Pit Realkalisation and its Role in the Electrochemical Repair of Reinforced Concrete

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Abstract

Open circuit steel passivity is induced by most electrochemical treatments used to arrest ongoing corrosion of reinforcement in concrete. This is achieved by the re-alkalisation of the acidic corrosion sites on the steel and may be induced by a charge density as low as 60 kC/m² in moderately aggressive environments. The rapid restoration of steel passivity is facilitated by using a sacrificial metal anode in an impressed current role. This allows the delivery of current densities at low driving voltages with no gas generation and limited acid generation.

Keywords: Corrosion, Chloride, Concrete, Cathodic Protection, Carbonation, Steel, Anode.

Introduction

Corrosion is the most important deterioration process affecting reinforced concrete. Prior to corrosion initiation, the reinforcing steel is protected by a passive film. The rate of steel corrosion is negligible with typically 0.1μm of section loss occurring each year [1]. Corrosion initiation involves the disruption of a normal passive condition. Its main causes are chloride contamination and carbonation of the concrete cover.

Many electrochemical treatments have been developed to arrest the corrosion process [2]. In most cases protection is achieved by the re-establishing steel passivity. This work is concerned with the mechanism of steel passivity, the magnitude of the treatment required to restore passivity and the delivery of such treatment.

Corrosion Cell Activity

Corrosion Initiation

An analysis of thermodynamic data illustrated in the interpreted Pourbaix diagram for iron in Figure 1 [3] shows that the oxides that make up the passive film on iron are thermodynamically stable in the alkaline environment in concrete. Carbonation may result in the loss of concrete alkalinity hence rendering the passive film unstable. However, chloride ions do not directly destabilise the passive film and insoluble oxides remain the most stable products at alkaline pH values when chloride ions are present [4].
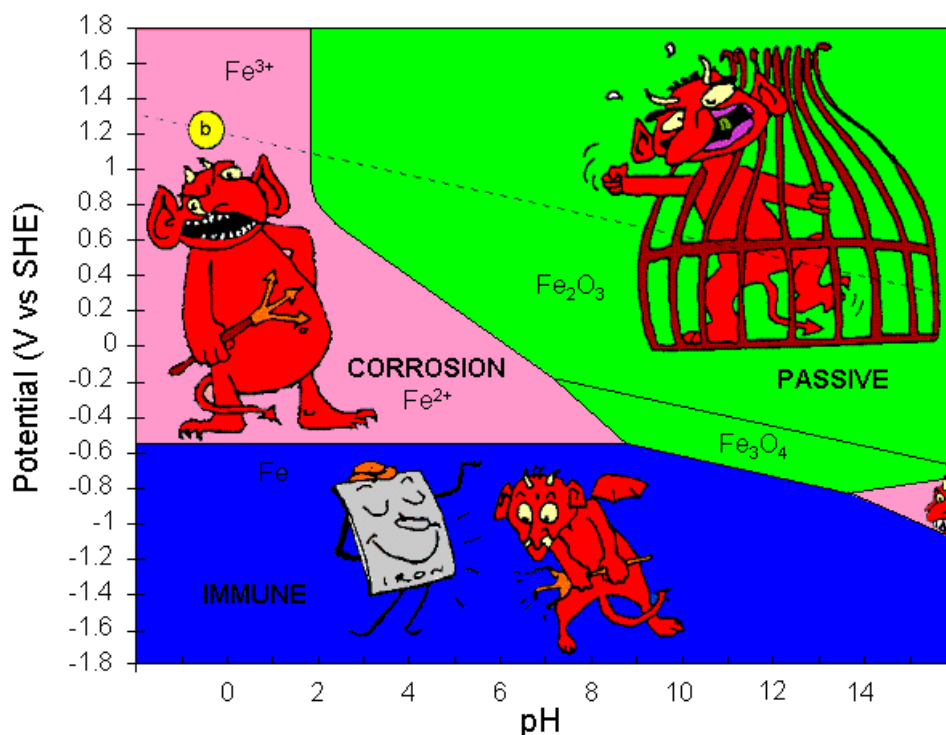
Figure 1 Interpretation of the stability of iron, its oxides and its soluble species. The presence of chloride has no effect on the stability of the iron oxides [3].

Chloride induced corrosion tends to be localised and the localised breakdown of the passive film in concrete follows the model of pitting corrosion. It is a two stage process in which the localised passive film breakdown, termed pit nucleation, is followed by the establishment of a sustained corrosion process, termed pit growth [4]. However, most nucleating pits do not grow. A pit nucleation event is likely to be followed by the restoration of the passive film.

To establish a sustained corrosion process, pit nucleation must be accompanied by a local fall in pH at the pit nucleation site. A local fall in pH arises from the hydrolysis of dissolving iron ions. Dissolving iron reacts with water to form iron hydroxides and hydrogen ions. The positively charged hydrogen ions are balanced by the presence of negatively charge chloride ions producing hydrochloric acid (Figure 2(a)). This stabilizes the local pH reduction and promotes further dissolution of iron.

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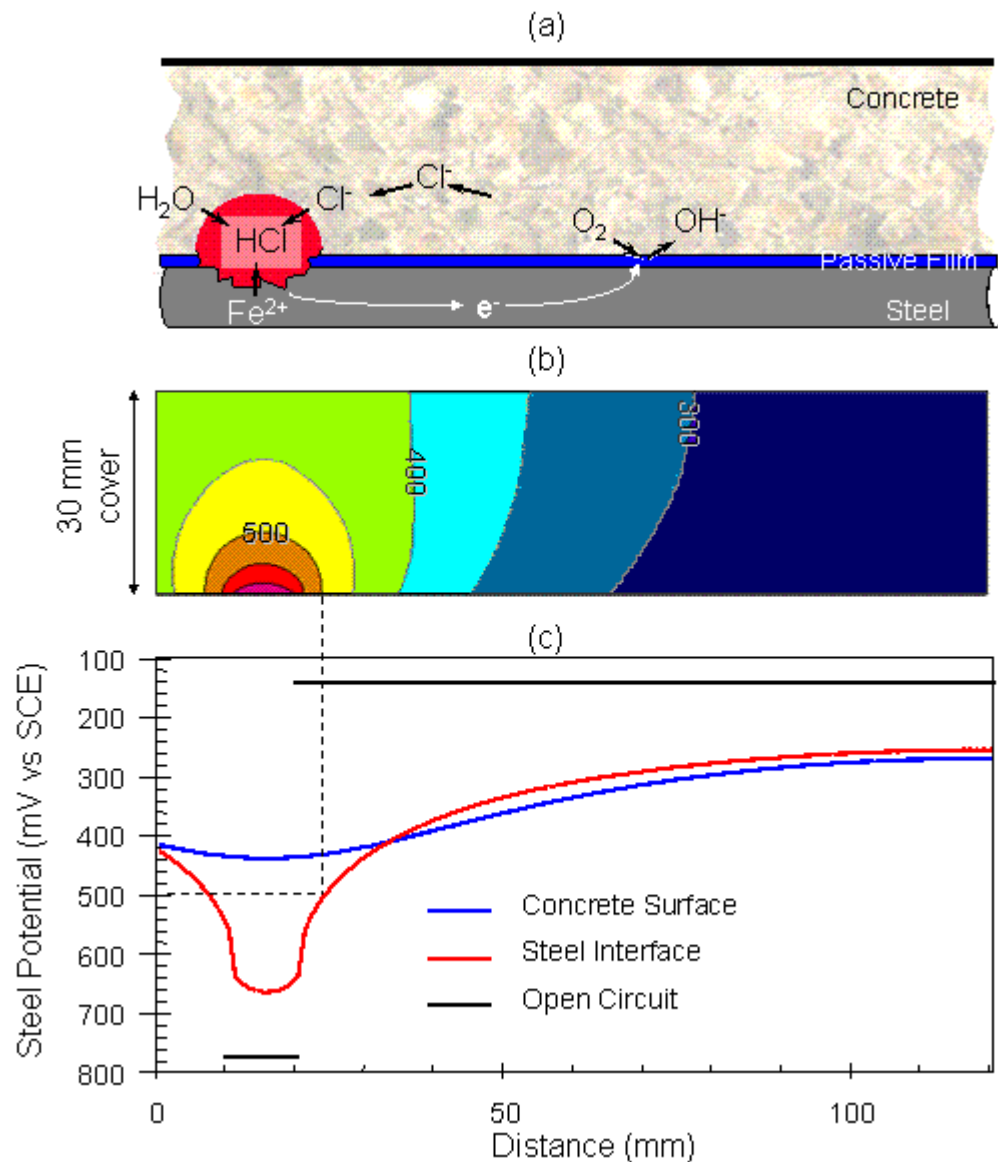
Figure 2 An illustration of the processes occurring in a corrosion cell on steel in concrete (a) together with the potential field in the concrete cover (b) and the potentials on the steel and concrete surface (c).
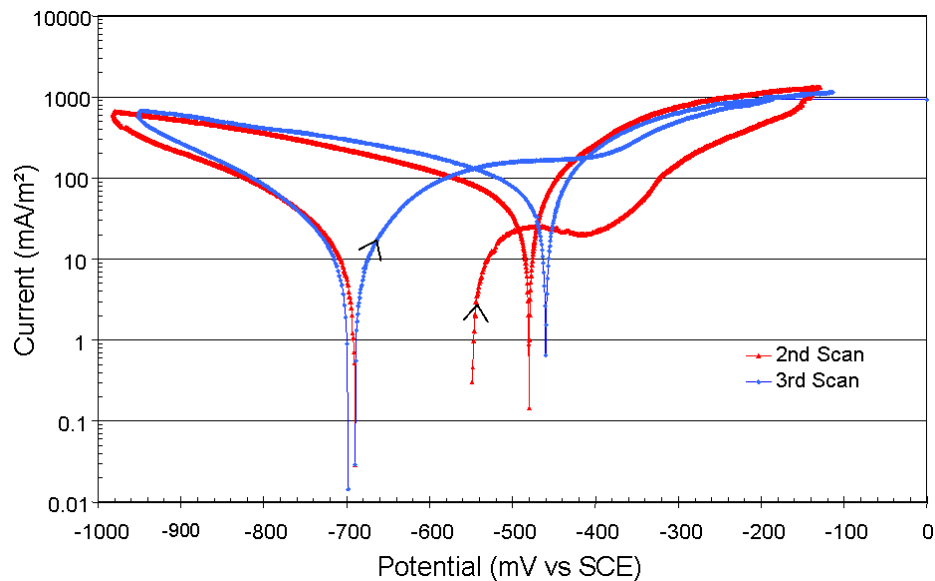
Macro–Corrosion Cell

Figure 2(a) illustrates the processes occurring in a corrosion cell in concrete. The dissolution of iron at a corroding site, also termed an anode, is at least in part supported by the consumption of oxygen (oxygen reduction) at a location (the cathode) away from the anode. This process was modelled using a 2 dimensional model that was governed by a description of the reactions occurring at the anode and the cathode as well as by ensuring conservation of current within the concrete [5]. It was assumed that 10 mm long anodes were located at 210 mm centres.

The corrosion potential of the isolated anode was –770 mV (SCE), while that of the isolated cathode was –140 mV. It should be noted that, when the anode is connected to the cathode as is normally the case, these potentials will move towards each other – the reactions are said to be polarised. The potential contours within the concrete cover are given in Figure 2(b) and the potential as a function of distance along the steel surface and along the concrete surface are given in Figure 2(c). The concrete resistivity was taken as 200 Ωm.

The behaviour of the anodic and cathodic reactions on active steel used in the model is shown in Figure 3. The combined behaviour, labelled micro–cell, represents the isolated behaviour of an active steel surface. These curves were calculated using an anodic Tafel slope (β_A) of 60 mV, a migration resistance (R_m) of 0.3 Ωm^2 a cathodic Tafel slope (β_c) of 120 mV and a cathodic limiting current (i_L) of 100mA/m^2. The migration resistance is an empirical parameter similar to the resistance in "pencil anode" models of pit growth or to the approach resistance described by Evans [6]. On passive steel the anodic reaction kinetics were limited to 0.1 mA/m^2. For comparison, the behaviour of active steel measured at a sweep rate of 1mV/min in a 350 kg/m^2 OPC concrete with a water cement ratio of 0.5 contaminated with 3 % cast in chloride added as NaCl to the mix water is shown in Figure 4.
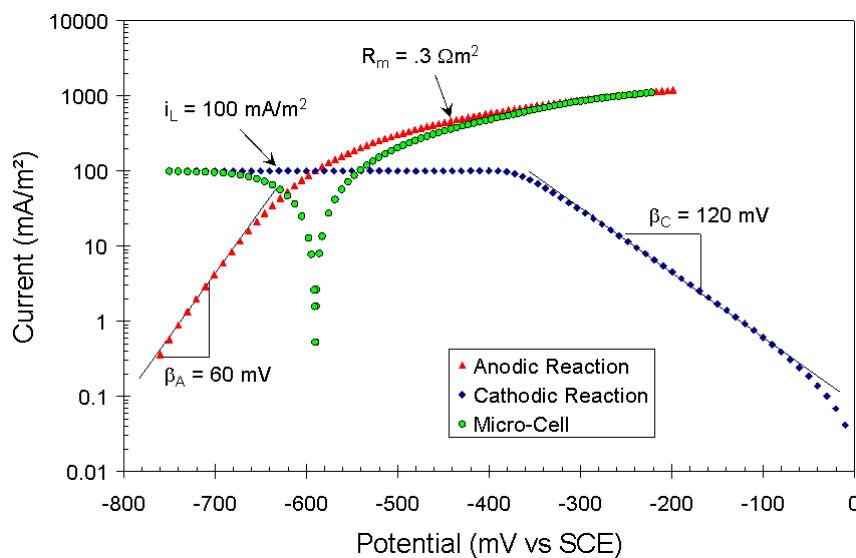
Figure 3 Theoretical potential–current behaviour of the anodic and cathodic reactions on active steel used in the model [5].

Figure 4 Measured potential-current behaviour of steel in concrete contaminated with 3 % cast in chloride.

The modelled corrosion cell in Figure 2 shows that, while a large potential gradient exists at the steel, the gradient at the concrete surface is much smaller. The modelling process also indicated that the corrosion rate of an isolated active area of steel is likely to be close to the limiting current for oxygen reduction and it may be increase by a factor of 3 if it is connected to an adjacent steel cathode. It may be noted that the potential of the passive steel adjacent to the anode area is shifted by more than 300mV in the negative direction.

Electrochemical Protection

One interesting view of the model in Figure 2 is that it shows an example of electrochemical protection. The actively corroding steel area is providing a form of sacrificial cathodic protection to the adjacent passive steel. However in this view an anomaly exists. The passive steel closest to the site of active corrosion receives the most protection as indicated by its large potential shift but this steel remains at a high corrosion risk because of the lateral growth of the corroding area. This risk is presented by the acidic nature of the environment local to the actively corroding site. Hence the damaging effect of the acidic nature of the environment overrides the substantial effect of protection current.

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In more typical electrochemical treatments applied to steel in concrete such as cathodic protection and prevention, intermittent cathodic protection, chloride extraction and re-alkalisation, the anode is installed at some distance from the steel. The protective effects include a negative potential shift that inhibits the dissolution of steel to form positive iron ions (corrosion), the removal of chloride ions from the steel surface to render the environment less aggressive to passive steel, and the generation of hydroxyl ions at the steel surface stabilising the formation of passive films on steel [7].

These effects are illustrated in Figure 5 which shows a section through a temporarily installed inert carbon – gel anode and a carbonated reinforced concrete beam after it had been treated with a high current short term electrochemical treatment [8]. A universal indicator was applied to the concrete and anode section. The red colour at the anode in indicates a pH less than 2, while the purple colour at the steel indicates a pH greater than 12.
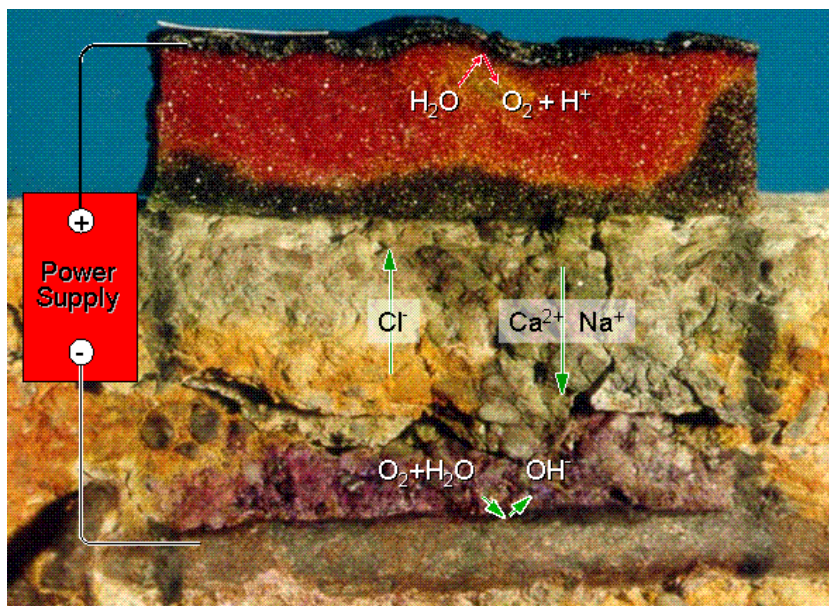

Figure 5 A section through an anode and carbonated reinforced concrete beam after it had been treated with a high current short term electrochemical treatment [8].

Traditional understanding of reinforced concrete electrochemical treatments suggests that different treatments rely on different protective effects. In this understanding, the basis for cathodic protection is the achievement of a negative potential shift. Re-alkalisation of carbonated concrete requires the generation of a

reservoir of hydroxide around the steel. Chloride extraction requires the removal of chloride ions from the concrete. Intermittent cathodic protection relies on changing the environment at the steel either by removing chloride or by generating hydroxyl ions to inhibit steel corrosion for a short period while the protection current is interrupted. However this traditional understanding is challenged below.

Pit Realkalisation

Analysis of published data

It is postulated in this work that one mechanism is likely to have a dominant effect on the success of all electrochemical treatments applied to steel, namely the generation of hydroxide at the steel interface. The applied charge (current for a given time) raises the pH at corroding sites such that the local environment naturally supports steel passivation. The generation of hydroxide at the steel is widely accepted as the protective effect that is relied on in the application of re-alkalisation to carbonated concrete. This is a less intensive treatment than chloride extraction and its application to arrest chloride induced corrosion would offer some practical advantages.

The importance of the generation of hydroxide at the steel is supported by the following existing evidence.

- The increase in the tolerance to chloride contamination of reinforced concrete following a limited period of electrochemical treatment prior to chloride contamination.

- The successful arrest of high corrosion rates using relatively low integrated protection current densities in intermittent cathodic protection.

- The widespread successful application of cathodic protection to chloride contaminated reinforced concrete at relatively low current densities.

The hypothesis that short term electrochemical treatments like chloride extraction result in the generation of a reservoir of hydroxide at the steel to increase the tolerance to chloride contamination has

previously been presented. An example of the data supporting this is given in Figure 6 [9]. In the absence of electrochemical treatment, the chloride content at the depth of the steel that is required to induce corrosion initiation (the chloride threshold level) is strongly dependent on the presence of defects at the steel concrete interface [10] with high chloride threshold levels being measured at low void contents. After electrochemical treatment, the effect of voids is largely lost and the chloride threshold levels are generally high. A similar series of tests showed the chloride threshold level increasing from between 0.2 to 0.6% by weight of cement for the controls to between 0.9 to 3.8% following a period of electrochemical treatment [11]. Because the electrochemical treatment was completed before exposure of the concrete specimens to a source of chloride ions in these tests, the hydroxide hypothesis is the only protective effect of those that are widely accepted that can induce these beneficial changes.
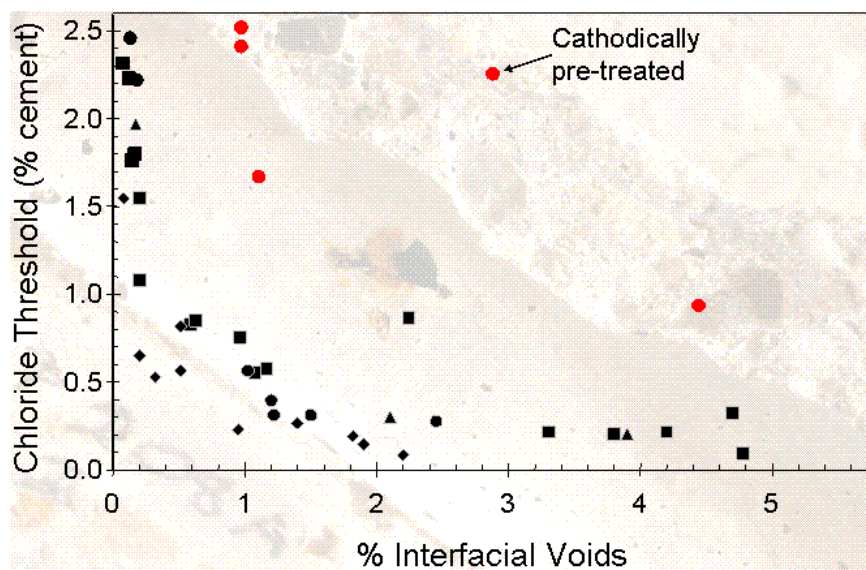
Figure 6 The effect of a limited period of electrochemical treatment prior to chloride contamination and interfacial voids on tolerance to chloride contamination [9].
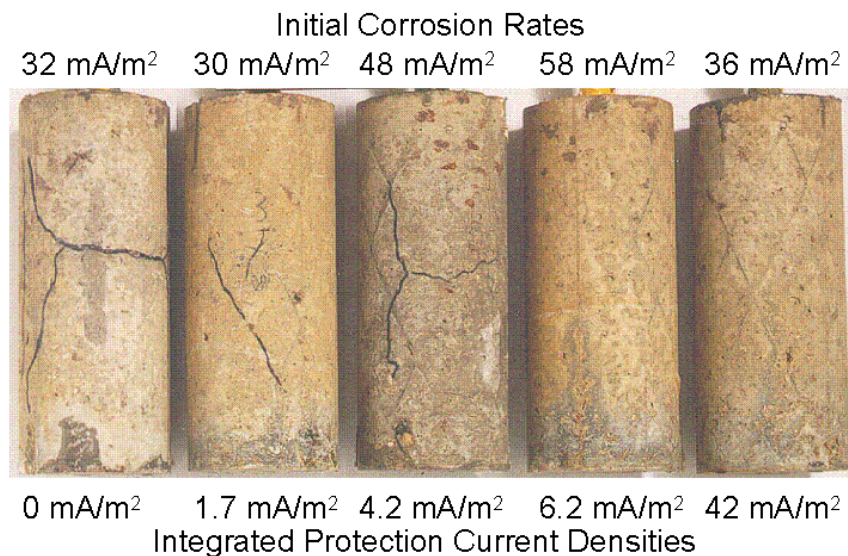
The precipitation of hydroxides at the steel surface to inhibit corrosion initiation introduces the novel concept of solid phase inhibitors. Visible evidence of the change in the environment at the steel is shown in Figure 7 [12]. The white deposit on the treated concrete that is more intense of the surfaces receiving the most electrochemical treatment is likely to be the result of a high concentration of sodium and potassium in these locations. This coupled with the high pH at the steel after treatment (cf. Figure 5) is likely to produce an alkaline

gel that would provide a reservoir of hydroxyl ions in a sparingly soluble solid phase at the steel surface. This stabilises the formation of passive films on steel by preventing the local pH reduction that accompanies localised corrosion and accelerates the deterioration process.
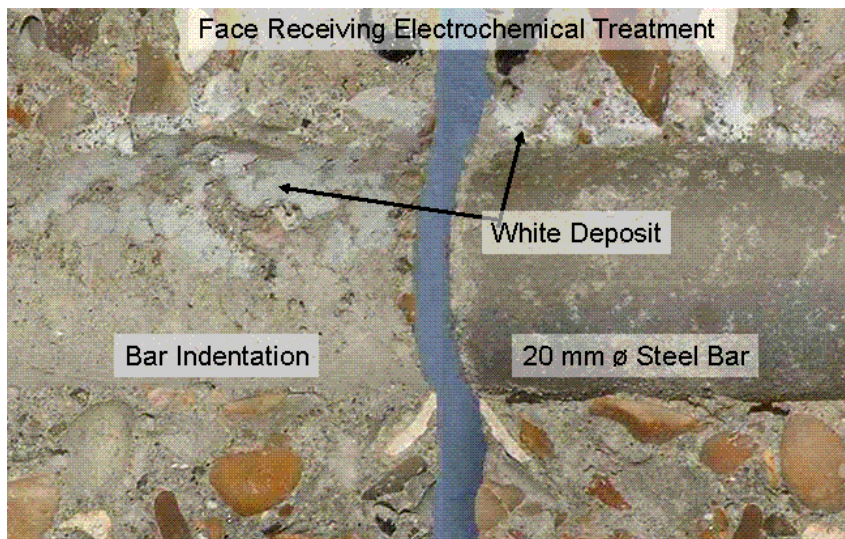

Figure 7 Visible evidence of the change in the environment at the steel is shown by a white deposit that is more intense of the surfaces receiving the most treatment [12].

A typical chloride extraction treatment requires the delivery of a current of 1 A/m^2 for 6 weeks. This is equivalent to an applied charge of 3630 kC/m^2. Intermittent cathodic protection, like chloride extraction, also relies on inducing steel passivity. It however uses a much lower charge. Figure 8 shows specimens that were subjected to 12 months of intermitted cathodic protection in which the current was applied for only 4% of the time [13]. The integrated current densities and initial corrosion rates are included. An analysis of the published data shows that passivity in one of the intact specimens was induced with a charge of less than 100 kC/m^2. This is very small compared to the charge applied in a chloride extraction treatment.

Initial Corrosion Rates

| 32 mA/m² | 30 mA/m² | 48 mA/m² | 58 mA/m² | 36 mA/m² |

| 0 mA/m² | 1.7 mA/m² | 4.2 mA/m² | 6.2 mA/m² | 42 mA/m² |

Integrated Protection Current Densities

Figure 8 Five specimens that were subjected to 12 months of intermitted cathodic protection in simulated marine exposure conditions with the current being applied for only 4% of the time [13].

Strong evidence of induced steel passivity and the arrest of chloride induced corrosion arising from the use of a relatively small charge density comes from an analysis of extensive data obtained in both field and laboratory cathodic protection studies. Figure 9 shows the change in the steel corrosion potentials determined on the Tay Road Bridge before and after the first year of cathodic protection [7]. Similar data has been reported for many other structures. The negative potentials initially observed, indicating the presence of areas of significant corrosion activity, were shifted to substantially more positive values indicating induced steel passivity. The protection current was reduced from approximately 10 mA/m² to 3 mA/m² over the period analysed and a charge of less than 200 kC/m² (more than an order of magnitude smaller than that required by chloride extraction) was delivered. This represents the upper limit of the charge required to induce open circuit passivity in this case.

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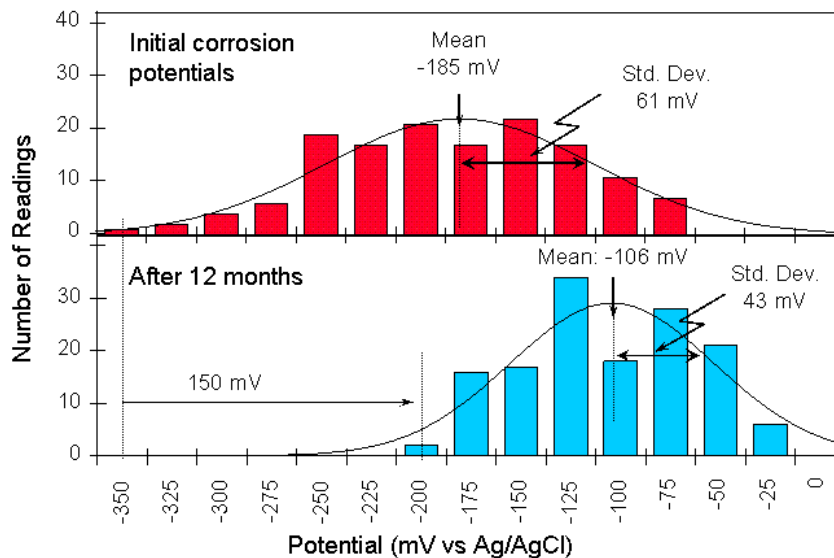
Figure 9 The change in the steel corrosion potentials on the Tay Road Bridge before and after a period of cathodic protection [7].

Steel passivity is likely to be induced after a relatively short period of cathodic protection. Indeed it has been shown that, in order to achieve the standard 100 mV potential decay criterion with a practical protection current, the steel must already be in a near-passive condition [14]. Figure 10 shows the steel potential decay over 2 hours determined after various periods of cathodic protection applied in a heavily chloride contaminated specimen in a laboratory environment [12]. The substantial potential shift to more positive values of the current-off potentials again indicates that steel passivity is being induced. It should be noted that this positive shift in corrosion potential occurs despite the observation that cathodic protection drives the steel potential to more negative values to reverse the process of iron dissolution (corrosion). This implies that the protective effect of the driven negative potential shift is negligible compared to the protective effects of changing the environment at the steel to induce passivity which is accompanied by a positive shift in corrosion potential.
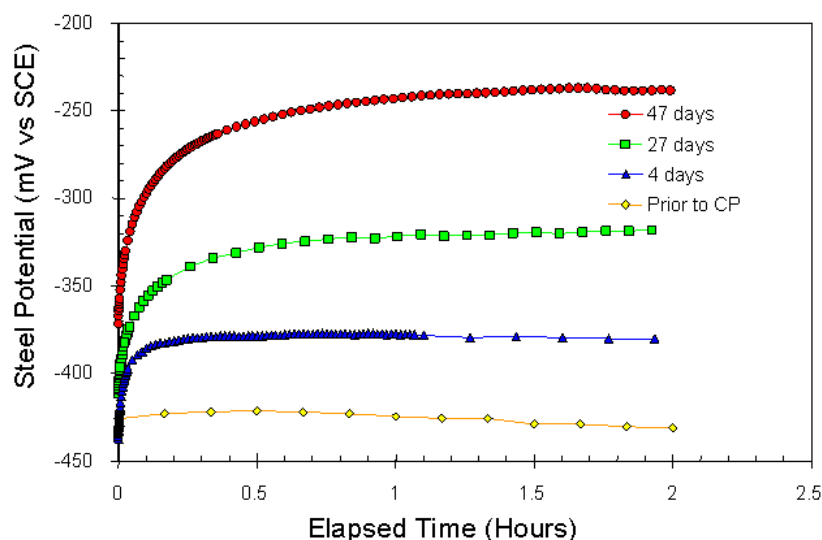
Figure 10 Steel potential decay determined after various periods of cathodic protection applied to a heavily chloride contaminated specimen [12].

The change in the corrosion potential observed in Figure 10 indicates that steel passivity has been restored after less than 50 days. A current of 20 mA/m^2 (the upper limit of the recommended range of reinforced concrete cathodic protection design current densities) delivered for 50 days is equivalent to a charge of only 80 kC/m^2 on the steel. Again this is a conservative value and 60 kC/m^2 (15mA/m^2) may be a more typical of the practical charge delivered in this period to a corroding reinforced concrete structure in a moderately aggressive environment.

There is overwhelming evidence that steel passivity is induced using cathodic protection current densities that are substantially lower than the localised steel corrosion rates in chloride contaminated concrete [13]. Average corrosion rates of 0.02 mm steel section loss per year and localised corrosion rates greater than 0.1 mm per year are not uncommon in chloride contaminated concrete. These equate to corrosion current densities of approximately 20 and 100 mA/m^2. However cathodic protection design current densities are nearly always less than or equal to 20 mA/m^2 and applied current densities are invariably lower than the design current densities (cf. Figure 8).

Two other factors further compound this surprising observation. Firstly, the applied protection current is very inefficient in reducing the corrosion rate in concrete exposed to the air. The technical reason for this is that the cathodic reaction kinetics are weakly polarised in this

environment. To reduce the corrosion rate to a negligible value, the protection current would need to be many times greater than the corrosion rate. Secondly a study of current distribution in reinforced concrete [13], showed that the current preferentially flows to the more positive cathodes rather than the corroding anodes of the natural corrosion cells that are formed in concrete.

In these conditions it is very unlikely that the applied current will result in the extraction of any chloride from the corroding anodic sites. Indeed a net anodic current will always be leaving sites of high corrosion activity at typical cathodic protection current densities (cf. Figure 2). However re-alkalisation of such sites is possible because a pH gradient between the surrounding concrete and the corroding sites will provide an additional force to move hydroxyl ions to these sites. Furthermore the strong electric fields that maintained these concentration gradients are weakened by the electric field imposed by the cathodic protection system. Thus the process of establishing actively corroding sites on the steel is reversed – the corroding sites begin to shrink until a point is reached where insoluble iron oxides are the most stable corrosion product over the whole steel surface and the passive film is re-established.

Delivery of Rapid Treatments

The above analysis has shown that a charge as low as 60 kC/m^2 may be sufficient to arrest the corrosion process on steel in concrete. It is preferable to deliver this treatment as rapidly as possible to prevent further corrosion induced damage. To achieve this, an anode system capable of delivering a high current density is required. Most impressed current systems utilise an inert anode with a long life. However a brief high current treatment may be delivered using a sacrificial anode metal in an impressed current role.

Figure 11 compares the current delivered of an aluminium anode embedded in plaster in a hole in concrete, with the current delivered of an MMO coated titanium anode in the same environment [15]. It may be noted that the instant off potentials in Figure 11 represent the potential of the anode reaction that is generating a current density

proportional to the anode reaction rate while the current–on potentials include a component of the voltage drop through the concrete.
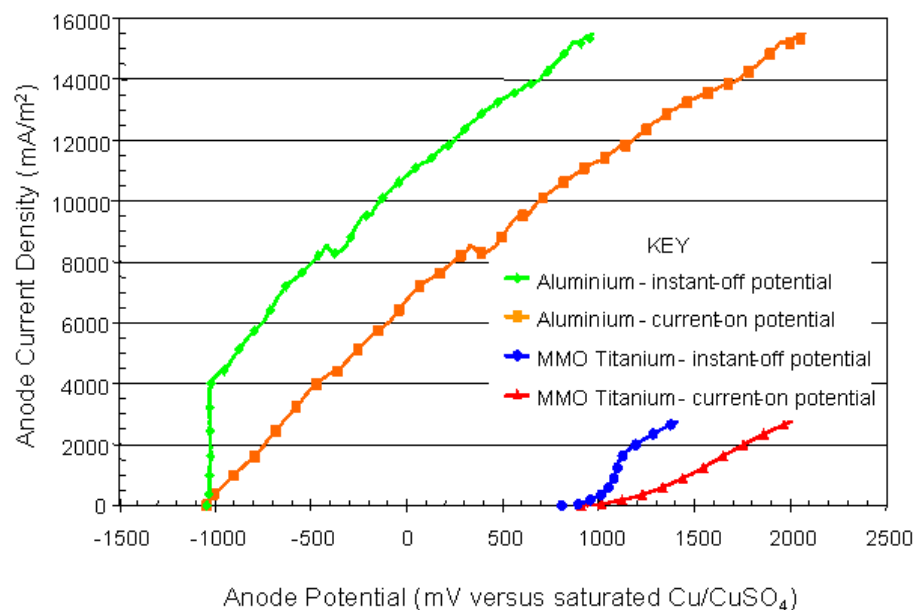
Figure 11 A comparison of the current delivered of an aluminium anode with that delivered of an MMO coated titanium anode embedded in plaster in concrete [15].

The aluminium anode delivers more than 10 000 mA/m^2 off its surface at anode potentials that are not sufficiently positive to result in any significant anode current being driven of the MMO coated titanium surface. This high current density may be compared with the 110 mA/m^2 that MMO coated titanium is normally limited to when embedded in concrete.

The principal anodic reaction on the sacrificial anode is the dissolution of the sacrificial metal. This is preferable to the oxidation of water that occurs on inert impressed current anodes as this latter reaction results in problems associated with the production of acid and oxygen gas which attack the concrete and hinder anode performance (cf. Figure 5). The dissolution of the sacrificial metal produces a metal salt. The production of gas may be avoided and the only acid that is produced is the result of the secondary hydrolysis reaction of the metal salt that is controlled by the equilibrium between the metal salt, the environment pH and the metal hydroxide.

The above analysis indicates that some substantial advantages may be obtained by using a sacrificial in this role. These advantages include

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very high current densities, low driving voltages, no gas generation and limited acid generation.

Conclusions

Open circuit steel passivity may be induced by most electrochemical treatments used to arrest ongoing corrosion of reinforcement in concrete. This is achieved by the re-alkalisation of the acidic corrosion sites on the steel.

Open circuit steel passivity may be induced by the application of a charge density that is less than 100 kC/m^2. A charge density as low as 60 kC/m^2 may be sufficient to restore passivity in moderately aggressive environments.

The rapid restoration of steel passivity may be achieved using a sacrificial metal anode in an impressed current role. This allows the delivery of current densities at low driving voltages with no gas generation and limited acid generation.

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