is low) because of the high current required to shift the potential.^[22]

Perhaps because of this, the criteria subsequently developed and listed in current standard practice are described as “not necessarily supported by theoretical considerations.”^[1] However the data in Figure 3 suggest that the least onerous of the listed criteria for concrete exposed to the air, namely the requirement for 100 mV of depolarization, when achieved with a low protection current density (typically less than 20 mA m^{-2}), is a criterion associated with passive or near passive steel in concrete.^[9]

The informative section of the current standard suggests that the repassivation potential of steel in concrete is more negative than -600 mV (Ag/AgCl 0.5M KCl) (figure A.3 in ref. [1]). This implies that to achieve passivity by polarising the steel, its potential should be polarized to more negative than -600 mV (Ag/AgCl 0.5M KCl). Typically such steel polarization is not achieved because the cathodic reaction kinetics are weakly polarized (Figure 2). Polarization will not necessarily, directly restore steel passivity in above ground concrete.

As noted above, concrete is unique in that it sustains a high pH that supports steel passivity. A broad objective of a protection system is to restore the naturally passive steel condition in above ground concrete. Factors such as the removal of chloride from, or the generation of hydroxide at the steel surface, which are related to the charge delivered, are often critical to restoring steel passivity in reinforced concrete cathodic protection systems.^[3]

Thus, polarization is generally not a cause of steel passivity in above ground reinforced concrete. It is not a dominant factor—chloride removal and hydroxide generation are the dominant factors. Instead, when the cathodic reaction is difficult to polarize (i.e., the resistance to cathodic polarization is low), achieving substantial polarization with a low current density is a consequence of the restoration of steel passivity arising from chloride removal and hydroxide generation at the steel. Adequate polarization (the acceptable

level of potential shift) is a subjective concept that is sometimes only supported by theoretical considerations when the protection current density is taken into account.

4.4 | Beneficial effects

The polarization delivered by a cathodic protection system is related to the protection current. A reduction in protection current may be used to address adverse effects associated with its delivery. The main adverse effects are associated with the anode systems. Sacrificial anodes are consumed by the delivery of protection current.^[1] However adverse effects are not restricted to sacrificial anodes.

The anodic reaction on inert anodes generates acid which attacks the cement paste in the concrete. Localized current dumping, which may occur when embedded steel bars pass close to the anode system or when water ponding occurs on a surface applied anode system, may lead to failure.^[23]

Evidence of the responsive current in a galvanic system is provided in Figure 2 above.^[24] For substantial periods of time the current output of this system was low and the polarization was negligible. Nevertheless, both corrosion rate data and visual assessment of the structure have suggested that the steel remains passive in this and other similarly treated structures.^[14,15] The fall in average current output has resulted in longer than expected predicted service lives of the anode system.^[25]

Thus flexibility over the degree of polarization required may be used in impressed current and sacrificial systems to reduce the protection current to limit the deterioration of the anode or surrounding concrete. For example a structure may require less onerous protection if the steel is already passive, or during dry or cold periods when the corrosion risk is lower.

5 | CONCLUSIONS

Criteria for reinforced concrete cathodic protection may be based on the observation that, at protection current densities typically used in reinforced concrete, the degree of polarization provides an indication of the steel corrosion risk in an unprotected condition. An example of such a criterion is, a steel polarization of 55 mV or more achieved by a protection current of 5 mA m⁻² or less is indicative of passive steel reinforcement. Such criteria are dependent on the applied protection current density. While not specifically listed, such criteria are allowed by current standard practice.

Corrosion risk based criteria are supported by both theory and practice. In practice corrosion risk assessment provided a bases for interrupting the protection current in aged impressed current cathodic protection systems for a period of at least 3 years. Responsive behavior was shown to be adequate in galvanic systems, in at least one case for more than 10 years.

In very aggressive laboratory conditions a residual corrosion risk, observed when 100 mV of polarization was achieved, is predicted by such an assessment.

Polarization is generally a consequence of steel passivity in systems where the cathodic reaction kinetics are difficult to polarize such as is often the case in above ground reinforced concrete. It is not generally a cause, or a dominant factor, but instead can be used to show the steel is passive. In such systems, the removal of chloride from, or the generation of hydroxide at the steel surface, which are related to charge delivered, dominate the restoration of passivity by restoring an environment that naturally supports passivity.

Flexibility over the degree of polarization required in cathodic protection systems may be used to address adverse effects associated with the delivery of protection current. For example, reducing the protection current at least during periods which require less protection would increase the anode life of a system.

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