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## Hybrid corrosion protection of chloride-contaminated concrete

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This paper examines steel corrosion initiation and arrest in chloride-contaminated concrete. Corrosion damage is, at least in part, attributed to the production of acid at sites of corrosion initiation. Solid phase inhibitors provide a reservoir of hydroxyl ions to inhibit damage. Pit re-alkalisation is identified as an important protective effect in electrochemical treatments used to arrest corrosion. An acidification-pit-re-alkalisation model is used to explain the lateral spread of chloride-induced corrosion across a steel surface, the time required to arrest corrosion in cathodic protection and the potential shifts observed as protection is achieved. The process of pit re-alkalisation may be achieved using a relatively small electric charge that is readily impressed off sacrificial anodes using a power supply. A simple but powerful electrochemical treatment comprises a hybrid of a brief pit-re-alkalisation process to arrest corrosion followed by low maintenance galvanic protection to prevent local acidification. Methods of monitoring the steel corrosion rate in electrochemically treated concrete have been developed and used to assess corrosion risk. The brief pitre-alkalisation process may be applied at any time using the existing anode system to manage future corrosion risk.

#### **I. INTRODUCTION**

Chloride-induced corrosion is a major cause of damage to steel in concrete structures (Fig. 1).<sup>1</sup> It is an electrochemical process in which iron dissolves as positive ions and there is a current flow that is proportional to the corrosion rate. Corrosion rates are usually expressed as a current density or steel section loss. A corrosion rate of 1 mA/m<sup>2</sup> is approximately equal to the loss of  $1.1 \ \mu m$  of steel per year. Average corrosion rates up to  $2 \ mA/m^2$ are considered to be negligible. Higher corrosion rates represent an increasing risk of significant localised corrosion activity.<sup>2</sup>

Treating corrosion damage after chloride has contaminated the concrete presents a challenging problem. In some cases it is preferable to remove the contaminated concrete. Electrochemical methods are considered to be the most powerful treatments when chloride-contaminated concrete is left in place. This paper reviews the processes of steel corrosion initiation and its arrest using electrochemical methods in chloride-contaminated concrete. Existing mechanisms are challenged and developed, and a basis for an improved treatment of chloride-induced corrosion damage, that relies on restoring and maintaining the

pH at the steel, is derived. Data from both laboratory studies and field installations of this new treatment are evaluated.

#### 2. CORROSION DAMAGE

Concrete normally provides a highly alkaline environment that promotes the formation of a protective passive film on reinforcing steel.<sup>3</sup> Chloride-induced corrosion starts as localised breakdown of this passive film and is termed pitting corrosion. It is usually explained using a pitting potential-repassivation potential model.<sup>4,5</sup> In this hypothesis, the presence of chloride affects the voltage that may be tolerated across the passive film before passive film breakdown occurs. At positive steel potentials achieved in the presence of oxygen, chloride ions induce local passive film breakdown.

A common illustration of this model adapted from the European cathodic protection standard for concrete is given in Fig. 2.6 At negative potentials iron is stable and steel is immune to corrosion (region A). As the potential increases iron dissolution becomes possible, but in the alkaline environment a passive oxide film forms (region B). At higher chloride content and more positive steel potentials a region exists in which corrosion may propagate but it will not initiate (region C). Further increases in steel potential and/or chloride content render the passive film unstable and pitting corrosion initiates (region D).

While the *x* and *y* axes in Fig. 2 are sometimes quantified, it should be noted that only the boundary defining steel immunity has been calculated from thermodynamic data and this is dependent on pH. Even experimental data defining the regions in this model are not readily available for reinforced concrete, although these regions have been observed in alkaline solutions.<sup>7</sup>

Another feature of chloride-induced corrosion is that acid is produced at the site of corrosion initiation. pH values below 5 have been measured on corroding steel in what is otherwise a very alkaline concrete environment.<sup>8,9</sup> However, the effect of acidification is not clear in the literature on steel corrosion in concrete because chloride-induced corrosion is distinguished from carbonation-induced corrosion with the observation that chloride-induced corrosion occurs despite the high pH of the concrete cover.<sup>10</sup> Thus the local pH reduction is sometimes regarded as simply a consequence of corrosion initiation rather than a cause of corrosion damage; however, this is not the case in solution environments.



In a second model, corrosion initiation may be divided into pit nucleation and pit growth.<sup>11</sup> A local pH reduction cannot be the cause of pit nucleation, but passive films are not perfect and pit nucleation events are frequent. Most pits do not grow and a local pH reduction is considered to be essential if pit growth is to occur. In this model, chloride-induced corrosion damage in reinforced concrete requires the production of acid at a pit nucleation site.<sup>12</sup>

The pit-nucleation—pit-growth model is illustrated in Fig. 3. A pit-nucleation event leads to the formation of soluble iron ions. These react with water to produce iron hydroxide and positive hydrogen ions. Chloride ions act as a charge balancing species. Hydrochloric acid is effectively produced. The local pH reduction promotes further iron dissolution and the acidification—dissolution cycle continues in the process of pit propagation. The soluble iron moves away from the steel surface before it precipitates and the repair of the passive film is prevented. Included within Fig. 3 are the mass transfer processes that maintain charge balance (the migration of positive and negative ions). Ion migration is relatively slow in a concrete environment.

Chloride-induced corrosion is sometimes termed autocatalytic (self-accelerating).<sup>9,13</sup> Chloride ions stabilise the formation of soluble iron in the acidic environment, but they are not consumed. To maintain charge balance the chloride ions move towards the pit, whereas the hydrogen ions (acid) move away. The movement of hydrogen ions away from the pit is equivalent to





the movement of hydroxyl ions towards the pit. There is some competition between chloride and hydrogen ion migration, but if the pH is to continue to fall and the corrosion rate is to continue to increase, an increase in the chloride content in the pit is required.

The above discussion introduces the concepts of pit nucleation, pit growth, corrosion initiation and corrosion damage. Two co-existing models (Figs 2 and 3) are used to explain these concepts. One of these is well established in the literature, whereas the other is less clear in texts on corrosion in concrete. These models place emphasis on either steel potential or local acidification. From an engineering perspective, arresting and preventing damage is important and this may be achieved by either maintaining a relatively negative steel potential, or by neutralising the production of acid at sites of corrosion initiation.

#### 3. SOLID PHASE INHIBITORS

Evidence of the effect of a local pH reduction in the corrosion process in concrete is provided by the observation that corrosion initiation tends to occur at the location of voids filled with pore solution.<sup>14,15</sup> Early work postulated that the calcium hydroxide phase in hydrated cement paste provides a reservoir of hydroxyl ions that act to inhibit corrosion initiation in chloridecontaminated concrete.<sup>16-18</sup> The absence of precipitated calcium hydroxide at voids results in a low resistance to a pH reduction and therefore a low resistance to corrosion initiation at these locations. This has been extended to include all solids with pH-dependent dissolution behaviour and a broad concept of solid phase inhibitors has been developed.<sup>19</sup> Solid phases in hydrated cement have an important influence on the steel corrosion risk.

A method termed differential acid neutralisation analysis was developed to identify acid-soluble phases in concrete that may inhibit corrosion.<sup>20</sup> The resistance to acid neutralisation (quantity of acid per unit of sample per unit of pH reduction) for an ordinary Portland cement (OPC) concrete is given in Fig. 4. There are many phases in hydrated cements that will inhibit a local reduction in pH. This localised effect is not replicated in solution-based experiments.

The effect of a reservoir of hydroxyl ions has been the subject of previous reviews.<sup>21,22</sup> Well-compacted laboratory specimens and specimens initially subjected to temporary electrochemical treatment have a high resistance to corrosion initiation.<sup>19</sup> Similarly, corrosion initiation will also be inhibited by the continuous low-level generation of hydroxyl ions at the steel in a preventative electrochemical treatment.



#### 4. CORROSION PROPAGATION

Figure 5 illustrates the processes occurring in a corrosion cell on steel in concrete. The dissolution of iron at a corroding site (anode) is at least in part supported by the consumption of oxygen (oxygen reduction) at a location (the cathode) away from the anode. This is termed a macro-corrosion cell. Corrosion usually spreads as a shallow pit from the point of initiation over the adjacent steel surface.<sup>23</sup>

Included in Fig. 5 are the results of a numerical model of the corrosion cell. This assumed that 5% of the steel was corroding and the concrete resistivity was 200  $\Omega$  m. The boundary conditions include the polarisation behaviour (the relationship between the reaction rate and the electrode potential) at the anodic and cathodic areas. Details have previously been reported.<sup>24</sup> The potential contours within the concrete cover are given in Fig. 5(b) and the potential as a function of distance along the steel surface is given in Fig. 5(c).<sup>19</sup> The potential values are the potential of the concrete relative to a saturated calomel reference electrode (SCE). The steel potential is inverted (negative) relative to the concrete.

The model predicted an average steel corrosion rate of approximately 15 mA/m<sup>2</sup> and a local rate at the anode of 300 mA/m<sup>2</sup> (0·3 mm of steel section loss per year). These predictions correspond with observations made in practice. The model suggests that the potential of the steel cathode adjacent to the anode is shifted in the negative direction by more than 250 mV. Similar potential shifts have been reported in other published models of this corrosion cell.<sup>25–27</sup>

It has been suggested that the adjacent steel cathode is protected by this potential shift.<sup>23</sup> This protection is lost if the anodic area is repaired with chloride-free concrete. This is sometimes referred to as the incipient anode problem. Corrosion damage often develops in concrete adjacent to a repaired area.

The published explanation is illustrated in Fig. 6.<sup>28</sup> This shows the potential at the steel interface as a function of distance before and after repair and the classical shape of the anodic polarisation curve for steel that obeys the pitting potential—repassivation potential model. Before the repair, the potential of the incipient anode is held in a region where pitting corrosion will not initiate, but after the repair its potential rises into the region where pitting can occur. Thus the pitting potential—repassivation potential model provides an explanation for the observed spread of corrosion following patch repairs to a chloridecontaminated structure.



with the potential field (contours at 50 mV intervals) in the concrete cover (b); and the potential on the steel surface (c)

However, the pitting potential—repassivation potential model fails to provide an explanation for the observed lateral spread of corrosion if patch repairs are not undertaken. Corrosion spreads to the cathode adjacent to the anode that receives the most potential shift.

In the pit nucleation—pit propagation model, the adjacent cathode falls within the pH gradient between the acidic anode and the alkaline cathode. The passive film becomes unstable as the pH falls. The effect of the more acidic environment overrides the protective effect of the negative potential shift. A corollary to this is the protective effect of the high pH may be more important than the protective effect of the negative potential shift. The conditions where this may be true are examined further in the next section.







#### 5. ELECTROCHEMICAL CORROSION ARREST

Cathodic protection is the most common electrochemical method used to arrest an aggressive corrosion process. The potential of the steel is driven to more negative values by the applied protection current and cathodic protection is sometimes defined in terms of this potential shift effect. Monitoring comprises interrupting the protection current and measuring the subsequent steel potential decay. Typically 100 mV of potential decay is required to indicate protection.<sup>6</sup>

Figure 7 shows the initial potential and the potential decays determined on steel in a laboratory concrete specimen containing 3% chloride.<sup>24</sup> The open circuit steel potential just prior to applying the cathodic protection was -430 mV (SCE). The potential decay starts with an instant off potential. This is the driven potential of the steel that excludes any voltage drop through the concrete arising from the current and concrete resistance (IR drop).

Figure 7 also includes the applied steel current density  $(i_{appl})$  measured just before the potential decay and the average steel corrosion rate  $(i_{corr})$ . The corrosion rate was determined from the applied current density and the potential decay. The method is discussed further below. After 47 days and the application of 30 A h/m<sup>2</sup> (100 kC/m<sup>2</sup>) of charge, the 100 mV decay criterion was achieved and the corrosion rate of the steel fell to 1·2 mA/m<sup>2</sup>. This is low and probably represents passive steel.

The data shows that it is difficult to achieve large potential shifts on actively corroding steel in the short term. Furthermore, while



the steel potential was driven to more negative values, it shifted to more positive values with time before the protection criterion was achieved. Even the driven potential (the instant off potential) after 27 days was 15 mV more positive than the initial corrosion potential and, after 47 days, the driven potential was 90 mV more positive than the initial corrosion potential. This implies that inducing steel passivity was a prerequisite to achieving the protection criterion.

The long time required to achieve protection and the positive shift in driven potential prior to achieving protection cannot be adequately explained by the pitting potential—repassivation potential model. The results indicate that slow processes such as diffusion and migration dominate. Even the repassivation potential must shift to more positive values before protection is achieved. In this case an improvement in the environment at the steel was a more important protective effect than a negative potential shift.

Two effects of electrochemical treatments that improve the environment at the steel are the production of hydroxyl ions at the steel and the migration of chloride ions away from the steel. These effects are related as hydroxyl ions, like chloride ions, are negative charge carriers and are an alternative charge balancing ion.

It has been noted that the direct extraction of chloride from actively corroding sites is not feasible at cathodic protection current densities.<sup>29</sup> The problem is modelled in Fig. 8 where an installed anode on the concrete surface delivering 50 mA/m<sup>2</sup> is added to the model in Fig. 5. This is a high current when compared with cathodic protection current densities.<sup>6</sup> Despite this high applied current density a net positive current still leaves the anode on the steel. Thus chloride ions may still be drawn to this local steel anode. The direct extraction of chloride from an acidic corrosion site on the steel is only possible when the applied current depresses the steel potential to a value below the open circuit potential of the isolated acidic corrosion site.

By contrast re-alkalisation is assisted by diffusion in the pH gradient and hydroxide migration which competes with chloride migration in the electric field. It is postulated that the production of additional hydroxide at the steel cathode coupled with a reduced migration of chloride and increased migration of hydroxide to the steel anode reverses the spread of the corrosion process. This is illustrated in Fig. 9. The pH rises at the periphery of the corrosion site which then reduces in size until a point is reached when the passive film is restored. This is a relatively slow process at cathodic protection current densities and would be

accompanied by more positive steel potentials associated with passive steel. This new concept is termed pit re-alkalisation.<sup>24</sup> In principle, pit re-alkalisation is similar to re-alkalisation applied to carbonated concrete, but it is also applied to non-carbonated concrete to re-alkalise localised acidic corrosion sites that result from chlorideinduced corrosion.

There is a thermodynamic basis for the acidification—pit-re-alkalisation model for chloride-contaminated concrete. The



was required in a laboratory concrete specimen containing 3% chloride at the depth of the steel (Fig. 7).<sup>24</sup> It is probable that less charge would be required at lower chloride contents. The high current density that may be achieved off sacrificial anodes allows the pit-re-alkalisation treatment to be delivered in a

calculated regions of stability for iron and its compounds as a function of potential (SCE) and pH is shown in Fig. 10.<sup>19</sup> Concrete normally provides an alkaline environment in which the oxides that make up the steel passive film are stable. Passive films are not perfect and some iron dissolution may result in a local pH reduction (acidification). Pit re-alkalisation restores the pH and renders the passive film stable.

# 6. PIT RE-ALKALISATION AND CORROSION PREVENTION

Electrochemical treatments for chloride-induced corrosion include cathodic protection and chloride extraction. Chloride extraction is a temporary treatment with the onerous objective of removing the chloride. Cathodic protection is a permanent treatment and may be applied using impressed or galvanic current. Impressed current systems require sustained management by skilled personnel to ensure successful installation and operation.<sup>30</sup> Galvanic systems are not as powerful and may not arrest an active corrosion process. However, they do function in a preventative role, they are very simple to install and they require very little maintenance.

A new treatment to arrest an active corrosion process and maintain steel passivity combines a brief pit-re-alkalisation treatment, impressed off a sacrificial anode system, with galvanic protection subsequently delivered from the same anode system. The high pH at the steel is restored by the pit-re-alkalisation process and maintained by galvanic protection. This novel combination is referred to as a hybrid electrochemical treatment.<sup>31</sup> The power of an impressed current electrochemical treatment is combined with the low maintenance requirements of galvanic protection. The maintenance of the impressed current treatment is limited to a brief period during installation when steel passivity is restored.

One advantage of the use of a sacrificial anode in an impressed current role is that a high current density is readily achieved. This is illustrated in Fig. 11, which compares the current from an aluminium anode with that from an inert mixed metal oxide (MMO)-activated titanium anode in a concrete specimen.<sup>32</sup> The aluminium delivers more than 10 000 mA/m<sup>2</sup> off its surface at a potential that is not sufficiently positive to result in any significant current being driven off the titanium anode. The dissolution of the sacrificial metal element occurs more readily than the conversion of water into oxygen gas on the inert anode.

The pit-re-alkalisation process requires the delivery of relatively little charge to the steel. As noted above, 30 A  $h/m^2$  of steel

very short time using a temporary DC power supply. In practice it typically takes less than 2 weeks.

The sacrificial anode is consumed in the delivery of the pit re-alkalisation and galvanic treatments. Its life is determined by the quantity of sacrificial metal. By way of example, a pure zinc bar, 17 mm in diameter and 100 mm long has a charge capacity of more than 125 A h. If six bars are installed for every square metre of steel, the available charge is 750 A h/m<sup>2</sup>. The pitre-alkalisation process may require 30 A h/m<sup>2</sup>. The remainder is available to deliver the galvanic current. A typical corrosion prevention current density for passive steel is 1 mA/m<sup>2</sup>.<sup>6</sup> The delivery of this current for 50 years equates to a charge of 440 A h/m<sup>2</sup>. Anode utilisation and efficiency need to be taken



Fig. 10. Acidification and pit re-alkalisation in the context of the stability of iron and its products



Fig. 11. Sacrificial and inert anode current densities as a function of anode potential  $^{\rm 32}$ 



into account as well as other contingencies such as a possible need to re-apply the pit-re-alkalisation process. Nevertheless it appears to be feasible to design a system with an anode life in excess of 50 years and pure galvanic systems have been applied to steel in concrete for more than 10 years.<sup>33</sup>

Data from a laboratory trial of the hybrid treatment applied to steel in a concrete block containing 4% chloride by weight of cement is presented in Figs 12 and 13.<sup>34</sup> Figure 12 shows the current delivered off a zinc bar to  $0.25 \text{ m}^2$  of steel. Initially an impressed current was driven off the anode using a 12 V power supply to achieve the pit-re-alkalisation process. The zinc was then connected to the steel and the current decayed to 170 mA/m<sup>2</sup> off the zinc.<sup>34</sup>

The steel potential prior to applying the hybrid treatment was -460 mV (SCE). The steel potential decay measured on disconnecting the steel from the zinc is shown in Fig. 13. The steel potential decay over a 10 h period was 346 mV. This excluded a 62 mV IR drop. The steel current density prior to interrupting the current was  $8 \cdot 2 \text{ mA/m}^2$  and the calculated steel corrosion rate was less than  $0.05 \text{ mA/m}^{2.34}$  The steel was passive. The open circuit potential of the steel had also shifted to significantly more positive values indicative of steel passivity.

This hybrid corrosion treatment has now been applied to several reinforced concrete structures. An

example of a treated bridge where the reinforced concrete substructure had previously suffered from chloride-induced corrosion is shown in Fig. 14.<sup>35</sup>

#### 7. CORROSION RISK MANAGEMENT

In the above discussion a hybrid electrochemical treatment comprising a temporary pit-re-alkalisation process to arrest corrosion followed by the application of a low galvanic current as a preventative measure is described. Both treatments are delivered using the same sacrificial anode system and it is possible in theory to have an anode life in excess of 50 years. The treated structure may be monitored using corrosion rate and corrosion

potential measurements to assess future corrosion risk. A corrosion risk management plan combines monitoring with a strategy to deal with adverse monitoring data.

Corrosion rates are related to the potential shift and applied current density. A common method uses polarisation resistance







Fig. 14. Whiteadder bridge following the installation of a Hybrid corrosion protection system on the concrete substructure



Fig. 15. The corrosion rate plotted as a function of potential shift and current density together with an example of its interpretation



theory. The polarisation behaviour (relationship between potential shift and applied current) of an electrode with activation controlled reactions is given by

$$i_{\text{appl}} = i_{\text{corr}} \left( \exp\left(\frac{2 \cdot 3\Delta E}{\beta_{\text{c}}}\right) - \exp\left(-\frac{2 \cdot 3\Delta E}{\beta_{\text{a}}}\right) \right)$$

where  $i_{app}$  is the applied current density,  $i_{corr}$  is the corrosion rate  $\Delta E$  is the electrode potential shift and  $\beta_a$  and  $\beta_c$  are constants.<sup>36</sup> In the 1950s this equation was simplified by assuming that the potential shift was small. The exponential functions were then approximated by linear functions and the linear polarisation resistance method was developed.<sup>37</sup>

If the potential shift is not small, the corrosion rate may still be calculated using equation (1). The

sensitivity of the calculation (1). The sensitivity of the calculation to errors in the various parameters has previously been assessed.<sup>38</sup> For a negative potential shift, the calculated corrosion rate will be reasonably accurate if the cathodic reaction kinetics are under activation control.

For steel undergoing electrochemical treatment, a conservative estimate of its potential shift is given by its potential decay measured on interrupting the protection current. This method was used to estimate the corrosion rates associated with Figs 7 and 13 above. The data in Fig. 7 suggests that the method gives a conservative estimate of corrosion rate when compared with the more traditional polarisation resistance method applied to calculate the initial corrosion rate.

Figure 15 shows an example of the theoretical corrosion rate as a function of the potential shift induced by an applied current density of 2 mA/m<sup>2</sup>.<sup>39</sup> Passive and active regions are included in the figure. At a current density of 2 mA/m<sup>2</sup>, a potential shift of 30 mV or more would indicate that the steel is passive. In practice the steel current density may be estimated from the current off an isolated segment of the anode at the location of the steel potential decay measurement.

An example of corrosion rate data calculated using steel potential decay and current density measurements on a concrete bridge element in the galvanic phase of a hybrid treatment is included in Fig. 16.<sup>40</sup> A brief pit-re-alkalisation process lasting 7 days had initially been applied using approximately 1400 discrete sacrificial anodes installed in the bridge substructure. The *x*-axis represents the elapsed time from the end of the pit-re-alkalisation process on a segment of the system. The potential of the sacrificial anode–steel couple is also shown. Six corrosion rate measurements were made during the 2 years that followed the pit-re-alkalisation process. The data suggests that the steel is passive. The corrosion rates are negligible (less than 2 mA/m<sup>2</sup>) and falling, while the potential of the anode–steel couple is moving to more positive values with time.

Another method of monitoring uses potential mapping. An example of a potential map obtained on a section of a concrete column in a car park containing sacrificial anodes that had previously been used to deliver a pit-re-alkalisation treatment to the column is shown in Fig. 17. The potential data was obtained by measuring the potential of a manganese dioxide reference electrode on the concrete surface relative to the embedded steel on a 50 mm grid.<sup>41</sup>

The presence of strong sacrificial anodes is indicated by strong peaks in the potential map and this indicates that the sacrificial anodes are functioning. When the steel falls within the potential field of the anode, it receives some protection. The absence of smaller peaks between the installed anodes indicates that there are no anodic areas on the steel and therefore the steel corrosion risk is negligible. The use of such a non-invasive potential



Fig. 17. Potential map (contours at 100 mV) showing the location of installed anodes in a concrete column supporting a car park



Fig. 18. A general view of a tidal barrage, corroded reinforced concrete supporting beams (lower left inset) and a repaired area with discrete anodes in holes just above the repair (lower right inset)

results when pit nucleation leads to local acidification which in turn leads to a cycle of increasing iron dissolution and local acidification.

Corrosion spreads from the point of initiation to adjacent steel surfaces in spite of the significant negative potential shift at this location because

been developed. While the theory may be debated further, a significant practical benefit has been achieved in the form of a new powerful but simple treatment for corrosion damaged concrete.

8. CONCLUSIONS An acidification-pit-

re-alkalisation model has been derived to improve the description of corrosion initiation and arrest in chloride-contaminated concrete. Significant damage

mapping technique is more compatible with low-maintenance galvanic treatments.

Risk management includes a strategy to deal with any future risk of corrosion identified by corrosion monitoring. Such a strategy may be included in the design stage of a hybrid electrochemical treatment by connecting the anodes to the steel at locations that are accessible at a later date. This allows the pit-re-alkalisation process to be applied in the future using the existing anode system and a temporary DC power supply if a corrosion risk is detected.

In one example, chloride-induced corrosion damage to a tidal barrage that harnessed the tide for power generation was repaired using a hybrid electrochemical treatment involving the installation of 5000 discrete zinc anodes. Figure 18 gives a general view of the structure, the condition of the soffits of the supporting reinforced concrete beams in this aggressive environment (lower left inset) and the targeted installation of the anodes in the high-risk parent concrete just above the repaired area on one beam (lower right inset). The anodes were subsequently covered with repair mortar. The restricted access in the tidal zone limited the time for concrete repair and anode installation. The anodes were connected to the steel at accessible locations outside the tidal zone to minimise the access requirement of the pit-re-alkalisation process. The pitre-alkalisation process was applied through these accessible connections at a later date. The pit-re-alkalisation process comprised driving a high current off the installed zinc anodes to the steel using a 6 V DC power supply for a period of 2 weeks.

The above discussion has challenged existing theory and proposed a new model for steel corrosion initiation and arrest in chloride-contaminated concrete. A hybrid of a temporary pitre-alkalisation process with a permanent galvanic treatment has the production of acid overrides the protective effects of the negative potential shift. Damage may be prevented by solid phase inhibitors that release hydroxyl ions and solid phases have an important influence on corrosion risk.

Pit-re-alkalisation is an important protective effect that breaks the acidification—iron dissolution cycle in electrochemical treatments applied to arrest an active chloride-induced corrosion process. It gives rise to the time dependence of the processes leading to corrosion arrest at cathodic protection current densities and the positive potential shifts observed as active corrosion is arrested. A relatively small charge is required to deliver a pit-re-alkalisation process to steel in chloridecontaminated concrete. The rapid delivery of this charge in a brief pit-re-alkalisation process is assisted by using a sacrificial metal element as an impressed current anode.

A hybrid electrochemical treatment consisting of a brief pitre-alkalisation process followed by supplementary galvanic protection to induce and maintain a high pH at the steel has been developed. The treatment combines the power to arrest an aggressive corrosion process with the simplicity and low maintenance requirements of galvanic technologies. In practice, both the pit-re-alkalisation and supplementary galvanic treatments are delivered from the same sacrificial anode system. The life of the anode system is related to the quantity of sacrificial metal and lives in excess of 50 years are theoretically possible from practical anode systems.

A strategy to manage future corrosion risk in reinforced concrete subject to galvanic protection combines corrosion monitoring with the option built into the galvanic system to apply a brief pit-re-alkalisation treatment from the installed sacrificial anodes. Corrosion risk may be assessed non-destructively using corrosion potential and corrosion rate measurements. Corrosion rates may be determined from the local galvanic current density delivered to the steel and the steel potential decay observed on interrupting the galvanic current.

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#### REFERENCES

- 1. HIGHWAYS AGENCY. *Repairs to M4 Elevated Section Supports*. See http://www.highways.gov.uk/roads/projects/12851.aspx for further details. Accessed 22/05/2008.
- 2. ANDRADE C., ALONSO C., GULIKERS J., POLDER R., CIGNA R., VENNESLAND O., SALTA M., RAHARINAIVO A. and ELSENER B. Test methods for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method. *Materials and Structures*, 2004, **37**, No. 273, 623–643.
- 3. POURBAIX M. Thermodynamics and corrosion. *Corrosion Science*, 1990, 30, No. 10, 963–988.
- LI L. and SAGÜÉS A. A. Chloride corrosion threshold of reinforcing steel in alkaline solutions—cyclic polarization behavior. *Corrosion*, 2002, 58, No. 10, 305–316.
- LI L. and SAGUES A. A. Chloride corrosion threshold of reinforcing steel in alkaline solutions—Effect of specimen size. *Corrosion*, 2004, 60, No. 2, 195–202.
- 6. BRITISH STANDARDS INSTITUTION (BSI). BS EN 12696:2000 Cathodic Protection of Steel in Concrete. BSI, London, 2000.
- 7. PEDEFERRI P. Cathodic protection and cathodic prevention. *Construction and Building Materials*, 1996, 10, No. 5, 391–402.
- NAM J., HARTT W. H., KIM K. and LI L. Effect of cement alkalinity upon time-to-corrosion of reinforcing steel in concrete undergoing chloride exposure. In: *Corrosion 2003*. National Association of Corrosion Engineers, Houston, Texas, Paper No. 03290 (CD-ROM).
- 9. BERTOLINI L., ELSENER B., PEDEFERRI P. and POLDER R. B. Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair. Wiley-VCH, Weinheim, Germany, 2003, pp. 92–93.
- 10. BROOMFIELD J. P. Corrosion of Steel in Concrete, Understanding, Investigation and Repair. E & FN Spon, London, UK, 1997, pp. 22–27.
- SZKLARSKA-SMIALOWSKA Z. *Pitting Corrosion of Metals*. National Association of Corrosion Engineers, Houston, Texas, 1986, pp. 377–404.
- GLASS G. K. Deterioration of steel reinforced concrete. In Encyclopaedia of Comprehensive Structural Integrity (MILNE I., RITCHIE R. and KARIHALOO B. (eds)). Elsevier Science, Oxford, 2003, vol. 6, ch. 7.
- COTTIS R. F. Introduction to Corrosion. January 2002. See http://corrosiontest.its.manchester.ac.uk/lecturenotes/civils/ Civils%20Corrosion%20Notes.pdf for further details. Accessed 14/05/2008.
- ANN K. Y. and SONG H. W. Chloride threshold level for corrosion of steel in concrete. *Corrosion Science*, 2007, 49, No. 11, 4113-4133.
- HARTT W. H. and NAM J. Effect of cement alkalinity upon chloride threshold and time-to-corrosion of reinforcing steel in concrete. In: *Corrosion 2008*. National Association of Corrosion Engineers, Houston, Texas, Paper No. 08322 (CD-ROM).

- PAGE C. L. Mechanism of corrosion protection in reinforced concrete marine structures. *Nature*, 1975, 258, No. 5535, 514–515.
- SYKES J. M. and BALKWILL P. H. Simulating the pitting corrosion of steel reinforcement in concrete. In: *The Use of Synthetic Environments for Corrosion Testing* (FRANCIS P. E. and LEE T. S. (eds)). ASTM, West Conshohocken, PA, USA, 1988, STP 970, pp. 255–267.
- YONEZAWA T., ASHWORTH V. and PROCTER R. P. M. Pore solution composition and chloride effects on the corrosion of steel in concrete. *Corrosion*, 1988, 44, No. 7, 489–499.
- GLASS G. K., REDDY B. and CLARK L. A. Making reinforced concrete immune from chloride corrosion. *Proceedings of the Institution of Civil Engineers, Construction Materials*, 2007, 160, No. 4, 155–164.
- GLASS G. K., REDDY B. and BUENFELD N. R. Corrosion inhibition in concrete arising from its acid neutralisation capacity. *Corrosion Science*, 2000, 42, No. 9, 1587–1598.
- 21. GLASS G. K. and BUENFELD N. R. The presentation of the chloride threshold level for corrosion of steel in concrete. *Corrosion Science*, 1997, 39, No. 5, 1001–1013.
- 22. GLASS G. K., REDDY B. and BUENFELD N. R. The participation of bound chloride in passive film breakdown on steel in concrete. *Corrosion Science*, 2000, **42**, No. 11, 2013–2021.
- 23. PAGE C. L. and TREADAWAY K. W. J. Aspects of the electrochemistry of steel in concrete. *Nature*, 1982, 297, No. 5862, 109–115.
- 24. GLASS G. K., DAVISON N. and ROBERTS A. C. Pit realkalisation and its role in the electrochemical repair of reinforced concrete, *Journal of Corrosion Science and Engineering*, 2007, 9, paper 10.
- 25. REDAELLI E., BERTOLINI L., PEELEN W. and POLDER R. FEM-models for the propagation period of chloride induced reinforcement corrosion. *Materials and Corrosion-Werkstoffe und Korrosion*, 2006, **57**, No. 8, 628–635.
- 26. WARKUS J. and RAUPACH M. Numerical modelling of macrocells occuring during corrosion of steel in concrete. *Materials and Corrosion-Werkstoffe und Korrosion*, 2008, **59**, No. 2, 122–130.
- 27. GULIKERS J. and RAUPACH M. Numerical models for the propagation period of reinforcement corrosion comparison of a case study calculated by different researchers. *Materials and Corrosion-Werkstoffe und Korrosion*, 2006, **57**, No. 8, 618–627.
- 28. PAGE C. L. and SERGI G. Developments in cathodic protection applied to reinforced concrete. *Journal of Materials in Civil Engineering*, 2000, 12, No. 1, 8–15.
- 29. GLASS G. K. and HASSANEIN A. M. Surprisingly effective cathodic protection. *Journal of Corrosion Science and Engineering*, 2003, 4, Paper 7.
- SHARP S. R. and BROWN M. C. Survey of Cathodic Protection Systems on Virginia Bridges. Virginia Transportation Research Council, Charlottesville, VA, USA, June 2007, Report FHWA/VTRC 07-R35.
- 31. GLASS G. K., ROBERTS A. C. and DAVISON N. *Treatment Process for Concrete*, UK Patent GB2426008B, November 2007.
- DAVISON N., GLASS G. K. and ROBERTS A. C. Inhibiting chlorideinduced reinforcement corrosion. In: *Corrosion 2006*. National Association of Corrosion Engineers, Houston, Texas, Paper No. 06353.
- 33. CLEMEÑA G. G. and JACKSON D. R. Evaluation of Anodes for Galvanic Cathodic Prevention of Steel Corrosion in Prestressed

*Concrete Piles in Marine Environments in Virginia.* Virginia Transportation Research Council, Charlottesville, VA, USA, July 1999, Report FHWA/VTRC 00-R3.

- 34. HOLMES S. Repair of corrosion damaged concrete using a 2-stage electrochemical treatment. In: *Structural Faults and Repair, 12th International Conference and Exhibition.* Engineering Technics Press, Edinburgh, UK, 2008, (CD-ROM).
- 35. NORTHUMBERLAND COUNTY COUNCIL. Vital Repairs To Whiteadder Bridge. Press Release Archives, 06 December 2006. See http://www.northumberland.gov.uk /BB\_News.asp?BB\_Bulletin\_ID=3259 for further details. Accessed 22/05/2008.
- 36. BURSTEIN G. T. A Hundred Years of Tafel's Equation: 1905–2005. *Corrosion Science*, 2005, **47**, No. 12, 2858–2870.
- ELSENER B. Corrosion rate of steel in concrete–Measurements beyond the Tafel law. *Corrosion Science*, 2005, 47, No. 12, 3019–3033.

- GLASS G. K. and BUENFELD N. R. On the current density required to protect steel in atmospherically exposed concrete structures. *Corrosion Science*, 1995, 37, No. 10, 1643–1646.
- 39. CHRISTODULUU C., GLASS G. K., WEBB J., NGALA V., BEAMISH S. and GILBERT P. Evaluation of galvanic technologies available for bridge structures. In: *Structural Faults and Repair, 12th International Conference and Exhibition*. Engineering Technics Press, Edinburgh, UK, 2008, (CD-ROM).
- DAVISON N., ROBERTS A. C. and GLASS G. K. Arresting and preventing corrosion of steel in concrete. In: *Corrosion 2008*. National Association of Corrosion Engineers, Houston, Texas, Paper No. 08302.
- GLASS G. K., ROBERTS A. C. and DAVISON N. Hybrid electrochemical treatment in the repair of corrosion damaged concrete. In: *Concrete Platform 07–An International Conference*. Queens University, Belfast, 2007, pp. 489–501.

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