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TOWARDS RENDERING STEEL REINFORCED CONCRETE IMMUNE TO CORROSION

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SUMMARY: This work reviews developments in the understanding of chloride induced corrosion of steel in concrete from both a kinetic and thermodynamic perspective. 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. A process like pit re-alkalisation is achieved more easily by impressing current off sacrificial anodes using a power supply and may then be 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. Some of these concepts have been adopted in the recent international standard on cathodic protection, ISO 12696:2012. This work also considers some of the amendments to this standard.

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

1. INTRODUCTION
Corrosion of reinforcing steel in concrete is the most significant deterioration process affecting reinforced concrete structures. It is accompanied by a loss of rebar cross-section and a build up of corrosion products. Very often the first indication of a problem is the appearance of a crack following the line of reinforcement. The most important causes are carbonation and chloride contamination of the concrete. This work is concerned with chloride induced corrosion of reinforced concrete.

One method of arresting corrosion is to use electrochemical treatments. The application of a cathodic current to a metal surface is accompanied by a negative shift in its potential and a reduction in the overpotential stimulating metal dissolution. This effect is embodied in the classical understanding of cathodic protection [1]. A cathodic current also has several other beneficial affects and much development has occurred in the field of electrochemical treatments of steel in concrete.

This work reviews developments in the understanding of chloride induced corrosion of steel in concrete from both a kinetic and thermodynamic perspective and considers the impact of these on the understanding of electrochemical treatments to arrest and prevent corrosion deterioration.

2. THE CORROSION PROCESS
The stability of compounds in a given environment in a potential range is determined by thermodynamics. This is commonly presented as a Pourbaix diagram. If the most stable products at a given electrode potential and pH are insoluble oxides, passivity is likely. Passivation is thus the primary mechanism of corrosion protection for steel in concrete. No significant corrosion will occur if this environment remains unchanged. However, concrete is exposed to a wide variety of external environments and the ingress of aggressive species may render it corrosive.

The oxides which make up the passive film on iron are thermodynamically stable in the alkaline environment in concrete even when chloride ions are present [2]. In this situation corrosion tends to be localised and chloride induced corrosion initiation in concrete follows the model of pitting corrosion. It is a two stage process in which pit nucleation is followed by pit growth [3]. The causes of pit nucleation are still subject to much debate. Most pits repassivate soon after nucleation. If the pits are to grow, pit nucleation must be accompanied by a local fall in pH and increase in chloride content at the pit nucleation site. The local fall in pH occurs as the result of the hydrolysis of dissolved iron ions given by:
The presence of an excess of chloride ions provides the charge balancing anion to stabilise the local reduction in pH. Hydrochloric acid (HCl) is effectively formed. Thus the presence of chloride ions promotes the continued dissolution of iron. The process of corrosion initiation as understood in thermodynamic terms is illustrated in Fig. 1.

\[ \text{Fe}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ \] (1)

The corrosion rate can be controlled by the kinetics of either the anodic or cathodic reactions, or by the resistance to current flow between the anodic and cathodic sites. The associated controlling mechanisms are termed anodic control, cathodic control or resistive control. Reinforced concrete is exposed to a wide variety of environments and any of these mechanisms may dominate depending on the exposure conditions [4]. This work is focussed on atmospherically exposed conditions which tend to be dominated by anodic control.

When concrete is periodically allowed to dry out, oxygen has relatively easy access to the steel. The kinetics of the cathodic reaction, oxygen reduction, are said to be weakly polarised because this reaction can occur relatively easily. The presence of a passive film may restrict the overall rate by limiting the rate of metal dissolution (the anodic reaction). The anodic kinetics are said to be strongly polarised and the corrosion rate is under anodic control. To increase the corrosion rate, passive film breakdown must occur.

A typical relationship observed between the corrosion potential and the corrosion rate for a concrete exposed to chloride ion contamination is given in Fig. 2. More negative corrosion potentials are associated with a higher corrosion risk [5].

To explain this observation, it should be noted that the corrosion potential is a mixed potential containing the effects of both the anodic and cathodic reactions. These two reactions are sometimes referred to as the half reactions making up the corrosion process. If the cathodic kinetics remain unchanged, the cathodic reaction rate will only increase if the electrode potential is shifted to more negative values. This is because the reaction products are more negative than the reactants (e.g. \( \text{O}_2 \) is converted into \( \text{OH}^- \)). By contrast, if the kinetics of the anodic reaction remain unchanged, the rate of anodic dissolution will only increase if the electrode potential is shifted to more positive values. This is because the reaction products are more positive than the reactants (e.g. \( \text{Fe} \) is converted in \( \text{Fe}^{2+} \)). The potential difference between the negative iron electrode and the positive oxygen electrode provides the driving force for the spontaneous corrosion process.
The decrease in corrosion potential with increase in corrosion rate observed in Fig. 2 results from a change in the anodic reaction kinetics. To a first approximation, the kinetics of the cathodic reaction, oxygen reduction, remain unchanged. The intersection between the lines representing the anodic and cathodic reaction kinetics gives the corrosion potential and the corrosion rate of the corrosion process. When only the anodic reaction kinetics change, more negative corrosion potentials will be associated with higher corrosion rates. Such a change may be brought about by chloride contamination at the steel which induces passive film breakdown.

3. INDEX OF CHLORIDE TOLERANCE

The index used to represent the tolerance to chloride contamination (the chloride threshold level), is subject to debate [6]. While it is practical to represent this as the ratio of total chloride to cement content expressed as a percentage (commonly referred to as the total chloride content), the use of the chloride/hydroxyl concentration ratio in the pore solution has been promoted on theoretical grounds [7,8]. However, this representation ignores the influence of the solid phases [9].

There is strong evidence that solid phases release hydroxyl ions to inhibit corrosion initiation. Furthermore bound chloride may, in theory, also be released to participate in the corrosion process. Indeed, published data have, on balance, produced very little evidence of a direct relationship between chloride binding and the chloride threshold level [10]. It is widely accepted that chloride and hydroxyl ions in solution have a strong impact on corrosion initiation. Chloride ions are the principal aggressive ions in concrete, while hydroxide is the principal inhibitor. However, chloride induced corrosion initiation has an impact on the local pH. Furthermore many solid phases have pH dependent dissolution characteristics and may in theory participate in the process of corrosion initiation.

Early work postulated that calcium hydroxide was a particularly important inhibitive solid phase in concrete as it provides a significant reservoir of hydroxyl ions that would be released to resist the local reduction in pH at the site of a nucleating pit [11]. Fig. 3 shows a SEM micrograph of a polished section through a steel-concrete interface [12]. Calcium hydroxide appears as a lighter cementitious phase in the backscattered electron image. It constitutes approximately 25% of the hydration products of ordinary Portland cement. However it is not always present at the steel-concrete interface.

Figure 2 The relationship between the potential and the corrosion rate in concrete exposed to air [5].

Figure 3 Backscattered electron image of a polished cross-section of steel in concrete [12].

Figure 4 The resistance to pH reduction and chloride content determined on chloride contaminated concrete [13].
Concrete is an inhomogeneous material (cf. Fig. 3) with many phases that provide a reservoir of hydroxyl ions to inhibit corrosion initiation. These phases most probably give rise to the fairly impressive resistance to corrosion at relatively high chloride concentrations. Air voids are one prominent type of defect that will dilute this hydroxyl reservoir, thus affecting chloride induced corrosion initiation. However other features like millscale, aggregate and bleed water will also provide zones where the resistance to the local reduction in pH occurring during corrosion initiation is lowered. If a high chloride content coincides with such features at the steel, corrosion initiation is more likely [17].

5. ARRESTING AND PREVENTING CORROSION

Arresting a chloride induced corrosion process is a problem that still presents many challenges. Chloride contaminated concrete remains at risk even after damaged areas have been repaired. Electrochemical treatments might be the most proven technologies when the aim is to avoid replacing contaminated concrete [1] but their complexity makes reliable
implementation difficult. Other technologies such as drying the structure or using penetrating corrosion inhibitors may slow the corrosion process but the effectiveness and value of these techniques is still debatable [18].

One view of localised steel corrosion is that it provides an example of sacrificial electrochemical protection. The actively corroding steel area provides a form of sacrificial cathodic protection to the adjacent passive steel. However, while the passive steel closest to the site of active corrosion receives the most protection current, this steel remains at a high corrosion risk and corrosion often spreads laterally over the steel surface to this area. This risk probably results from the acidic nature of the adjacent corroding site and the disruption caused by expansive steel corrosion products. Thus, the damaging effects override any protective effect of the cathodic current.

Cathodic protection traditionally relies on achieving a negative potential shift and such a basis is enshrined in many criteria for achieving protection. A negative potential shift is induced while cathodic current is applied and is referred to as cathodic polarisation. By contrast a positive shift in the open circuit steel potential associated with anodic polarisation, results from an increase in pH and reduction in chloride ion content that stabilises the formation of a stable passive film (Fig. 1). An improvement in the environment is generally considered to be the principal protective effect of temporary electrochemical treatments that rely on continued protection after the current is removed. However it also appears to be the dominant protective effect during cathodic protection.

To illustrate this, the effects of a negative potential shift induced by a current of 40mA/m² (steel surface area) are compared with a change in the environment that might induce a 200 mV positive shift in the open circuit potential in Fig.7. The steel was initially assumed to be corroding at 30 mA/m². Fig.7 shows that a negative shift in steel potential induced by a high cathodic protection current density (40mA/m²) is relatively small when the steel is corroding. Indeed it has been shown that even the application of a very high protection current density (in practical terms) cannot reverse the direction of a macro-cell corrosion current on a corroding steel bar. It is postulated that the generation of hydroxyl ions at the cathode has a much more significant effect in inhibiting the corrosion process [19].

![Figure 7 Comparison of the effects of a cathodic polarisation with those of anodic polarisation when the concrete is periodically allowed to dry [19].](image)

When it comes to preventing corrosion initiation, there are two approaches that may be adopted. The first is to prevent chloride contamination of the concrete. This may, for example, be achieved by improving the barrier properties of the concrete cover, applying coatings to the concrete surface and by removing the source of chloride [1]. The second is to increase the tolerance to chloride contamination. In this case chloride contamination is considered to be inevitable. An increase in tolerance to chloride contamination may be achieved by changing the reinforcement material, stainless steel reinforcement being one example. Another alternative is to modify the environment at the steel. This is discussed in greater detail below.

6. INCREASING THE TOLERANCE TO CHLORIDE CONTAMINATION

6.1.1 Defect Reduction

As indicated above there is strong evidence that defects in the cement paste at the steel-concrete interface have a significant effect on the chloride threshold level. (cf. Fig. 6). Indeed, it has been postulated that the reason for the large variability in the chloride level required to initiate corrosion in concrete structures is the presence of defects which disrupt the integrity of
the layer of cement hydration products at the steel-concrete interface [20,21]. Thus, from a materials viewpoint, one method of increasing the tolerance to chloride contamination is to reduce the incidence of defects in the cement paste at the steel.

Evidence for the effect of concrete placement comes from the observation that it is relatively easy to produce specimens with a high chloride threshold level in a laboratory environment. Indeed some laboratory programs have produced chloride threshold data that exceed 1.5% chloride by weight of cement in all tests performed [21]. Laboratory specimens tend to be small and are often compacted on a vibrating table. By contrast, large elements cast on site are more difficult to compact and will therefore contain more entrapped air [21]. They will also be subject to structural loads that may induce cracks in the cover concrete [22].

6.1.2 Chemical Treatment
The protective solids that deposit on the steel may be termed solid phase inhibitors. Chemical treatment of the steel may be used to promote the formation of these solid phase inhibitors. Such treatments may involve placing either chemicals or coatings on the steel prior to casting the concrete [23]. Chemicals that react with a alkaline pore solution in concrete may precipitate hydroxides against the steel. In effect, hydroxyl ions are taken out of the solution and precipitated against steel and the resulting concentration gradient draws more hydroxyl ions to the steel to replenish those removed from the pore solution. In this way it is postulated that a local reservoir of hydroxyl ions will build up at the steel to resist any subsequent fall in pH that is an essential part of the development of a sustained corrosion process [14].

6.1.3 Electrochemical Treatment
Another method of precipitating solid phase inhibitors on the steel involves the use of electrochemical treatment. A cathodic reduction reaction occurring on steel bars will generate hydroxyl ions there and at the same time the current will carry positive ions towards a cathode. The positive ions could include sodium, potassium and calcium and there is evidence that sparingly soluble hydroxide compounds will form at the steel [24,25]. Visual examination of electrochemically treated specimens showed a white deposit on the faces that received treatment (Fig. 8) [26]. The precipitation of inhibitive solid phases on the steel may be improved by adding admixtures to the concrete to improve the solubility of calcium. Calcium is not normally soluble in a high pH environment. However the addition of calcium nitrate increases the soluble calcium content and therefore lowers the pH.

7. 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 [1]. Galvanic systems are not as powerful and may not arrest an active corrosion process although they do function in a preventative role. However, they are much simpler to install and, in theory, require no maintenance.

A new treatment to arrest an active corrosion process and maintain steel passivity combines a brief pit re-alkalisation treatment, delivered using a power supply, with galvanic protection. The pit re-alkalisation process is preferably delivered from the same sacrificial anode system used to provide galvanic protection. This novel combination is referred to as a “hybrid” electrochemical treatment [27]. It combines the power of an impressed current electrochemical treatment with the
low maintenance requirements of galvanic protection. The maintenance of an impressed current treatment is limited to a brief period (weeks) 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 because 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. 30A.hrs per square meter of steel was required in a laboratory concrete specimen containing 3% chloride at the depth of the steel [27]. It is probable that less charge would be required at lower chloride contents [28]. The high current density that may be achieved off sacrificial anodes allows the pit re-alkalisation treatment to be delivered in a 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, 17mm in diameter and 100 mm long has a charge capacity of more than 125A.hrs. If 6 bars are installed for every square meter of steel surface, the available charge is 750A.hrs/m². The pit re-alkalisation process may require 30A.hrs/m². The remainder is available to deliver the galvanic current. A typical cathodic prevention current density for passive steel is 1mA/m². The delivery of this current for 50 years equates to a charge of 440A.hrs/m². Anode utilisation and efficiency need to be taken 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.

Data from a laboratory studies of the hybrid treatment applied to steel in a concrete block containing 4% chloride by weight of cement is presented in Fig. 9 [29]. This shows the current delivered off a zinc bar to 0.25m² of steel. Initially an impressed current was driven off the anode using a 12V power supply to achieve the pit re-alkalisation process. The zinc was then connected to the steel and the current decayed to 170mA/m² off the zinc.

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. 10.

Figure 9 The current delivered from zinc to steel in a hybrid impressed-galvanic treatment applied in concrete containing 4% chloride by weight of cement.

Figure 10 Tongue bridge during the installation of a hybrid electrochemical treatment on the concrete substructure.

8. CORROSION RISK MANAGEMENT

While galvanic protection is in theory not dependent on monitoring a maintenance, the new ISO standard on cathodic protection (ISO 12696:2012) [30] requires a strategy to manage future corrosion risk in a reinforced concrete structure subject to galvanic protection. A 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 theory. The polarisation behaviour (relationship between potential shift and applied current) of an electrode with activation controlled reactions is given by

\[ i_{\text{appl}} = i_{\text{corr}} \left( \frac{2.3\Delta E}{\beta_c} - \exp \left( \frac{-2.3\Delta E}{\beta_a} \right) \right) \]  

(2)

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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 [31]. In the 1950's this equation was simplified by assuming that the potential shift was small. The exponential functions were then approximated by linear functions and the polarisation resistance method was developed [32].

If the potential shift is not small, the corrosion rate may still be calculated using equation 1. The sensitivity of the calculation to errors in the various parameters has previously been assessed [33].

For steel undergoing electrochemical treatment, a conservative estimate of its potential shift is given by its potential decay measured on interrupting the protection current. Fig. 11 shows an example of a corrosion rate calculated from this data [34]. In practice the steel current density may be estimated from the current off an isolated segment of the sacrificial anode system 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. 12 [27]. A brief pit re-alkalisation process lasting 7 days had initially been applied using discrete zinc based anodes installed in the bridge substructure. The x-axis in Fig. 12 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. The data suggests that the steel is passive. The corrosion rates are negligible (less than 2 mA/m²), while the potential of the anode - steel couple is moving to more positive values with time.

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 re-applied in the future using the existing anode system and a temporary DC power supply, if a corrosion risk is detected.

The above discussion has challenged existing theory, but it is important to test the theory and re-assess the understanding of the corrosion process to progress towards rendering steel reinforced concrete immune to chloride induced corrosion.

9. CONCLUSIONS

The mechanism of chloride induced corrosion initiation on passive steel in concrete involves a reduction in the local pH at the site of a nucleating pit on the steel. Solids with pH dependent dissolution behaviour release hydroxyl and chloride ions as the local pH falls. Corrosion spreads from the point of initiation to adjacent steel surfaces in spite of the protective effects of a negative potential shift because the production of acid and the damage caused by expansive iron corrosion products overrides any protective effects of an adjacent corroding steel anode.

These effects may be taken into account when addressing the chloride induced corrosion risk. Chloride induced corrosion initiation will be inhibited by inhibiting the local pH reduction occurring during the corrosion initiation process. A major factor affecting the chloride threshold level on steel in concrete is the presence of defects at the steel-concrete interface that dilute the reservoir of inhibitive hydroxyl ions available.

Damage may be prevented by solid phase inhibitors that release hydroxyl ions to prevent a local pH reduction. It is in theory possible to achieve a tolerance to chloride contamination in steel reinforced concrete that is sufficiently high to effectively render the steel immune to chloride induced corrosion in many environments. A high tolerance to chloride contamination has been repeatedly obtained in laboratory concrete specimens. By reducing the entrapped air void content at the steel to values below 0.2% by volume in laboratory conditions, it was possible to increase the chloride threshold level from 0.2% to above 2% chloride by weight of cement.
A significant increase in the tolerance of steel to the presence of chloride ions in atmospherically exposed concrete may also be generated by electrochemical treatments that increase the reservoir of hydroxyl ions at the steel-concrete interface. When it comes to repairing concrete, the process is known as pit re-alkalisation. This breaks the acidification -iron dissolution cycle and gives rise to the time dependence of the processes leading to corrosion arrest at cathodic protection current densities as well as the positive potential shifts observed as active corrosion is arrested. 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 pit re-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 may be delivered from the same sacrificial anode system.

The new ISO standard on cathodic protection requires a strategy to manage future corrosion risk in a reinforced concrete structure subject to galvanic protection when substantial negative shifts are not achieved. 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.

10. REFERENCES

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11. AUTHOR DETAILS

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