MONITORING THE PASSIVITY OF STEEL SUBJECT TO GALVANIC PROTECTION

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SUMMARY: This work investigates the assessment of the passivity of steel in concrete subject to galvanic protection. Under atmospherically exposed conditions the kinetics of the cathodic reaction often exhibit activation controlled behaviour. It is shown that in these conditions the corrosion rates estimated from a large negative potential shift are very similar to those determined using the more widely accepted polarisation resistance method. The results are considered in the light of the potential decay cathodic protection criterion, and show how criteria based on potential shift may be improved to monitor steel passivity induced in a galvanic cathodic protection system. This provides the basis for an improved reinforced concrete acceptance criterion that is focussed on the condition of the structure and is included within the ISO standard cathodic protection when applied to galvanic systems.

Keywords: Steel, Concrete, Chloride, Corrosion, Electrochemical Protection.

1. INTRODUCTION

Electrochemical treatments are widely used in the mitigation of steel reinforcement corrosion and galvanic (sacrificial) anodes are increasingly being used in these treatments. One basis for protection is provided by achieving adequate cathodic polarisation of the steel. Indeed cathodic protection is an electrochemical treatment that is often defined by its achievement of adequate polarisation. Galvanic anodes have not generally sustained a condition of adequate polarisation. Thus one definition of galvanic anodes that still persists today is galvanic anodes "do not have sufficient driving voltage to overcome the relatively high resistance of even wet concrete, except when fully immersed" [1].

The new ISO standard for cathodic protection [2] caters for galvanic anodes. In the event that these systems do not achieve polarisation criteria, a system which informs the user of the condition of the structure is then required. Action is taken if corrosion is identified. This provides for a system acceptance criteria focused on the condition of the structure. In an ideal system, the treatment will arrest corrosion as quickly as possible, monitor the structure to inform the user of its condition and provide a facility to address any corrosion risk identified in the future. The changes to the standard allow the secondary protective effects of cathodic protection, which modify the environment at the steel and also stop steel corrosion, to be taken into account. Such effects include Pit Re-alkalisation and pH Maintenance [3-5] and may halt corrosion, or delay its onset in concrete that is contaminated with chloride even when the protective current has been removed and there is no cathodic polarisation at all [6, 7]. A key feature of the system is a monitoring facility that informs the user of any increase in corrosion activity.

A strong link between the current applied, its induced negative potential shift and the corrosion rate allows an estimate of the corrosion rate (i_{corr}) to be obtained from the local current density (*i*) and resulting negative potential shift (η) [8]. The relationship between these parameters is described by the equation:

$$i = i_{\rm corr} \left(\exp\left(\frac{2.3\eta}{\beta_{\rm c}}\right) - \exp\left(-\frac{2.3\eta}{\beta_{\rm a}}\right) \right) \tag{1}$$

where β_a and β_c are the anodic and cathodic Tafel slopes. Support for the use of equation 1 to estimate the corrosion rate of steel in concrete comes from the widely successful application of the polarisation resistance method [9]. This is based on an approximation of the exponential function in equation 1 that may be made when the potential shift (η) is small, namely:

$$i_{\rm corr} = \frac{i}{\eta} \frac{\beta_{\rm a} \beta_{\rm c}}{2.3(\beta_{\rm a} + \beta_{\rm c})}$$
(2)

The polarisation resistance may be viewed as the resistance to current flow across the metal-environment interface at the

rest (corrosion) potential and is given by η/i in equation 2.

The most commonly applied cathodic protection criterion requires a minimum potential decay of 100 mV on interrupting the current [1]. Equation 1 has previously been used to derived this 100mV polarisation criterion. In this derivation, it is assumed that the applied current density was 20 mA./m² and the corrosion rate had to be less than 4 mA/m². Equation 1 then shows that to achieve this, more than 85 mV of potential shift will be required [8, 10].

Galvanic anodes typically exhibit 'Responsive Behaviour' [10, 12]. The current passed by galvanic anodes in site installations fluctuates depending on the local and seasonal weather conditions. Under these conditions, the historical potential shift criteria may not be met, and this is more likely to occur in benign conditions, such as very cold or very dry conditions.

This brief review looks at methods of monitoring the condition of atmospherically exposed concretes structure subject to galvanic protection and compares these with the more traditional polarisation based criteria applied to cathodic protection. The responsive behaviour of anodes is demonstrated, and the use of potential mapping to complement corrosion rate data when assessing corrosion risk is considered.

2. EXPERIMENTAL OBSERVATIONS

2.1 Cathodic Polarisation and Corrosion Rate

Previously reported examples of the current and potential response to both small and large potential step perturbations are given in Figure 1 [8]. The specimens consisted of reinforced concrete cylinders, 100 mm in diameter and 250 mm long. Each specimen contained a centrally located 20 mm diameter mild steel bar with an exposed length of 180 mm. Chloride was added to the mix water as sodium chloride to give initial chloride ion contents between 0 and 3 % by weight of cement. The specimens were periodically exposed to simulated sea water for 30 minutes in every 12 hours and then allowed to dry in circulating air with a relative humidity varying between 50 and 70% for 10 weeks prior to obtaining this data. This resulted in 17 specimens in a range of corroding states [8].



Figure 1 Typical examples of the current and potential response to (a) a small and (b) a large potential step perturbation.

The corrosion rates were determined using equations 1 and 2 above for the large (cathodic shift of Figure 1(b)) and small (polarsation resistance of Figure 1(a)) potential perturbations respectfully assuming anodic and cathodic Tafel slopes of 120 mV. The potential shift was corrected for the effects of the electrolyte resistance as illustrated in Figure 1. The corrosion rates are plotted against each other in Figure 2. It is evident that, while a small potential shift (polarisation resistance) results in a marginally higher corrosion rate than the large potential shift (cathodic shift), there is a fairly close agreement between the two sets of values.



Figure 2 The relationship between the corrosion rate determined from the large cathodic (negative) potential shift and that determined using the polarisation resistance method.

2.2 Responsive Behaviour

In the above example, a range of corrosion states were produced in 17 laboratory specimens. In practical applications, monitoring is more limited and is directed to the most aggressive or highest risk locations on a structure. The aggressive nature of the environment and the corrosion rate of the steel at these locations will, however, vary with time.



Figure 3 Zinc and steel anodic current response to rainfall and changes in temperature.

The previously reported output of a cylindrical zinc anode 65 mm long by 15 mm in diameter was compared with a similarly sized steel anode in an elongated steel reinforced concrete block [10]. The anodes were activated with the same sodium chloride contaminated mortar surround and were located at either ends of the concrete block approximately 600 mm apart. The concrete block was otherwise chloride free. The steel anode represents a small section of corroding steel in a largely passive structure.

Figure 3 shows the zinc and steel anode current densities, along with temperature and rainfall data. Both currents increased or decreased with increases or decreases in temperature and degree of wetness. Daily variations in both zinc and steel anode current were largely the result of variations in temperature. The large increase in the anode current densities on day 67 was as a result of rainfall after a period of dry weather. The relative changes in zinc current output were greater than changes in the steel current output. In drying conditions up to day 67, the current outputs decayed to 15 and 30 mA/m² for the steel and zinc respectively. However the zinc anode responded more quickly to an increase in moisture following the rainfall rising to 600mA/m² which compares with 100mA/m² from the steel anode.

2.3 Potential Mapping

While monitoring in practical applications covered by the ISO standard is undertaken at selected locations on a structure at highest risk, not all galvanic systems are installed with the minimum monitoring requirements specified by the standard when they are applied in a limited and targeted way. In these cases, and also to complement the requirements of the ISO standard, close interval potential mapping may be applied to selected locations on a structure protected with galvanic anodes.

Close interval potential mapping data was previously obtained on selected sections of a bridge substructure and car park deck subject to corrosion damage concrete patch repair [13]. Proprietary galvanic anodes containing approximately 65 grams of zinc, were installed in pre-drilled holes in the parent concrete, as close as practically possible to the edge of the patch repairs. A wire integrated with the galvanic anodes made a connection to the steel reinforcement within the repair area. The facility to disconnect the anodes as part of the minimum monitoring requirements of the ISO standard was limited to a few selected locations. However, the performance of the system in the first 6 months of its life was more rigorously assessed using potential maps of selected areas throughout both structures. The maps were obtained on a 50 mm square grid using a portable Ag/AgCl/0.5M KCl reference electrode and a high impedance multi-meter [13].

Figure 4 shows the polarisation effect afforded by galvanic anodes at a distance away from the edge of a patch repair area in the car park over a period of 215 days. The potentials are plotted relative to the most positive value obtained. In this case, the anodes affected the potentials to a distance of approximately 500 mm away from the edge of the repair.



Figure 4 Polarisation effect of the anodes at a distance from the edge of a patch repair over a period of 215 days.

The above results are typical and re-occurring findings on the polarisation effect of the anodes at a distance from the edge of a patch repair throughout the repaired car park. The polarisation distance varied between 500 mm and 750 mm depending on the prevailing environmental conditions at the time of testing.

The bridge structure exhibited less of an effect, extending to between 200 and 450 mm from the edge of the patch. It also had a substantially higher steel density which would reduce the extent of the effect of the anodes [14].

3. DISCUSSION

As noted above a commonly accepted cathodic protection criterion is the achievement of 100 mV of potential decay on interrupting the applied current. This implies that the potential shift is at least 100 mV. To achieve this, the applied current should be five times greater than the corrosion rate [8]. However design current densities seldom exceed 20 mAm⁻² and are often lower. Thus the achievement of this criterion already implies that steel is approaching a passive state (corrosion rate less than 2 mA/m^2).

In the above argument, equation 1 provides a theoretical basis for the commonly adopted cathodic protection criterion. It also indicates ways in which such a criterion may be developed. Thus, when less than 100 mV of polarisation is achieved at the location of a particular reference electrode, a knowledge of the local applied current density may be used to determined the unpolarised steel corrosion rate. The factors that affect the degree of polarisation also affect the measurement of corrosion rates. No additional uncertainties are introduced when using an acceptance criterion based on corrosion rate, as opposed to a potential shift, and more of the monitored data is used in the assessment of the condition of the structure.

Figure 5 illustrates a circuit that may be used to obtain monitoring data in accordance with the ISO standard. A segment of the anode system (green circuit) associated with a reference electrode is used to determine the local current density and the steel potential shift (yellow circuit) induced by that current. A conservative estimate of the potential shift is given by the potential decay on interrupting the galvanic current. This provides the data for insertion into equation 1. The rest of the anode system (blue circuit) acts as a guard electrode to confine the measured current to the area that is monitored.



Figure 5 Schematic arrangement of a monitoring circuit in a galvanic anode cathodic protection system.

Figure 2 shows that larger potential shifts gave rise to slightly lower corrosion rates than smaller potential shifts. This is probably because the theory behind equation 1 does not include all contributions to polarisation when large potential shifts are induced. Thus, for example, diffusion effects may make a contribution to the polarisation and give rise to more potential shift and therefore a lower estimate of the corrosion rate.

Monitoring the local current density allows changes in the unpolarised corrosion rate with time to be determined. A sustained period of protection current may change the environment at the steel and cause the steel to go passive [3, 6]. The high corrosion rate data in Figure 2 was obtained after a very short period of cathodic polarisation. In this case, high steel current densities were required to induce the associated large potential shifts on corroding steel.

An initial period of current application is often required before steel passivity is achieved. Indeed, it would be preferable if, when a repair to a corrosion damaged structure was completed, the steel in the structure was passive. This may be achieved using a temporary but high impressed current treatment. Some patented galvanic systems facilitate such a brief high current treatment (typically less than 3 weeks in duration) [12]. In a purely cathodic protection system a sustained period of cathodic protection may be necessary to induce passivity.

Other factors that affect corrosion rate include temperature, moisture and chloride content. In dry cold conditions, the steel may not be corroding and protection current may not be required. Galvanic anodes exhibit responsive behaviour to changes in the aggressive nature of the environment, passing a high current when required to address a high steel corrosion risk [11]. For example, rainfall on day 67 caused an order of magnitude increase in the zinc current output in Figure 3. Because current is not delivered in benign conditions, anode life is preserved.

Figure 3 does not represent a protected structure, but just shows the responsive behaviour of a zinc anode relative to the steel corrosion process. Figure 3 includes a section of unprotected steel - namely the steel anode. Its corrosion rate would be greater than its anode current output (50 to 100 mA/m^2). The acceptance criterion for passive steel is less than 2 mA/m² [9]. Figure 3 shows that if the conditions become more aggressive, the galvanic anode current output will respond accordingly.

Figure 4 suggests that potential mapping is another technique that may be used to complement the assessment of structure condition and of galvanic anode performance. It can provide valuable information on whether the anodes are active or not, and also identify the condition of the adjacent reinforcement. Anodes on the adjacent steel reinforcement will show up in a close interval (50 mm) potential map. Because of the quantity of data that is required to make these assessments, it is necessary to restrict monitoring to selected areas considered to be at a high risk in accordance with the ISO cathodic protection standard [2].

Another criterion may be to demonstrate that there are no corroding spots between locations of galvanic anodes in a potential map. In this case, the polarisation effect afforded by the galvanic anodes to the adjacent reinforcement in the parent concrete should be at least equal to half the distance between the anodes. The effect of anodes in heavily reinforced concrete is reduced because of the higher surface area of the steel. Anode spacing is dependent on steel density. This probably resulted in the differences in the extent of polarisation between the car park and bridge structures repaired with galvanic anodes (see section 2.3 above).

It is possible to undertake potential mapping without a direct steel connection, by measuring changes in the electrical field of the concrete induced by electrochemical activity of the zinc - steel couple against a fixed point on the surface of the concrete. Such an approach may be advantageous where connection to the reinforcement is not possible, or when galvanic systems, targeted to limited areas of corrosion damage, are not installed with the full monitoring facilities.

The ISO cathodic protection standard requires the facility to address corrosion risk by increasing the protection current in galvanic systems when such a risk is identified during monitoring. Such a facility is provided in a proprietary hybrid anode which may be used, when required, to deliver a temporary impressed current treatment. It can also deliver galvanic protection. A short impressed current treatment lasting less than 3 weeks has been sufficient to arrest active corrosion in concrete contaminated with 4% chloride by weight of cement for at least 7 years [12].

4. CONCLUSIONS

Cathodic protection monitoring data, consisting of the level of cathodic polarisation (potential shift) and the applied current density that caused the polarisation, may be used to estimate the unpolarised corrosion rates of steel in protected structures. The results correlate well with the polarisation resistance method of corrosion rate determination. This effect provides a theoretical basis for other acceptance criteria for atmospherically exposed reinforced concrete. It does not introduce any additional uncertainties when compared with the existing 100 mV polarisation criterion, but instead uses more of the collected data to draw a conclusion on the condition of the structure.

The current output of a zinc anode responds to a changing environment at least in the same way that corroding steel would respond. A high current is passed when required to address a high steel corrosion risk and a low current is passed when there is a low steel corrosion risk. A lack of galvanic current and therefore an absence of steel polarisation is acceptable in galvanic systems, provided that the low protection current corresponds to conditions which also represent passive steel (typically a corrosion rate of less than 2 mA/m²). Responsive behaviour means that anode life is conserved in benign environments, while the current output responds accordingly if conditions become more aggressive.

Another method of assessing the performance of galvanic anodes requires the anodes to have a dominant influence on steel potentials, and therefore mask any effect of a steel anode, to a distance of at least half the spacing between anodes. This can be assessed using close interval potential mapping (50 mm measurement spacing). The extent of the protective effect afforded by the anodes is dependent on the steel density.

The 2012 ISO cathodic protection standard requires the monitoring system for galvanic protection to inform the operator of any increase in corrosion activity and it requires a facility to take preventative action if corrosion activity is identified. Such a facility may be provided by a proprietary hybrid anode which can be energized to deliver a brief impressed current electrochemical treatment (typically less than 3 weeks) to arrest an active corrosion process when it is required.

5. REFERENCES

- 1. The Concrete Society, Cathodic Protection of Steel in Concrete, Technical Report No. 73, August 2011.
- 2. ISO 12696:2012, Cathodic protection of steel in concrete, British Standards Institute, 2012.
- 3. Glass, G.K., Roberts, A.C., Davison, N., Hybrid corrosion protection for chloride contaminated concrete, Construction Materials 161 (2008) 163-172.

- 4. Glass, G. K., Reddy, B. and Clark, L. A., 2007. Making concrete immune from corrosion. Proceedings of the Institution of Civil Engineers, Construction Materials, 160 (4) (2007) 155-164.
- 5. Glass, G.K., Davison, N., Roberts, A.C., Pit realkalisation and its role in the electrochemical repair of reinforced concrete, Cathodic Protection Conference, University of Manchester, 2006.
- 6. Christodoulou, C., Glass G.K., Webb, J., Austin, S.A. and Goodier, C.I., 2010 Assessing the long term benefits of Impressed Current Cathodic Protection. Corrosion Science, 2010, 52 (8), pp. 2671-2679.
- 7. Christodoulou C., Goodier C.I., Austin S.A, Webb J., Glass G., Diagnosing the cause of incipient anodes in repaired reinforced concrete structures, Corrosion Science, 2013, 69, pp. 123 129.
- 8. Glass, G. K., Hassanein, A. M. and Buenfeld N. R., "Monitoring the passivation of steel in concrete induced by cathodic protection", Corrosion Science, 39(8) (1997) 1451-1458.
- 9. The Concrete Society, Electrochemical tests for reinforcement corrosion, Technical Report No. 60, 2004.
- Glass, G. K., "Technical Note: The 100-mV Potential Decay Cathodic Protection Criterion", Corrosion 1999, 55, 286-290.
- 11. Holmes S.P., Wilcox, G.D., Robins, P.J., Glass G.K. and Roberts A.C. "The Responsive Behaviour of Galvanic Anode Current in Concrete and the Basis for its Utilisation", Corrosion Science 2011, 53, pp. 3450-3454.
- 12. Holmes S.P., Wilcox, G.D., Robins, P.J., Glass G.K. and Roberts A.C. "Long term assessment of a hybrid electrochemical treatment", Materials and Corrosion 2011, 62, 1-7.
- Christodoulou C., Glass G., Webb J., Austin S.A. Goodier C.I., A new approach for the patch repair of car parks using galvanic anodes, Concrete Solutions 2011, : Grantham, M., Mechtcherine, V. and Schneck, U. (eds). Concrete Solutions 2011: Proceedings of the International Conference on Concrete Solutions 2011. London: CRC Press, ISBN 978-0-203-13468-9.
- 14. Christodoulou C., Austin S.A. Goodier C.I., Glass G., Webb J., A new arrangement for galvanic anodes in the repair of reinforced concrete structures, Construction and Building Materials, 2013, In Press.

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Gareth Glass is a Director of Concrete Preservation Technologies with extensive experience in materials technology, durability and rehabilitation of structures. He is a leading expert in the repair of corrosion damaged concrete and is responsible for design, product development and product support in this field. He has over 100 publications to his name in the area of corrosion protection. He obtained his PhD from the Corrosion and Protection Centre, University of Manchester, in 1984.