CORROSION OF REINFORCED CONCRETE: ADVANCES IN REMEDIAL TREATMENT BY CATHODIC PROTECTION

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Summary

Impressed current cathodic protection (CP) has been shown to provide an effective means of restraining corrosion associated with the presence of chloride ions in reinforced concrete structures. Advances in extended anode systems and monitoring methods, together with improved understanding of how to minimise the risks of adverse side-effects, have led to widespread acceptance of the approach for treating such problems. Interesting developments in recent years have included the use of very low current density CP for preventing the initiation of corrosion in new structures (cathodic prevention) and intermittent or temporary forms of CP for restoring the passivating character of contaminated cover concrete. Progress is also being made in the application of sacrificial anode CP, particularly as a means of enhancing the performance of patch repairs, which have hitherto not been considered a durable method of restoring chloride-contaminated reinforced concrete.

1. CORROSION OF STEEL IN CONCRETE

It is well established that dense concrete normally contains an alkaline pore liquid phase which protects embedded steel from corrosion by passivation under conditions where oxygen is available. This form of protection can be undermined, however, if the concrete undergoes either carbonation or chloride contamination to a substantial extent in the vicinity of the steel. These effects, which lead to cracking and spalling of the cover concrete, have been considered in detail elsewhere [1].

In cases of chloride-induced degradation, the form of corrosion that develops is termed pitting because the anodic regions of the metal, from which iron dissolution occurs, are localised at sites of breakdown of the passive oxide film, whilst the remainder of the surface remains passivated providing a large cathodic area for oxygen reduction. At a given temperature, the risks of corrosion pits forming on an initially passive steel surface and propagating once formed, depend on several factors. These include the electrode potential of the metal, the chloride ion concentration near its surface and the hydroxyl ion concentration near its surface [2].

For alkaline concrete (of approximate pH 13) at normal ambient temperature, the electrochemical behaviour of the steel may be expected to vary with potential and chloride content of the concrete, as illustrated in a simplified form by Figure 1, adapted from Bertolini et al [3]. The area of the diagram labelled as *'Pitting'* represents conditions that are conducive to the initiation and stable propagation of pits on initially passive steel; the region of *'Imperfect Passivity'* indicates conditions that

allow pre-existing pits to propagate but that do not favour the initiation of new pits on initially passive steel; the domain labelled as 'Pitting Unstable' signifies conditions that inhibit the initiation and propagation of pits, so that pre-existing pits tend to repassivate; the region labelled as 'Hydrogen Discharge' denotes conditions of highly negative potential that are sufficiently reducing to render a passive film of oxide thermodynamically unstable and enable hydrogen to be formed cathodically.
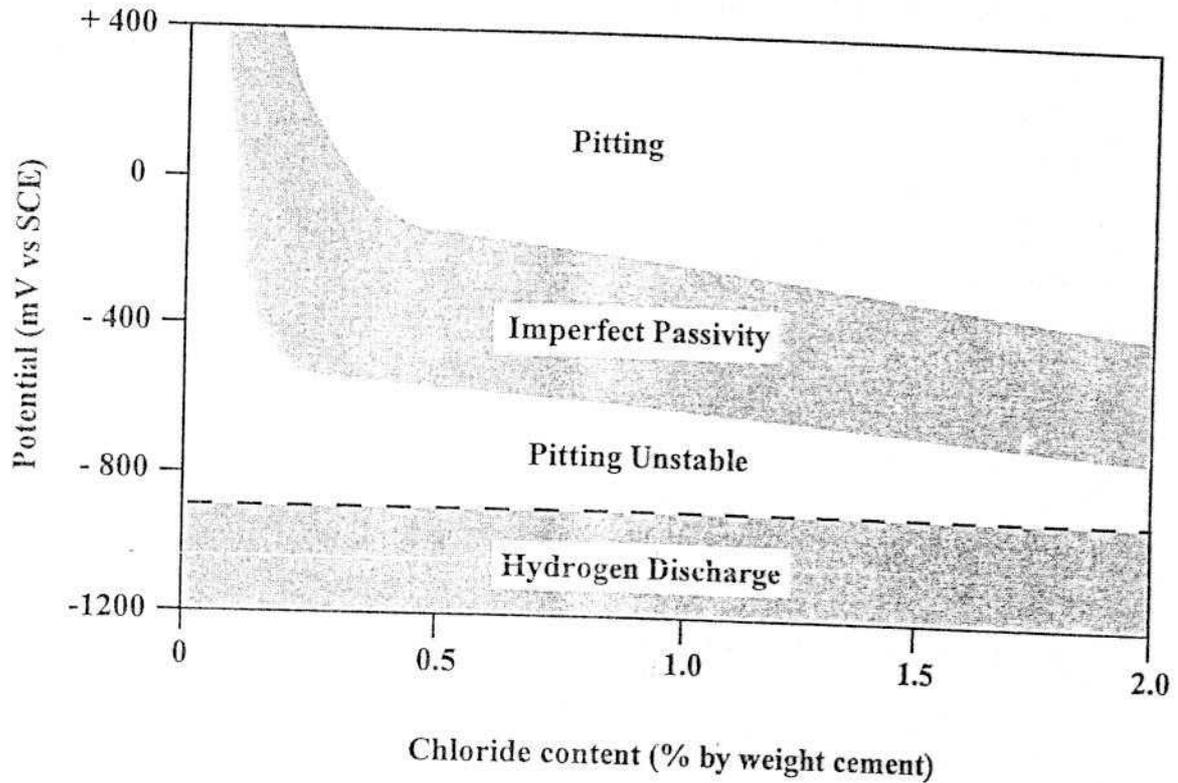

Fig. 1: Approximate domains of electrochemical behaviour of steel in concretes with different levels of chloride contamination.

2. BASIC PRINCIPLES OF CATHODIC PROTECTION

2.1 Influence of Potential

Cathodic protection (CP) is a long-established method of reducing the tendency of steel to corrode in neutral media such as seawater or groundwater and, in this context, the usual objective is to polarize the steel to an 'instantaneous-off' (IR-free) potential more negative than about -850 mV (Cu/CuSO$_4$ scale). This is close to the boundary of the immunity domain of the Pourbaix diagram for Fe in a solution of neutral pH at an equilibrium interfacial concentration of Fe^{2+} ions of approximately 10^{-3} g ions/l, although there is still some debate as to the significance of the protection criterion (4). When CP is applied to reinforcing steel in concrete, however, the objective is not to achieve a condition close to immunity but simply to reduce the susceptibility of the metal to pitting in the presence of chloride ions. The means of achieving this may be understood by reference to Figure 1.

If, as is normally the case, CP is to be applied as a remedial treatment to a structure in which chloride-induced corrosion has already been occurring for some time, then the desired intention is to polarize the steel from its condition of pitting to the domain where pitting is unstable so that complete repassivation will be effected. Even if the required extent of polarization to do this cannot be achieved, it will still be of benefit to depress the steel potential by a more modest amount, from a position within the pitting domain to one in the region of imperfect passivity, as this will at least reduce considerably the rate of propagation of existing pits and prevent the initiation of new ones. There is of course no advantage to be gained in applying excessive polarization, as this would reduce the passive film as well as promoting hydrogen discharge and other unwanted side-effects, to be discussed later.

If, on the other hand, CP is to be used as a means of preventing the initiation of corrosion in a structure, which has not been exposed for sufficient time to a chloride-rich environment to have accumulated concentrations of chloride at the reinforcement that are likely to cause depassivation, then only modest polarization is needed to maintain the steel at a potential where pits cannot initiate *(Cathodic Prevention)* (3). This implies that potential must remain below the upper boundary of the imperfect passivity domain as chloride penetration progresses.

2.2 Concentration Gradients

As a result of applying CP to steel in concrete, a porous medium which restricts the transport of ions and molecules that participate in the electrode reactions or in the electrolytic conduction processes involved, several forms of concentration gradient may be induced. In particular, there is a tendency for the material in the vicinity of the steel cathode to become enriched with respect to OH^-, Na^+ and K^+ whilst being denuded of Cl^- and O_2. Correspondingly, at the CP anode the surrounding material becomes progressively acidified and enriched with Cl^-.

The aforementioned effects have a number of consequences that will be referred to in the following sections of this paper. Here it is sufficient to note that the enhancement of the OH^- concentration and reduction of the Cl^- concentration near the steel surface are both beneficial in reducing the risk of corrosion. They account for the fact that, even when the CP current is interrupted, protection will be maintained for a time until the concentration gradients have been dissipated by diffusion. This gives rise to the possibility of applying CP intermittently in certain situations (5) or of applying very high current densities for periods of several days or weeks with a view to achieving more persistent protection of the sort associated with electrochemical realkalisation (6) or electrochemical chloride extraction (7,8).

3. APPLICATION OF CP TO REINFORCED CONCRETE

3.1 Development of Anode Systems

The earliest recorded applications of CP to steel in concrete were concerned with buried pipelines (9,10) and in such cases where the material is surrounded by a conductive electrolyte it is possible to use conventional discrete anode systems to distribute the current to the reinforcement. Many such uses of CP have been described involving both impressed current and sacrificial anodes (11).

The problem of how to apply CP to atmospherically exposed reinforced concrete is considerably more difficult technically because of the need to ensure a reasonably uniform current distribution in an electrolyte of fairly high resistivity (the concrete) which provides only a few tens of millimetres of cover to the embedded steel. To satisfy this requirement, it has been necessary to develop extended anode systems that meet the following conditions:

(i)   capable of being applied to concrete surfaces, often of various orientations, in such a way as to allow uniform electrolytic conduction,

(ii)   acceptable in terms of weight, cost and durability in service under a wide range of environmental exposure conditions.

Substantial progress has been made in achieving these requirements since the earliest reported successful application of CP to a reinforced concrete bridge deck in the USA in 1974 (12). In this and similar cases, the system comprised high silicon cast iron primary anodes in a conductive asphalt overlay, some 50 mm in thickness, to which a non-conductive asphalt wearing course was applied. Problems of added weight and difficulties of applying the technique except to horizontal top surfaces, however, effectively prevented the system from being used for structures other than bridge decks and car parks. Since the early 1980's, there have been many alternative anode systems developed to enable CP to be applied to reinforced concrete in a much wider range of situations, including highway bridge substructures, buildings and marine structures (13). A number of these systems have now been used quite extensively for a minimum of 5 years and are considered sufficiently well-proven to be described in some detail in a draft European Standard which has recently been circulated for comments under the CEN Enquiry Procedure (14). The draft Standard also recognizes that further new and effective anode systems are likely to become available for CP of steel in atmospherically exposed reinforced concrete.

Amongst the anode systems described by the draft Standard are the following:

(i)   organic conductive coatings, normally applied to a dry film thickness in the range 0.25 to 0.5 mm,

(ii)   metallic conductive coatings of thermally sprayed zinc, normally applied to a thickness in the range 0.15 to 0.2 mm,

(iii)   activated titanium, commonly in the form of mesh mounted on the surface of the structure and embedded in a cementitious overlay.

Organic conductive coatings containing graphite dispersed in acrylic or chlorinated rubber binders have been successfully used in trials and full-scale applications on highway bridges, car parks and buildings. They show variable performance but have a range of effective service lives of 5 to 15 years when properly applied and operated at current densities of up to 20 mA/m^2 in an appropriate environment (13). They do not withstand conditions of continuous wetting or abrasion and undergo gradual degradation at a rate dependent on the applied current density. Reported failure mechanisms involve disbondment, blistering and flaking related to degradation of the cementitious matrix by anodic acidity and oxidation of the organic binder (15). They are relatively easy to reapply and are commonly overcoated with grey or white paint

to improve appearance, to provide UV protection and to limit heat gain to the structure.

Thermally sprayed zinc may be applied to reinforced concrete by arc or flame spraying and shows greater tolerance than that of organic conductive coatings to conditions of moisture at the time of application or during service. Adhesion problems may arise, however, if the coating thickness exceeds about 0.2 mm and calculated rates of zinc anode consumption suggest that sustained operation at 20 mA/m^2 would oxidise completely a 0.2 mm coating in less than 6 years (13,14). The reported failure mechanism involves gradual increase in the resistance of the coating owing to zinc corrosion so that the current distribution becomes ineffective (15). Like organic conductive coatings, thermally sprayed zinc is easy to reapply and there have been reports of its use with apparent success as a sacrificial anode in limited trials in warm marine conditions (14).

Activated titanium electrodes with proprietary electrocatalytic coatings are available in several forms, the most widely used being an expanded mesh which is normally attached to the surface of reinforced concrete by means of non-metallic fixings and covered with a cementitious overlay of appropriately low resistivity. A variety of such overlays, applied by different means, has been used and their performance is critical to the durability of the anode system. Some failures have occurred due to disbondment of the overlay and these have generally been attributed to deficiencies in surface preparation, pre-treatment or application procedures. Evidence as to whether the substrate/overlay bond strength may be significantly affected by sustained application of CP in certain instances is somewhat inconclusive (15). The ability of the activated titanium anodes themselves to operate at high current densities (>> 100 mA/m^2) for long periods is well established but can give rise to acid attack of the surrounding cementitious material (14,15). This needs to be considered particularly when such anodes are not applied to the surface of a structure but inserted in holes drilled into the concrete and embedded in a cementitious repair mortar with or without a graphite-based backfill.

3.2 Monitoring Systems and Criteria

Apart from the development of anode systems, the area of most intensive debate within the field of CP applied to reinforced concrete in recent years has been concerned with the development of acceptable monitoring techniques and criteria. Here it has proved necessary to strike a compromise between what can be justified in theoretical terms and what can be achieved practically with reasonable convenience.

Recognizing the practical impossibility of arriving at a single performance criterion that could be applied successfully to all reinforced concrete structures under all conditions of exposure, the draft European Standard (14) adopts the pragmatic approach of endorsing a number of alternative criteria, any of which may be used as means of demonstrating the effective operation of a given CP installation. The recommended criteria are essentially as follows:

(i)   An 'instantaneous off' (IR free) steel potential (measured between 0.1s and 1s after switching off the d.c. circuit) more negative than -720 mV with respect to a Ag/AgCl/0.5M KCl electrode.

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(ii) A potential decay over a maximum of 24 hours of at least 100 mV from the 'instantaneous off' (IR free) steel potential.

(iii) A potential decay over an extended period (> 24 hours) of at least 150 mV from the 'instantaneous off' (IR free) steel potential, subject to a continuing decay and the use of reference electrodes that are stable over the period of measurement.

In addition, it is specified that no 'instantaneous off' (IR free) steel potential may be more negative than -1100 mV (for reinforcing steel) or -900 mV (for prestressing steel) with respect to a Ag/AgCl/0.5M KCl electrode.

The above criteria are intended to ensure that the potential of the steel is shifted either to a value where pitting is unstable, or at least depressed to an extent that will ensure a substantial reduction in the corrosion rate, whilst preventing adverse effects associated with overprotection. They are subject to a number of caveats, related first to the need to ensure that monitoring is undertaken at representative positions within each anode zone, avoiding areas within or close to concrete repairs, and secondly to the need to ensure that extended potential decay measurements are not vitiated by significant changes in temperature or moisture content over the monitoring period.

The need for a flexible approach to monitoring of CP applied to bridge substructures in marine environments, where vagaries of climate and water level can greatly influence the choice of acceptance criteria appropriate to different locations, has been well illustrated by long-term measurements on two Swedish bridges (16). Advances in instrumentation for automated collection of the large quantities of monitoring data that may be required when CP is applied to major structures of this kind have been reported recently, based on experience from work on the Tay Bridge in Scotland (17).

3.3 Understanding of Potential Side-Effects

Aside from the consequences of anodic acidity which can affect the durability and performance of CP anode systems as discussed above, there are a number of potential side-effects that require consideration in relation to the interfacial reactions and ionic migration processses occurring at and around the steel cathode. These have been reviewed in detail elsewhere (18) and a brief summary will suffice here. The principal concerns are as follows:

(i) hydrogen embrittlement of the steel,
(ii) degradation of the steel/concrete bond,
(iii) alkali-aggregate reaction in the interfacial region.

Hydrogen embrittlement is a very serious potential hazard when CP is applied to prestressing steels and much research has been aimed at quantifying the likelihood of this effect as it could lead to structural failure. The risk of significant embrittlement depends on a number of factors and, for steels other than chromium-containing microalloyed grades, it appears to be acceptably low provided the potential is maintained at a level less negative than -900 mV (SCE scale) (19). This is similar to the lower potential limit of -900 mV with respect to a Ag/AgCl/0.5M KCl electrode, proposed for prestressing steel in the draft European Standard (14).

Degradation of the steel/concrete bond, associated with softening of the cement matrix in contact with the metal, has been reported in several previous studies which involved the passage of high cathodic current densities for prolonged periods (20-22). At lower current densities, more typical of those used in practical applications of CP to reinforced concrete, however, the magnitude of this effect does not appear to be of major concern (23). Similarly, the enhanced risk of expansive alkali silica reaction (ASR) developing in cathodic regions of reinforced concrete containing susceptible types of siliceous aggregate has been found to be insignificant, provided that the cathodic current density is uniformly and consistently maintained at a low level (< 20 mA/m^2) (24). It should clearly be borne in mind, however, that if the current distribution to the cathode is not reasonably uniform, as can easily be the case if the CP system is not designed with appropriate care, the risk of locally induced ASR will be greatly increased. Hence the draft European Standard contains a necessary warning that the risk of alkali silica reaction shall be considered (14).

4. RECENT DEVELOPMENTS

A number of relatively recent developments in the application of CP to concrete structures have already been mentioned. Notable amongst these, has been the application of 'cathodic prevention' as a means of improving the corrosion resistance of new structures exposed to chloride-laden environments. This elegant practical application of electrochemistry, which requires cathodic current densities of only about 1-2 mA/m^2, has been used since about 1990 in Italy on prestressed concrete viaducts. The modest polarisation needed to achieve perfect passivity obviates the risk of hydrogen embrittlement (3).

Interesting proposals have been made recently concerned with the application of intermittent CP both in marine tidal locations where remote anode systems in seawater might be employed despite the periodic nature of their electrolytic contact with the concrete surface and in cases where the use of solar powered CP might be contemplated (5). Sacrificial anode CP, which has been used with success on buried structures and on the substructures of reinforced concrete bridges in warm marine environments, is now being evaluated for use on bridge decks in the USA (25). Whilst the approach has obvious advantages in terms of cost and simplicity, there are a number of limitations related, in particular, to the rather low driving voltages of sacrificial anodes which restrict their 'throwing power' in concrete of high resistance and render them ineffective if the corrosion rate of the steel is high.

An alternative possibility for the effective application of sacrificial anode CP is in conjunction with conventional patch repairs, which involve the removal chloride-bearing concrete from around the reinforcing steel in areas where corrosion is detectable, cleaning of the exposed metal and reinstatement with fresh alkaline concrete or mortar. As discussed elsewhere, the major problem with such an approach is that, unless stringent measures are taken to remove all significantly chloride-contaminated material from around the corroding areas, the likelihood of corrosion reappearing and cracking the concrete adjacent to the repairs is high (2). This is because replacement of the most intensely anodic regions of the reinforcement with passive steel in the repaired zones effectively removes the adventitious form of

sacrificial anode CP that was formerly being applied to the steel in the neighbouring regions. Hence the potential of the metal in these less severely contaminated areas can rise to a value at which pitting is liable to be initiated. To avoid triggering this problem of corrosion at incipient pits around the repair zones, it is desirable to reinstate some form of intentional 'cathodic prevention' and this can be accomplished with sacrificial anodes of an appropriate design, which are embedded near the periphery of the repair patches. The throwing power requirements and long-term current demand should be very low, assuming a reasonably competent attempt has been made to remove most of the chloride-bearing material prior to patching. A form of sacrificial anode, which is proposed for used in such applications, consists of zinc in a mortar of pore solution pH value > 14, containing LiOH. The high alkalinity of the pore solution promotes and sustains the anodic activity of the zinc, whilst the presence of lithium ions serves to inhibit problems of alkali silica reaction in the surrounding concrete if susceptible aggregates happen to be present (26).

5. CONCLUSIONS

During the past two decades, the application of CP to reinforced concrete has advanced rapidly to become a widely-accepted technology for dealing with problems of chloride-induced corrosion. Certain important features of this progress have been reviewed in this paper and an indication of some of the areas of current development has been provided. The publication of appropriate standards will be of major benefit in ensuring that CP is properly applied and monitored in Europe and elsewhere.

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