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**A Suggestion for a Two-Stage Corrosion Mitigation System for
Steel Reinforced Concrete Structures**

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Abstract

Cathodic protection of steel reinforced steel is a well-established technique for controlling reinforcement corrosion of structural elements. Long-term maintenance of the system, however, is seen as a burden to most structure owners and managers as it involves additional and continual costs. There is, therefore, a requirement for simpler CP systems to be made available which will involve less maintenance and monitoring requirements. This paper demonstrates a methodology, backed by laboratory experiments, that has enabled such a user-friendly system to be developed and applied.

The paper presents results that demonstrate corrosion arrest of steel samples, corroded by embedding in a range of chloride-containing mortars and delay in the onset of corrosion in chloride-free mortars subsequently exposed to external chlorides. This process is suggested as Stage-1 of a two-stage process for long-term protection of steel reinforcement, Stage-2 being corrosion or cathodic prevention, after corrosion arrest has been demonstrated, for which galvanic anodes have been proven to adequately achieve. The key element of the two-stage process is to establish that corrosion arrest has been attained. The paper suggests, with examples, monitoring of the depolarisation and depolarised potentials and use of the Butler Volmer equation for the estimation of the steel corrosion rate as possible validation techniques that can be simply achieved with minimal monitoring throughout the service life of the structure.

Keywords

“Cathodic Protection”; “Cathodic Prevention”; “Corrosion Arrest”; “Two-Stage CP”

Introduction

Cathodic protection of steel reinforced steel has become a well-established technique for controlling reinforcement corrosion of structural elements. The expectation of long life protection has, however, been somewhat reduced as some anode systems fail, monitoring equipment become antiquated and lack of adequate maintenance makes the systems inoperable with the average service life of any CP system falling to 15 years [1]. Inevitable additional costs are involved in maintaining and prolonging correct operation of the system. It appears that there is a requirement by structure managers and owners for simpler CP systems which will involve less maintenance and monitoring requirements.

EN 12696:2015 has clear performance criteria that need to be continuously satisfied to ensure that the system is working. A much-used criterion is that a depolarisation potential of 100mV should be achieved when the system is temporarily turned off for a period of 24 hours. The standard also defines that a successful CP system either passivates the steel or reduces the corrosion rate of the steel reinforcement which implies, correctly, that achieving 100mV of polarisation does not necessarily mean that corrosion has been arrested. Nonetheless, it has been shown in several cases that if a CP system is running for an extended period, e.g. 5 years, and is then turned off, corrosion of the steel does not reinitiate over a significant time period [1]. This phenomenon is believed to be achieved by some secondary effects, primarily, the increase in alkalinity and reduction in chloride concentration at the steel/concrete interface [2] which in effect reduces the $[Cl^-]/[OH^-]$ ratio considerably below the critical ratio for initiation or maintenance of corrosion. It has also been suggested that realkalisation of the acidified pits occurs which allows steel repassivation within them [3]. Once repassivation of the steel is achieved, the application of cathodic prevention can then maintain the passive conditions long-term [4].

A system that can arrest steel corrosion relatively early and can then switch to cathodic prevention mode over the longer term is thus realistically possible. It is important, however, to identify the desired current density and overall charge delivery to the steel reinforcement for successful corrosion arrest to occur before the current density is reduced to the lower cathodic prevention current density levels ($0.2\text{-}2\text{mA/m}^2$) which have been shown to be easily achieved by galvanic anodes [4].

This paper describes experimental work aimed at developing a viable Stage-1 procedure in which corrosion arrest of corroding steel can be achieved and follows on from a small piece of fundamental work published elsewhere [2]. This and the earlier work formed part of a process that has enabled the recent development of a simple to install and operate Two-Stage Corrosion Mitigation system [5].

Experimental

Preparation of Steel-Mortar Specimens

Multiple duplicate steel-mortar specimens were prepared using portland cement and sand in the ratio of 3:1 and a water-cement ratio of 0.5:1 (Fig. 1). The steel plate had an exposed circular surface area of 8.55cm^2 located in the centre of the steel plate; the remaining area was masked with beeswax. A wooden block was used to hold the steel plate in a constant and reproducible height within a standard plastic container used as a mould. The mortar was cast in two stages. A plastic tube was used to separate the chloride-dosed mortar from the mortar without chlorides. The plastic tube, being smaller in diameter than the exposed area of steel to avoid crevice corrosion at the exposed edges, was kept centrally in place above the

exposed steel area while mortar was cast on the outside. Once the mortar was set (within a few hours), the plastic tube was removed and mortar containing chloride was cast in the hole. The mortar above the exposed steel plate contained either 2% or 4% chloride as sodium chloride by weight of cement. Specimens made in this way were termed Set-1. Mixed metal oxide (MMO) coated titanium mesh ribbon was embedded in the chloride mortar, serving as the counter electrode. The specimens were vibrated for 2 minutes in a repeatable way to ensure relatively good compaction and the removal of most trapped air. They were then cured for 30 days in a 100% RH environment at $20 \pm 2^\circ\text{C}$ by enclosing in a sealed container with the base holding a small amount of water.

Set-2 specimens were prepared in the same way but with the tubes slightly raised. This ensured that the non-contaminated mortar could flow beneath the tube and rise to around half the height of the tube. MMO coated titanium mesh was once more embedded in the mortar within the tube. The tubes were subsequently used as reservoirs for introducing chloride to the central area of the mortar, just above the steel plates (Fig.1).

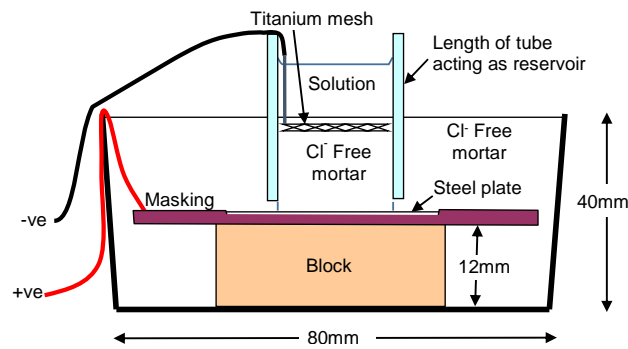


Figure 1 Schematic diagram of Set-2 steel-mortar specimens with built-in reservoir. Set-1 had the plastic tube removed and a chloride-dosed mortar was cast in the hole left behind.

Methods of Assessment

Corrosion of all control steel samples had initiated in mortars containing either 2% or 4% chloride by weight of cement within the 30-day curing period. Additionally, to enhance the level of steel corrosion, several duplicate specimens were anodically polarised at 20mA/m^2 to 3 different charge levels, for 2 weeks (low pre-corrosion), 4 weeks (medium) or 6 weeks (high) after their initial 30 days of curing, which had already initiated a level of corrosion. Table 1 illustrates the different experimental conditions for each group of specimens. After corrosion was established, weekly cycles of cathodic polarisation were applied to attempt to arrest corrosion, as defined in Stage-1 above. A current density of 20mA/m^2 was applied for 5 days followed by 2 days of depolarisation, this constituting one cycle of treatment. Instant-off potentials vs Saturated Calomel Reference Electrode (SCE) of the steel were measured before the CP system was interrupted, followed by measured depolarised potentials at different intervals (4 hours, 24 hours and 48-hours). Instant-off potentials are the potential measurements of the steel, taken within half a second of the CP system being interrupted. This practice eliminates the IR drop, which is the potential drop due to the resistance of the solution in the steel-mortar specimens whilst the current is flowing. After the 48-hour period, the corrosion current density of the steel was calculated by using the Butler Volmer equation (Eq. 1).

$$i_{corr} = \frac{i_{appl}}{\left\{ \exp\left(\frac{2.3\Delta E}{\beta_c}\right) \exp\left(-\frac{2.3\Delta E}{\beta_a}\right) \right\}} \quad \text{Eq.1}$$

Where,

i_{corr} is the corrosion current,

i_{appl} is the applied current,

ΔE is the observed potential shift (depolarisation potential),

βa is the anodic Tafel slope (120mv) and

βc is the cathodic Tafel slope (120mV).

Subsequently, the cathodic current density was increased to around 60mA/m² (see Results and Discussion) so that the overall mean at termination of the tests was 50mA/m². All the specimens had remained in their sealed containers during the whole period of testing, these being opened only when potential values were recorded by resting the reference electrode on a marked location on the surface of each specimen.

Table 1 Experimental conditions for each group

Level of additional corrosion (weeks of applied anodic current density of 20mA/m ²) after natural corrosion during 30 days of curing							
None		Low (2 weeks)		Medium (4 weeks)		High (6 weeks)	
2% Cl ⁻	4% Cl ⁻	2% Cl ⁻	4% Cl ⁻	2% Cl ⁻	4% Cl ⁻	2% Cl ⁻	4% Cl ⁻

The group of steel mortar specimens which had not been additionally corroded with an anodic charge ('natural' corrosion) were also subjected to weekly cycles of cathodic polarisation at a mean of 50mA/m². When passivation of the steel was achieved, and their potentials had remained passive for a period of 6 weeks, they were anodically polarised to determine the amount of charge required for the passive film to break down.

The potentials of the pre-corroded specimens were monitored for the same 6-week period, but their potential values gradually moved in a negative direction signifying increasing corrosion activity. They were again cathodically polarised at a constant 50mA/m² current density repeating the same weekly cycle. Potentials once more started to shift in a positive direction but more slowly than during the first treatment. Some of the more corroded specimens had started to suffer from cracking at which point the test was terminated.

Results and Discussion

Effect of Cathodic Charge on Depolarisation and Depolarised Potentials

The experiments were terminated when a total cathodic charge of the order of 110kC/m² was applied to all the specimens. This charge level was chosen because both the naturally corroded specimens had reached passivity (Fig. 2) as indicated in EN 12696:2015 of -150mV vs Ag/AgCl, 0.5M KCl (-141mV vs SCE). Passivity was reached quicker for the 2% Cl⁻ specimens (74kC/m²) compared to the specimens dosed with 4% Cl⁻ (108kC/m²). These values appear to be an improvement compared to earlier work [2] in terms of required level of charge to achieve passivation of steel. As is evident from Table 2, delivering the charge faster, i.e. increasing the current density from 30mA/m² to 50mA/m², has enabled steel passivation at a lower cathodic charge, i.e. 38% lower at the 2% Cl⁻ level where direct comparison can be made.

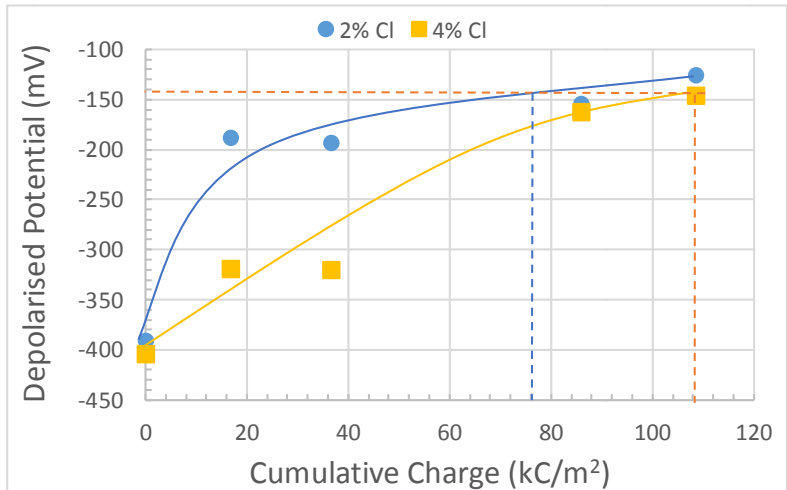


Figure 2 Depolarised potentials (mean of two) vs SCE with cumulative charge of naturally-corroded specimens.

Table 2 Cathodic Charge required to passivate steel at the chloride levels and current densities shown

Current Density (mA/m ²)	30			50	
% Cl ⁻ in Mortar	1	2	3	2	4
Cathodic Charge (kC/m ²)	15	120	190	74	108

In all cases, the steel depolarised potentials moved relatively quickly towards passive conditions, each polarising cycle improving the depolarised potential from the previous cycle. As termination of the cathodic polarisation occurred after the naturally corroded specimens had reached passivation, none of the pre-corroded specimens were able to reach passivity over the same charge delivery (Fig. 3) and only the ‘Low’ pre-corroded specimens dosed with 2% Cl⁻ approached passivation levels of around -200mV vs SCE. The depolarised potentials reached at termination by the pre-corroded specimens were in exact order of the corrosivity level, the potential reaching less negative values in the sequence ‘Low’, ‘Medium’ and ‘High’ pre-corrosion for the 2% Cl⁻ dosage levels followed by the same sequence for the specimens containing the 4% Cl⁻ addition.

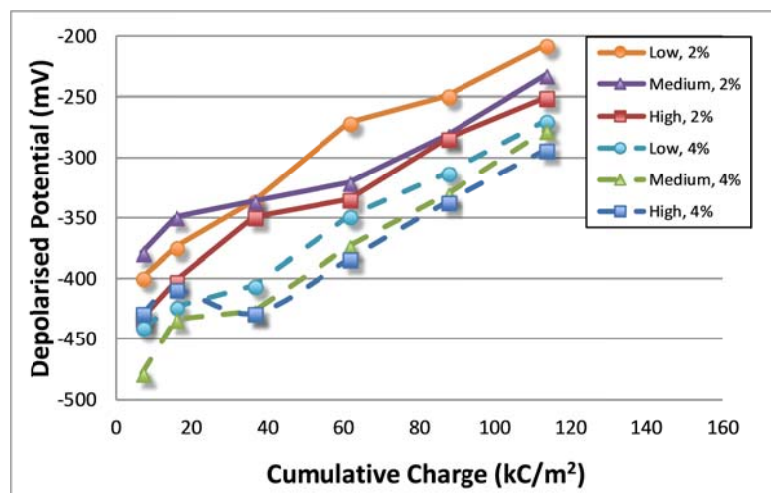


Figure 3 Depolarised potentials (mean of two) 24 hours after each cycle of cathodic polarisation against the cumulative charge delivered

Figure 4 shows the cumulative charge plotted against the depolarisation shift, the change in potential between the polarised instant-off and depolarised potentials at 24 hours. The lower current density originally employed (20mA/m^2) was considered to be insufficient as the 100mV depolarisation criterion stipulated in EN12696:2015 was not achieved, as indicated by the first two data points in the figure. The best depolarisation level reached up to that point was no more than about 30mV . Considering that the current density was at the upper level of the range stated in the standard, it is likely that the level of corrosion in the specimens had exceeded what would normally be encountered in real structures where it normally requires a current density less than 10mA/m^2 to achieve 100mV depolarisation. The current density was increased to around 60mA/m^2 and straight away depolarisations exceeded the 100mV criterion for the 2% chloride specimens, except for the high pre-corrosion condition and the 4% chlorides all of which reached 100mV depolarisation after a total charge of around 75kC/m^2 was applied.

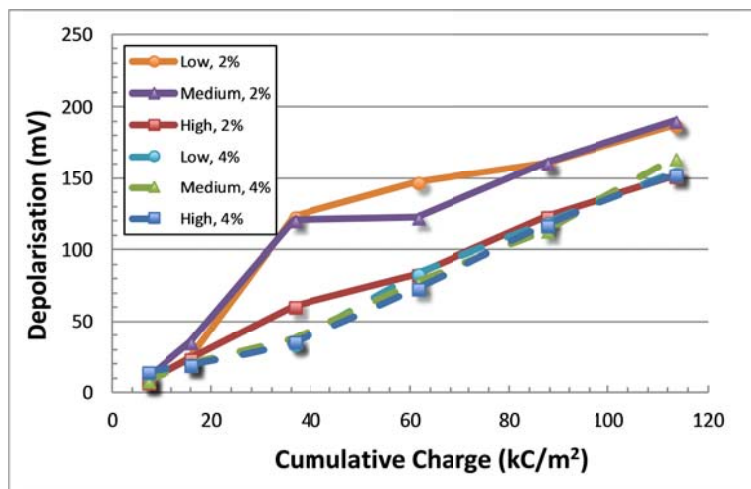


Figure 4 Depolarisation potentials (mean of two) after 24 hours with cumulative charge for pre-corroded specimens

All the pre-corroded specimens subsequently exceeded 150mV depolarisation at the end, but the depolarised potentials had not reached less negative values than -141mV vs SCE when passivation is likely to have been achieved. As the trends were relatively linear, the depolarised data with cumulative charge from Figure 3, were extrapolated to a potential of -141mV vs SCE to estimate the amount of charge that would have been required to passivate the steel when using an average current density of 50mA/m^2 . The results revealed that a significantly higher charge would have been required to passivate steel for the 4% chlorides compared to the 2% chlorides. For the high pre-corroded condition, a charge of $170\text{-}180\text{kC/m}^2$ would have been required to passivate the 2% chloride specimens whereas for the 4% chloride specimens it would have required $240\text{-}250\text{kC/m}^2$. For the same chloride levels, increasing the level of pre-corrosion also meant that, overall, a higher dosage of charge would have been required to passivate the steel.

Contrary to the naturally corroded specimens, which had remained passive for 6 weeks, the potentials of the pre-corroded steel had, over that period, become more negative indicating either that further corrosion had initiated or that the rate of corrosion at the corrosion sites had increased, as the original applied charge was not adequate to stop corrosion but only reduce it. This clearly implies that the 100mV criterion is not sufficient on its own to suggest that corrosion has been mitigated in all cases. An opportunity had, therefore, arisen to

demonstrate the short-term effects on the steel when terminating CP when only the 100mV shift criterion had been achieved.

After the 6 weeks, a further charge of 208 kC/m² at a current density to 50mA/m² was delivered to the pre-corroded specimens to significantly reduce corrosion but was still not sufficient to passivate the steel over reasonable timescales. As mentioned earlier, cracks in the mortar were observed in the more corroded specimens so the treatments were terminated. In practice, once corrosion-induced cracking appears, it is necessary to remove the affected concrete, clean the steel and apply a fresh repair mortar prior to applying CP.

Figures 5 and 6 summarise the average 24-hour depolarised corrosion potentials, or rest potentials when no charge was applied, of the pre-corroded steel specimens during each stage of the experimental process. For most of the 2% chloride specimens it can be seen that cathodic polarisation was able to reduce the corrosion activity of the steel further after the second period of applied charge, bringing the potentials closer to -141 mV. The specimens containing 4% chloride and the highly pre-corroded 2% Cl⁻ specimens were more difficult to polarise after the same second period charge and at best, it required nearly double the charge (208kC/m² compared to 110kC/m²) to bring the potentials to roughly the same level as after the first treatment.

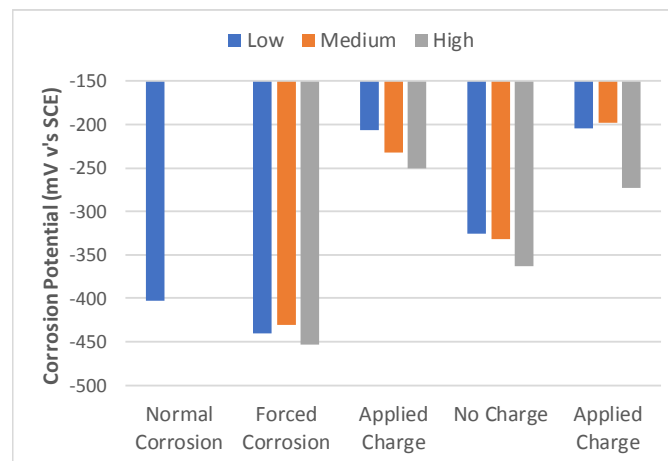


Figure 5 Summary of corrosion potentials for 2% chloride specimens indicating the evolution of potentials at the end of every stage of the process

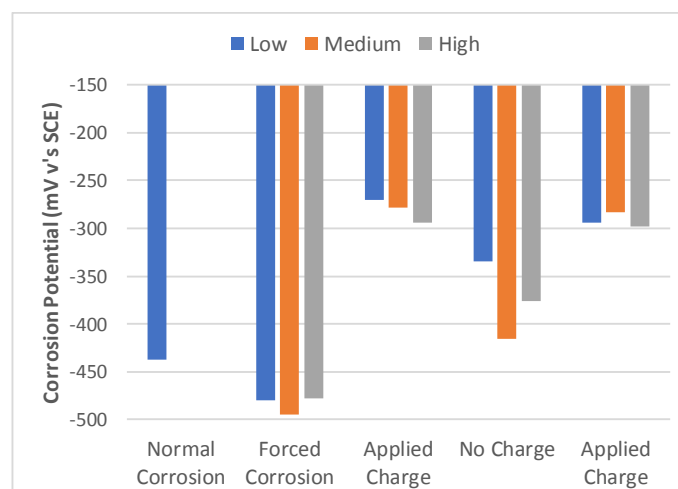


Figure 6 Summary of corrosion potentials for 4% chloride specimens indicating the evolution of potentials at the end of every stage of the process

Anodic Polarisation

The specimens from the naturally corroding group were anodically polarised after they remained passive for 6 weeks to determine how resistant the formation of the passive film on the steel was against corrosion. Probably because the cathodic charge was terminated as soon as passivation was achieved, the passive film was not seen to be very strong as it only required a small anodic charge of $1-10\text{kC/m}^2$ for it to break down. In a separate piece of work, similarly corroded specimens containing 3% Cl^- by weight of cement subjected to extensive cathodic polarisation of $800-2500\text{kC/m}^2$ (mean 1650kC/m^2) at a current density of 500mA/m^2 , a level more appropriate for electrochemical chloride extraction, had required an anodic charge of $30-600\text{kC/m}^2$ (mean 300kC/m^2) to break down the passive layer indicating that the strength of the passive film is related to the level of cathodic charge used to build it up.

Work by Pedeffferri et al [6] and Presuel-Monreno et al [7] had demonstrated that passivity of the steel can be maintained in a corrosive environment for considerable periods by a process they termed Cathodic Prevention by applying a current density of $0.2-2\text{mA/m}^2$. Even constant exposure to highly corrosive environments could not initiate corrosion at a current density of 1mA/m^2 [8]. Once corrosion is arrested it would appear reasonable to suggest that a second stage of a process based on Cathodic Prevention is likely to protect the steel from corrosion. Thus, a Cathodic Protection system based on a Two-Stage process appears to be a viable corrosion mitigation method.

Corrosion Rates

The corrosion currents of the pre-corroded and naturally corroded specimens were calculated using the Butler Volmer equation. This is a simple process if the polarisation in Eq. 1, ΔE , is assumed to be the depolarised potential, in this case at 24 hours. This may be an underestimate of the true level of polarisation, so some further work is required to establish how best to estimate polarisation but in the context of this work where conditions and geometry of samples were constant, using the 24-hour depolarisation was thought to allow comparable results.

The applied current density was assumed to be the current density as measured just before polarisation was turned off, the value never varying by more than 5% from the pre-set value. The anodic and cathodic Tafel slopes were assumed, as in the case of Linear polarisation, to be 120mV/decade . A straight-line relationship was observed between the depolarised potential of the steel and the log of corrosion current density (Fig. 7). The gradient of the data is 110mV/decade which is very close to the assumed cathodic Tafel slope of 120mV (Eq. 1). Linear polarisation resistance (LPR) is a widely used method to measure the corrosion rate, which is derived from the Butler Volmer equation. It is generally accepted that from LPR determinations, steel is assumed to be passive if the corrosion rate is $0.1\ \mu\text{A/cm}^2$ or less with a range of $0.1-0.2\ \mu\text{A/cm}^2$ in which passivity may or may not be signified [9]. Figure 7, however, indicates that for a mean potential considered to be passive ($-141\ \text{mV}$ vs SCE) the corresponding corrosion rate based on the Butler Volmer calculations is only a little more than $0.01\ \mu\text{A/cm}^2$, an order of magnitude lower than that suggested for Linear Polarisation techniques.

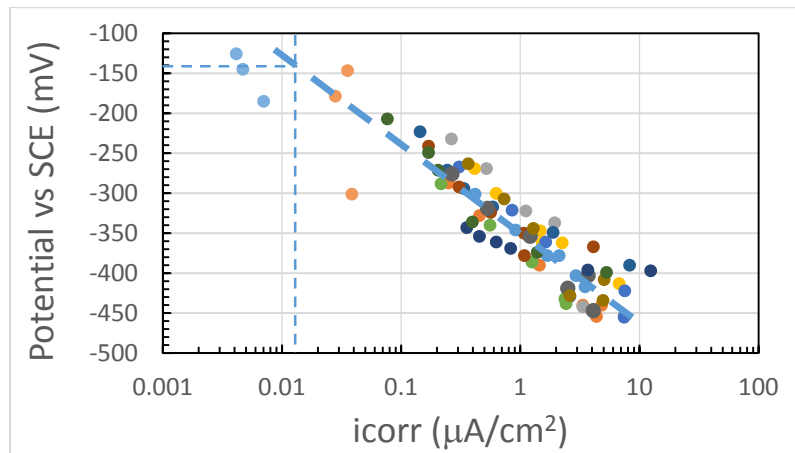


Figure 7 Correlation of corrosion current densities calculated by the Butler Volmer equation and steel depolarisation potentials for pre-corroded and naturally-corroded specimens

During the second stage of cathodic polarisation of the pre-corroded specimens, the corrosion current density after the 48-hour depolarisation measurements was measured several times by Linear Polarisation in order to compare to the Butler Volmer calculations. The correlation of the measurements is shown in Figure 8. Once again, the corrosion current density through the Butler Volmer equation is almost an order of magnitude lower than the equivalent density determined via Linear Polarisation at the assumed passive level. Nonetheless, the results are consistent enough to suggest that using a combination of the depolarisation potential and the cathodic current density just before switch-off of the system potentially provides a simple method of estimating the corrosion rate of steel at the time by utilising the Butler Volmer equation and, in combination with the 24-hour depolarised potential, a decision can be made if passivation of the steel has been achieved. The methodology can be extended to all cathodic protection systems to establish the state of the steel reinforcement and, in cases where the 100mV criterion is not satisfied, an estimation of the corrosion rate can be determined as an alternative criterion for the performance of the CP system.

In situ, a potential limitation is that the current density can only be assumed as the precise steel area being protected is estimated but, more importantly, the current density at the vicinity of the reference electrode measuring depolarisation is not accurately known. On the plus side, the position of the reference electrodes is fixed, as is, to a large extent, the current distribution so the evolution of measurements performed in the same way over time will show trends of behaviour which can be used for the corrosion assessment of the structural element.

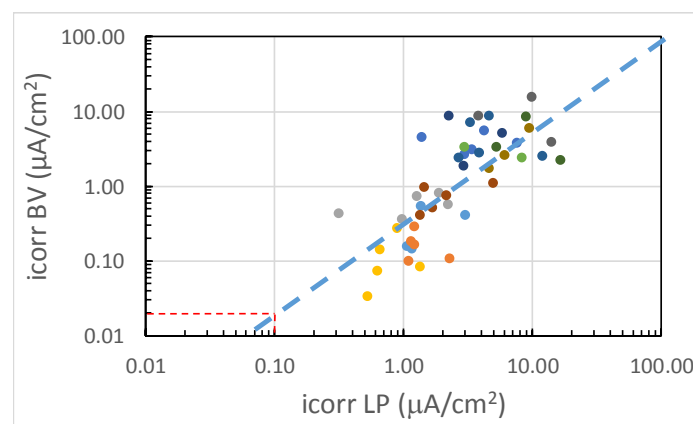


Figure 8 Relationship between the corrosion current densities determined by either the Butler Volmer equation or by Linear Polarisation at corresponding times

Corrosion prevention by early application of charge

Several Set-2 specimens, after their initial 30 day curing period in a 100% environment, were cathodically polarised, as described earlier, at a mean current density of 50mA/m^2 to three levels of total charge, viz. 82kC/m^2 , 176kC/m^2 and 245kC/m^2 . Once the polarisation was completed, the specimens were dosed with 5ml of 1M sodium chloride solution introduced through the reservoir. The specimens were subjected to bi-weekly wet dry cycles by wetting the exposed surface of the specimens around the reservoir, which were covered with thick tissue, with 10ml of deionised water. The drying cycle involved exposing the specimens in a room maintained at $65\pm 5\%$ RH for two weeks. This maintained the bulk of the specimens in a dry condition compared to the central region beneath the reservoir which was wet throughout in an attempt to accelerate penetration of chloride. The chloride solution was replenished whenever the level dropped by 2mm. The steel potential of each specimen was monitored by resting a reference electrode on a pre-marked point on the surface of each specimen. Owing to the dry surface at the location of the measuring point, the potential values reached extreme positive values and were very sensitive to wetting. In hindsight, it would have been more realistic to measure the potentials through the reservoir which would have avoided the extreme potentials recorded. Nonetheless, the points at which steel depassivation had occurred remain very clear (Fig. 9).

The striking result is the breakdown of steel passivity at increasing times of exposure to chloride depending on the level of applied cathodic charge. The trend is made clear in Figure 10 where the time for breakdown is seen to have a linear relationship with the applied charge. Two mechanisms may have caused the phenomenon. First, an increased alkalinity may have decreased the $[\text{Cl}^-]/[\text{OH}^-]$ ratio so that the onset of corrosion requires more chloride to initiate corrosion. Secondly, the steel concrete interface may have become more compact from the formation of additional alkali-based products so that migration of chlorides had become more difficult. Either way, it is clear that an initial cathodic charge is beneficial for the prevention of corrosion of steel.

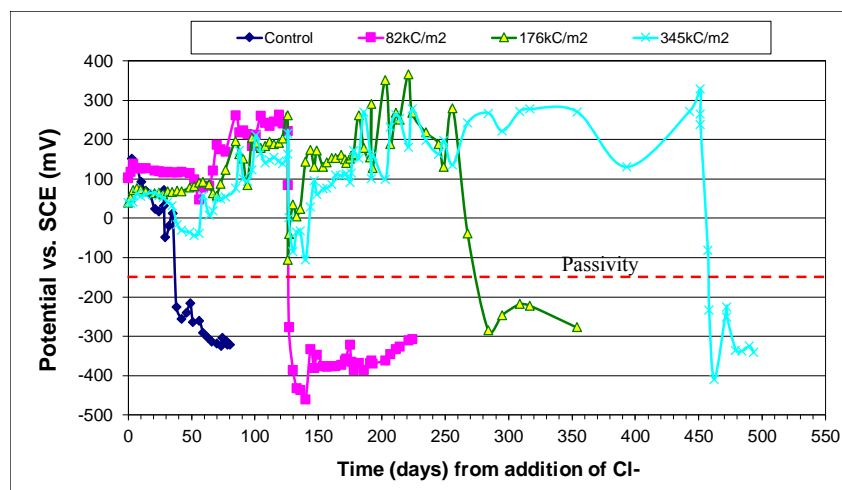


Figure 9 Corrosion initiation of steel subjected to various cathodic charge deliveries

The implication of these results is that when cathodic protection is applied to corroding steel reinforcement, corrosion can be arrested if the current density is adequate but also, especially in regions where steel is still passive, the steel can become more resistive to corrosion initiation.

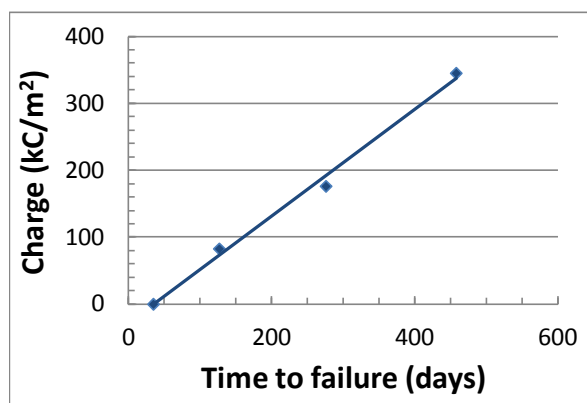


Figure 10 Time to failure (initiation of corrosion) of the steel related to cathodic charge delivered

There are concerns that excessive amounts of charge can result in damaging the microstructure of the concrete both in the bulk and at the steel concrete interface [10–12]. It is believed that a cumulative charge of up to 300-400kC/m², levels regularly exceeded in most current CP applications, delivered at current densities not exceeding 30-40mA/m² are not likely to be detrimental to concrete but this is being investigated further.

The results were used for the development of a Two-Stage Corrosion Mitigation System which has been applied to a bridge column and a coastal wall. These are being carefully monitored with a view of finalising the product and, primarily, to relate site results to the results obtained in the laboratory. Depolarised and depolarisation values in conjunction with corrosion current densities obtained with the Butler Volmer equation will be critically analysed with the aim of establishing sound performance criteria, especially on whether corrosion arrest had been achieved.

Conclusions

Under laboratory conditions, it has been shown that corrosion of steel can be arrested by the application of a constant current density of up to 60mA/m², provided no physical damage, e.g., cracking, delamination, has occurred at the steel-concrete interface. The total charge required for corrosion arrest is dependent on the level of corrosion and corrosivity of the environment. A charge as low as 74kC/m² was seen to passivate corroding steel in mortar containing 2% Cl⁻ when polarisation is applied with a constant 50mA/m² current density but pre-corroded steel in a 4% chloride mortar can require up to 250 kC/m² to arrest corrosion.

Initiation of chloride-induced corrosion can be delayed significantly if the steel is cathodically polarised when in a passive condition, the time before corrosion initiation being dependent on the level of polarisation.

The results conclude that depolarisation, depolarised potentials and corrosion current densities easily calculated by the Butler Volmer equation are suitable parameters for validating the performance of cathodic protection. As it stands, none of the criteria in EN12696:2015 can demonstrate whether steel reinforcement corrosion has been arrested. The only implied parameter is that a steel potential of -150mV vs Ag/AgCl, 0.5M KCl is likely to signify that corrosion is not occurring.

The results were used as a basis for the development of a Two-Stage corrosion mitigation system, prototypes of which have been installed on actual structures. Careful monitoring of these is being undertaken in order to substantiate the experimental results reported in this paper and to establish a workable procedure to confirm corrosion arrest of the Stage-1 process.

Acknowledgements

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