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A REVIEW OF CORROSION AND PROTECTION OF STEEL IN CONCRETE

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Abstract

Corrosion of reinforcement is one of the major durability challenges which leads to a reduction in the design life of reinforced concrete. Due to an increasing demand for longer service lives of infrastructure (typically 100-120 years) and the high cost involved in building and maintaining it, the repair of concrete structures has become extremely important. This paper discusses mechanism of corrosion in reinforced concrete and its thermodynamic and kinetic behaviour. It also presents and compares different corrosion prevention and protection techniques available and recommended by BS 1504-9:2008; including the use of corrosion inhibitors, alternative reinforcement, steel and concrete coating and electrochemical techniques. It is concluded that the electrochemical techniques are more effective than conventional methods.

Keywords: Reinforcement Corrosion, Electrochemical Techniques, Corrosion Protection, Corrosion Inhibitors, Alternative Reinforcement, Coating

1 Introduction

Durability issues associated with concrete structures are some of the biggest problems the civil engineering community is facing today around the world. One of the most significant durability issues is the corrosion of steel reinforcement, which leads to rust formation, cracking, spalling, delamination and degradation of structures. This is considered to be the main factor causing damage in bridges and other infrastructure [1, 2]. Atmospheric corrosion, galvanic corrosion and stress corrosion cracking can impact the performance and appearance of concrete structures. Therefore, to deal with these issues, research around the globe is oriented towards developing methods or materials to prevent this corrosion of steel in concrete. This paper presents a review of reinforcement corrosion, its mechanisms, and prevention.

2 Corrosion of Steel in Concrete

In general, when metals and alloys interact with their environment chemically, biochemically or electrochemically, surface loss occurs, and they convert to their oxides, hydroxides, or carbonates which are more thermodynamically stable. This process is termed as corrosion [1].

Along the surface of an embedded steel bar, when there is a difference in electrical potential, the concrete acts as an electrochemical cell which consists of anodic and cathodic regions on the steel, with the pore water in the hardened cement paste acting as an electrolyte [3]. This generates a flow of current through the system, causing an attack on the metal with the more negative electrode potential i.e. the anode while the cathode remains undamaged [4]. Thus, corrosion of rebar is initiated.

2.1 Mechanism of Corrosion of Steel in Concrete

As soon as the hydration of cement starts, steel in concrete develops a protective passive layer on its surface which consists of ɣ-Fe_2O_3 adhering tightly to the steel with a thickness in the range of $10^{-3}$to 10^{-1} µm [5]. This layer, blocks the movement of ions between the steel and surrounding concrete; thereby reducing the corrosion rate [6]. The presence of this oxide layer prevents damage of steel. It is only stable at high pH i.e. 12-14 [1, 3]. For corrosion to take place, this layer must be broken down. This occurs in presence of carbonation or chloride ions or poor quality concrete, and, in the presence of water and oxygen, corrosion occurs [7].

The process of corrosion can be understood through **Fig. 1** and equations. 1-5 [8]:

Anodic Reaction

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad (2)$$
(Ferrous hydroxide)

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \quad (3)$$
(Ferric hydroxide)

$$2Fe(OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O \quad (4)$$
(Hydrated Ferric oxide)

Cathodic Reaction

$$4e^- + O_2 + 2H_2O \rightarrow 4OH^- \quad (5)$$

Hydrated ferric oxide, i.e. rust, is formed as a result of these reactions and it is highly porous and has a volume 6-10 times that of steel, causing cracking and spalling [9]. The overall reaction mechanism is explained in **Fig. 2**. At the cathode, oxygen reduction occurs and at the anode reduction of iron occurs through either of the reactions in equations 6 and 7 [1]:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad e^o = -0.688\ V_{SCE} \quad (6)$$

$$Fe + OH^- \rightarrow [Fe(OH)]_{ads} + e^- \rightarrow$$
$$Fe(OH)^+ + H^+ + 2e^- \quad e^o = -0.404\ V_{SCE} \quad (7)$$

Formation of $Fe(OH)^+$ depends upon availability of OH^- ions. To maintain the electro neutrality, as Fe^{2+} ions are formed, OH^- ions shift from the bulk towards the surface. At high pH, equation 7 is more favourable on the surface of iron than equation 6. Holding $Fe(OH)^+$ ions, the electrode potential shifts in a more anodic

direction and increases the $Fe(OH)^+$ concentration at the steel surface. The $Fe(OH)^+$ oxidizes to ferric oxide, resulting in a barrier oxide layer (Eq. 8) [1]. This is the passive layer that protects the steel. For corrosion to be initiated, this passive layer must be penetrated by aggressive agents such as chloride ions or by a reduction in pH.

$$Fe(OH)^+ + H_2O \rightarrow Fe_2O_3 + 4H^+ + 2e^-$$

$$e^o = -0.084\ V_{SCE} \quad (8)$$

2.2 Chloride Induced Corrosion

Steel remains in passive state, i.e. free from corrosion, when it is embedded in a sound concrete layer; but it converts to an active state (corrosion initiates) when the concrete around it deteriorates. Chloride ions may penetrate from the environment or be mixed internally and reach the reinforcement.

When chloride penetrates into concrete, the alkalinity near the reinforcement increases as per, Eq. 5. To maintain electro-neutrality, Cl^- and OH^- ions diffuse to the interface. Because of their greater movement, the chloride ion concentration will build up close to the surface, saturating the interface with (Fe^{2+}) and (Cl^-). This will reduce the formation of $Fe(OH)^+$ shifting the potential in a more cathodic direction [1].

The chloride content required for steel depassivation and corrosion initiation is known as critical chloride content. If the chloride ion concentration goes beyond this threshold value, the passive layer gets locally destroyed and it leads to localized pitting corrosion [10]. The steel surface where chloride ions attack becomes an anode and the passivated surface becomes a cathode [8]. The reactions involved are in equations 9 and 10:

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \quad (9)$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl \quad (10)$$

The reactions in Eqs. 9, 10 break both ferric oxide and magnetite (Fe_3O_4) layers on the steel [1].

Chlorides in concrete that are soluble in nitric acid (sometimes referred as total

chlorides) include bound chlorides which can be chemically bound with cement hydration products such as the C_3A or C_4AF or loosely bound chlorides with the C–S–H. It is only the remaining chlorides, namely, free or water-soluble chlorides which react with steel and are responsible for its corrosion [11].

The passivity of steel depends on chloride content. The pitting potential of steel reduces with an increase in the chloride content. The pitting potential (E_{pit}) reduces from 500 mV to -500 mV in a chloride free structure if it becomes chloride contaminated (**Fig. 3**). For a typical corrosion potential, the critical total chloride content varies between 0.4 - 1 % by weight of the cement [12]. According to BS 1504-9:2008, the chloride content limit for reinforced concrete and prestressed structures is 0.4% and 0.1% respectively [13, 14]. However some studies, showed that the ratio $[Cl^-]/[OH^-]$ is a better representation of the chloride limit in concrete and is more critical for corrosion [15, 16]. Higher chloride binding for a given total chloride content, will lead to a higher chloride threshold ratio [17]. A threshold ratio varying from 0.3 to 40.0 has been reported [14].

In the presence of chlorides, corrosion can even takes place when the pH is very basic i.e. around 12 [5]. However, more recent research showed that this threshold limit can be as low as 0.2% or less or even more than 1% depending upon the environmental and exposure conditions [13]. Therefore, there is no scientific agreement about the corrosion threshold limit. Hence, for each structure, corrosion risk should be evaluated depending upon the actual site conditions without assuming any safe limits. From authors' practical experience, the risk of corrosion should also be calibrated against the actual conditions of the structures and not only based on half-cell or chloride values.

The effect of temperature and humidity on chloride ion transport, concrete resistivity and rate of corrosion should be considered

when assessing corrosion risk. The threshold level for chloride ion contamination can vary in different parts or components of a structure.

In practice, following approach is adopted:

- Below 0.4%, chloride ion concentration by mass of cement protection of reinforcement is not required.
- 1.0% chloride ion and evidence of reinforcement corrosion and concrete delamination are the upper limits above which intervention is required as soon as practicable.
- Between 0.4% and below 1.0%, intervention may be deferred providing that risk and consequence of corrosion is evaluated as low. Monitoring of corrosion and defects is necessary.

For chloride ion concentration above 0.4%, following options should be considered and assessed based on whole life cost analysis:

- Removal and replacement of contaminated concrete,
- Patch repair with galvanic anodes at the perimeter of concrete repair patches
- No treatment to chloride contaminated concrete but monitor for future deterioration
- Use of Impressed Current Cathodic Protection Technique (ICCP)
- For post-tensioned or pre-stressed structures, the presence of lower chloride values as low as 0.2% can lead to stress corrosion cracking, especially if there are voids in the duct systems of the tendons.

2.3 Carbonation

The porosity of concrete ranges from the micrometre to the nanometre level [18]. In concrete's pores, apart from liquid water, adsorbed water and structural water are present, which affects different structural and mechanical concrete properties. This porous structure and the natural reactivity of concrete make it prone to a natural

degradation, called as carbonation [18]. Penetration of CO_2 into the concrete layer and subsequent neutralization of alkalis in the pore fluid is called carbonation. It reduces the pH of concrete to around 9 where the passive layer is not stable and corrosion may occur [19]. CO_2 attacks not only $Ca(OH)_2$ but also C-S-H gel and the unhydrated cement components C_3S and C_2S. Corrosion induced by carbonation can take place over the whole surface of steel bars due to the complete dissolution of the passive layer around the steel [9].

The mechanism in equations 11 and 12 controls the carbonation process:

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad \text{(Carbonic Acid)} \qquad (11)$$

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \quad \text{(Calcium Carbonate)} \qquad (12)$$

Carbonic acid formation neutralizes the calcium hydroxide in pore water, dropping the pH to 8 [18]. At this pH, destruction of the passive layer is initiated and rebar corrosion takes place with rust formation as shown in **Table 1** [9, 11, 20]. The maximum rate of carbonation is observed at 50-70% RH [4, 17].

2.4 Stress Corrosion Cracking (SCC)

SCC is defined as the process in which a crack grows on a metal due to simultaneous action of both tensile stresses and a corrosive environment, leading to failure without warning [1, 4, 10]. Certain conditions lead to crack propagation due to the anodic part of the corrosion process, this is called anodic stress corrosion cracking [10]. The conditions required for this type of SCC can only rarely be reached in concrete structures.

Another form of SCC is caused by absorption in the metal of hydrogen gas produced by a cathodic reaction and is called hydrogen induced stress corrosion cracking [10]. This causes loss of ductility and crack propagation and leads to a brittle-like fracture surface and is termed hydrogen embrittlement [4]. This form of cracking can be generally observed in high strength steel used for prestressed / post-tensioned concrete elements [10]. Other materials that

may cause this type of corrosion are hydrogen sulphide and a high concentrations of ammonia and nitrate salts. When the metal potential becomes more negative than the equilibrium potential ($E_{eq,H}$), hydrogen evolution occurs, which decreases linearly with pH according to Nernst's law [10] (**Fig. 4**).

2.5 Stray Current Induced Corrosion

In concrete, electrolytic corrosion occurs when a current from an external source enters and leaves the reinforcing steel. This is referred to as stray-current corrosion. The currents can be generated from nearby cathodic protection systems, railways, high voltage power supplies etc. and travel through electrical paths other than their intended path [21, 22]. The currents deviate from their intended path if they find a lower resistance or an alternative route to flow such as metallic pipe buried in soil [10, 21]. The current may be AC or DC depending upon the source [10]. However, AC is exceptionally unlikely to cause corrosion. A cathodic reaction occurs where current enters the structure and an anodic reaction occurs where it leaves and returns to its original path, leading to metal loss at the anodic site.

In case of reinforced concrete, stray-current interference can result in localized corrosion where current leaves the steel and in hydrogen embrittlement of prestressing steel where current enters the steel if the potential is negative enough to generate hydrogen gas [21].

2.6 Thermodynamics of corrosion

Corrosion is a complicated process that relies on the surrounding environment and material, and is governed by underlying thermodynamic and kinetic factors [23]. The thermodynamics of a corrosion process decides the theoretical tendency of metals to corrode. Thus this concept helps in deciding conditions under which corrosion happens and also its prevention strategy [1]. The rate at which corrosion will proceed is controlled by kinetics of the electrochemical reaction and is determined by Faraday's law of electrolysis [1].

In any electrochemical process, at equilibrium, all reactants and products are at unit state. Deviation from the unit activity can be determined using Nernst equation, Eq. 13 [1]:

$$E_{cell} = E^o - 2.303\frac{RT}{nF} log \frac{a_C^{VC} a_D^{VD}}{a_A^{VA} a_B^{VB}} \quad (13)$$

Where, 'a' is activity of reaction, V is the stoichiometric number, A & B are the reactants and C & D are the products of electrochemical reaction, R is gas constant, F is Faraday's constant, T is absolute temperature, n is number of electrons taking part in the reaction, E_{cell} is the equilibrium cell potential and E^o is called as standard electromotive force of a corrosion system.

The corrosion potential of steel in concrete is the sum of two electrode potentials i.e. the reaction potential at the anode E_{Fe} (Eq. 14) and the reaction potential at the cathode E_{O2} (Eq. 16).

Referring to the anodic reaction (Eq. 1),

$$E_{Fe} = E_{Fe}^o - 2.303\frac{RT}{nF} log \frac{[Fe^{2+}]}{[Fe]} \quad (14)$$

Substituting the values of $E_{Fe}^0 = 0.440$, n=2, 2.303RT/F = 0.059 at T =25° C and [Fe] =1

$$E_{Fe} = 0.440 - 0.0295 log[Fe]^{2+} \quad (15)$$

Similarly, referring to cathodic reaction (Eq. 5),

$$E_{O2} = E_{O2}^o + 2.303\frac{RT}{nF} log \frac{[O_2][H_2O]^2}{[OH^-]^4} \quad (16)$$

Substituting the values of $E_{O2}^0 = 0.401$, n=4, 2.303RT/F = 0.059 at T =25° C and log[OH-] = pH-14

$$E_{O2} = 1.229 + 0.0148 log[O_2] - 0.0591 pH \quad (17)$$

The E (emf) for any equilibrium system is sum of two electrode potentials as shown in equation 18:

$$E = E_{Fe} + E_{O2} \quad (18)$$

Thus

$$E = 1.229 + 0.0148 log[O_2] - 0.0591 pH + 0.440 - 0.0295 log[Fe]^{2+} \quad (19)$$

And

$$E = 1.669 + 0.0148 log[O_2] - 0.0591 pH - 0.0295 log[Fe]^{2+} \quad (20)$$

It can be observed from Eq. 20, that the rate of corrosion is controlled by the pH of the

concrete electrolyte, the oxygen availability and the Fe^{2+} ion concentration [11]:

The stability of different metals is estimated by using potential-pH diagrams called Pourbaix diagrams. A typical Pourbaix diagram for iron in a chloride solution is shown in **Fig. 5** [9]. This depicts the change in potential and pH as iron moves from corroding areas to areas of passivity and finally to an area immune from corrosion. It can be observed that the steel is passive in alkaline media. In concrete, the formation of calcium hydroxide ($Ca(OH)_2$) increases alkalinity [18]. When chlorides enter concrete, there is conflict between OH^- and Cl^- to either passivate the steel or corrode it, where Cl^- dominates, as result pH drops and steel moves to corrosion zone of Pourbaix diagram from passive zone. Similar is the case with carbonation. Ideally, to protect the steel, the potential of iron should be depressed sufficiently to reach the immune zone by adopting a suitable protection technique. However, that is very close to the hydrogen evolution potential (lower dotted line) at pH 12 which is where steel in concrete lies. Thus, to avoid hydrogen evolution, it is brought down to the area below the pitting potentials [9].

2.7 Kinetics of corrosion

At equilibrium, at any given point on a metal surface, the rate of forward and backward reactions are equal [24]. In concrete, at equilibrium, the reactions, given by Eqs. 1 and 5, are equal at steel surface. However, when cathodic and anodic half cells are connected ionically i.e. through concrete pore solution and metallically i.e. through the reinforcement, a net current flows between them and the equilibrium potential shifts through polarization [20, 24]. When the concentrations of the reactants and products at the rebar surface are the same as in the bulk solution, the potential difference from the reversible potential for a given reaction is called the activation overvoltage [23]. For such reactions, the relationship between the current density i, and potential E, is

given by the Butler-Volmer equation, Eq. 21 [1, 23]:

$$i = \underset{i}{\rightarrow} - \underset{i}{\leftarrow} = i^o\{\exp\left(\frac{-\alpha_c F\eta}{RT}\right) - \exp\left(\frac{\alpha_a F\eta}{RT}\right)\} \quad (21)$$

Where $\eta = E\text{-}e_{eq}$, e_{eq} is a reversible half-cell potential, R is the gas constant and T is absolute temperature.

At a large anodic over potential (η) the cathodic term becomes negligible and equation 21 is simplified to:

$$i = -i_a = \underset{i}{\leftarrow} \quad (22)$$

$$i = i^o \exp\left(\frac{-\alpha_a F\eta}{RT}\right) \quad (23)$$

Anodic sites on steel surface mainly polarize through activation polarization [20, 24]. Rearranging equation 23 gives,

$$\eta_a = E_a - E_{Fe} = \beta_a \log\frac{i_a}{i^o} \quad (24)$$

Where, E_a (V) is the polarized anodic potential, $E_{Fe\ is}$ as given in Eq. 15, β_a (V/dec) is the anode Tafel slope given by $\beta_a = (2.3RT/\alpha nF)$, i^o (A/m^2) is anodic exchange current density and i_a (A/m^2) is the anodic current density.

Cathodic sites on the steel surface can also polarize through both activation and concentration polarization [24], given by:

$$\eta_c = E_c - E_{O2} = \beta_c \log\frac{i_c}{i^o} - \frac{2.303RT}{nF}\log\left(\frac{i_L}{i_L - i_c}\right) \quad (25)$$

Where, E_c (V) is polarized cathodic potential, $E_{O2\ is}$ as given in Eq. 17, β_c (V/dec) is the cathode Tafel slope given by $\beta_a = (2.3RT/\alpha nF)$, i^o (A/m^2) is cathodic exchange current density, i_c (A/m^2) is cathodic current density and i_L is limiting current density given by:

$$i_L = \frac{DnFC_{O2}}{d} \quad (26)$$

Where d (m) is diffusion layer thickness, D (m^2/s) is the oxygen diffusion coefficient, CO_2 (mol/m^3 of pore solution) is the concentration of dissolved oxygen on the concrete surface [24]. Concentration polarization only occurs when oxygen availability at cathodic sites is not enough to sustain the oxygen reduction process [20].

The corrosion process kinetics can be graphically represented on a potential vs

current plot called as Evan's diagram (**Fig. 6**). As shown on the plot, the point where the cathodic and anodic curves meet gives the value of corrosion potential (E_{corr}) at which the external current is maximized [1]. The current at this potential is called the corrosion current (I_{corr}) which can be used to calculate the corrosion rate of any metal.

The protection current (i_{pro}) required in the external circuit to stop corrosion can also be estimated from the Evan's diagram by extending the cathodic polarization line until it reaches the anodic equilibrium potential [1]. This forms the basis of cathodic protection.

3 Corrosion Mitigation Techniques

Due to the increasing demand for longer service lives for infrastructure and the high cost involved in building and maintaining it, the repair of concrete structures has become extremely important [25]. The repair and protection techniques for concrete are based on chemical, electrochemical or physical principles [13]. Since corrosion is an electrochemical process, its main components are the cathode, the anode and the electrolyte (in form of concrete pore water). The absence of any of these three components can restrict the corrosion process.

Repairs to corrosion damaged concrete structures are broadly categorised into two classes: conventional repair methods and electrochemical methods:

Conventional repair methods involve the removal of delaminated/spalled concrete and replacement with new alkaline concrete and also patching, coatings, sealers, membranes and barriers, encasement and overlays, impregnation and the use of corrosion inhibitors [26]. These are generally temporary techniques for corrosion prevention and can lead to acceleration of corrosion in nearby repaired areas [27]. After serious damage has occurred, they are generally costly and less effective than electrochemical methods [28, 29].

Electrochemical techniques include cathodic protection, cathodic prevention,

electrochemical realkalisation and electrochemical chloride removal and are effective methods for corrosion prevention and mitigation [10, 30, 31]. In electrochemical techniques, the chemical reactions and current flows due to corrosion are suppressed by the application of an external DC supply with the help of an anode (temporary or permanent). Direct current is passed from the artificial anode to the reinforcing steel to be protected. The current passes as a flow of ions through the pore water of the concrete to the reinforcement [32]. The advantage of such techniques is that only broken concrete needs to be removed and repaired [10].

The following sections describe different corrosion protection methods as suggested by BS 1504-9 [13]:

3.1 Corrosion Inhibitors (CI)

Corrosion inhibitors are chemical substances that reduce corrosion rates without significantly changing the concentration of any other corrosion agents [1, 33]. These inhibitors are chromates, nitrites, benzoates, phosphates, stannous salts and ferrous salts [1]. They are relatively of low cost and easy to handle as compared to other preventive measures for corrosion protection. Depending on the basis of their action, they can be anodic, cathodic or mixed inhibitors. Anodic inhibitors, for example calcium nitrite, supress the anodic corrosion reaction, hence reducing the corrosion rate by increasing the corrosion potential of steel, (**Fig. 7a**). This is the most widely used inhibitor for concrete [34]. Cathodic inhibitors, for example sodium hydroxide, supress the cathodic corrosion reaction, hence acting on the oxygen reaction and reducing the corrosion rate by decreasing the corrosion potential of steel, (**Fig. 7b**). The other type is mixed inhibitors which supress both anodic and cathodic reactions and reduce corrosion rates without changing the corrosion potential by surface adsorption over steel bars and thus forming a protective layer (**Fig. 7c**) [35]. However, anodic inhibitors have more pronounced

effect [36]. Lee et al., 2018 [37]reviewed various types of inhibitors and suggested that more extensive investigation is required to study the effectiveness of mixed/organic inhibitors in long term applications under various scenarios such as chloride content, types of cement etc.

Integral corrosion inhibitors are substances which, while not preventing ingress of chlorides into concrete, inhibit corrosion of steel. Only those inhibitors that can prolong the service life due to chemical or electrochemical interactions with the reinforcement can be considered as CI for concrete [10]. Neville (1995) states that nitrites of sodium and calcium have been found to be effective in corrosion protection [8]. The action of the nitrite is to convert ferrous ions at the anode into a stable passive layer of Fe_2O_3. The nitrite ion reacts specifically with the chloride ion. However, it is has not been demonstrated that corrosion inhibitors are permanently effective, they may simply delay corrosion. If desirable, the accelerating effect of nitrites can be controlled by the use of a retarding admixture. A potential problem with sodium nitrite is that it increases the hydroxyl ion concentration in the pore water, and this may increase the risk of alkali-aggregate reaction.

Other type of inhibitors are migratory inhibitors, which are applied as liquid to the concrete surface and form a self-replenishing monomolecular protective layer on steel [34, 38]. They reach the steel surface by migrating through concrete by capillary infiltration and vapour diffusion and gets deposited on it by polar attraction [38]. Malik et al. (2004) studied the performance of migratory corrosion inhibitors (MCI) which are proprietary blend of surfactants and amine salts in a water carrier and can either be applied on concrete surface or can be used as corrosion inhibitors on rebar. [39]. Bavarian et al. (2003) stated that MCI based on amino-carboxylate chemistry are the most effective at interacting at the anode and cathode simultaneously [40]. Soylev and

Richardson (2008) [33] presented a review on the most commonly used corrosion inhibitors in concrete viz. aminoalcohols (AMA), calcium nitrites, and sodium mono fluorophosphates (MFP). The research showed great concern on the long term effectiveness of CI in real environments and proposed a detailed analysis to study the factors influencing migrating CI's protection efficiency. From practical experience, the major problem with migrating CI is the depth of penetration. It may not be deep enough to reach the steel. This depends on quality of concrete and the porosity. The depth of penetration can also vary in different parts of the structure resulting in non-uniform protection.

Corrosion inhibitors are water soluble and may leach out from concrete [36]. Moreover, the commonly used inhibitors are costly and toxic in nature [41]. Thus, there is great need for replacing harmful inhibitors with cost-effective, environmentally friendly, non-hazardous alternatives. Abdulrehman et al. 2011 [33] reviewed various possible CI effective in concrete and their mechanism. Their review concluded that Amines, alkano amines, amino acids, mono, poly carboxylates, amino–alcohol based inhibitors, BTAH, organic heterocycles and green products could be successfully used as an effective inhibitors for concrete protection. Green Inhibitors as the future of CI in concrete should be explored in more detail. Some of the options available as green inhibitors were reviewed. Agro-waste/natural products and medical waste such as heena, neem, bamboo, penicillins, cefatrexyl etc. are non-toxic and have negligible harmful environmental impacts, and thus may replace traditional toxic corrosion inhibitors [42–44]. However, this is still a new concept and needs to be researched.

Huang and Wang, 2016 [26] studied the combined effect of ECR and CI (Calcium Nitrite) in chloride removal. They concluded that penetration of CI increases in presence of electric field which accelerates passivation of rebar. Similar

results were reported by Lee et al., 2018 [37] suggesting enhanced effectiveness of CI when electrochemically injected to improve protect steel in both carbonated and chloride contaminated concrete. However, the concept is of great interest but requires more study.

3.2 Using Alternative reinforcement

To prevent corrosion of reinforcement in concrete, an alternative is to use reinforcement made of corrosion resistant material such as stainless steel or Fibre Reinforced Plastic (FRP).

3.2.1 Stainless Steel (SS) Rebars

Pitting is the only form of corrosion that can occur in SS in concrete. Other forms of corrosion such as intergranular corrosion, stress corrosion or crevice corrosion requires an extremely aggressive environment which is very unlikely to occur [10]. The corrosion resistance of SS bars is significantly higher than carbon or mild steel because of the higher stability of their passive film [10]. The film is rich in chromium, and has a good bond with the parent metal and is self-healing in an oxygen rich environment [45].

In an alkaline solution, Moser *et al.* (2012) reported that all high-strength stainless steels HSSSs (Austenitic, Martensitic and Duplex) show high corrosion resistance at Cl^- concentrations from 0 to 0.25M. But as the Cl^- concentration increases to 0.5M and for a carbonated solution, only S32205 and S32304 i.e. duplex grades exhibit low and moderate corrosion susceptibility respectively. S32205 even shows high corrosion resistance at 1.0M Cl^-. Enhancement of nickel (Ni) and nitrogen (N) in the austenite phase enhances its corrosion resistance when compared with the ferrite phase [46].

Duplex steel 1.4362 (AISI S2304) and austenitic steel 1.4401 (AISI 316) have very good corrosion performance when exposed to a chlorine environment [47]. This is due to good protective properties of the passive film, enriched with Cr, Ni and Mo. Also, steel types with low Ni content, but with

high N and Molybdenum content perform well in a chloride rich environment. The Concrete Society technical Report 51 recommends austenitic and duplex steel for use as reinforcement in concrete [45].

However, it is too expensive to use SS as a replacement for mild steel reinforcement in most applications (the cost is almost 6 to 9 times higher) [45]. Though, its use can be prioritised with an outer layer of stainless steel but leaving the rest as carbon steel. But, when they are coupled with carbon steel, there is risk of galvanic corrosion of carbon steel [10, 45]. However, the corrosion rate is low when carbon steel is coupled with stainless steel compared to when corroding carbon steel is coupled with passive carbon steel [45, 48]. For the application of CP to structures having Austenitic and Duplex SS bars, the minimum negative potential recommended for protection is 0.6V [49]. The risk of hydrogen embrittlement should be assessed on a case by case basis by determining the safe potential of the specific type of SS used in the structure.

3.2.2 Fibre Reinforced Plastic (FRP) Rebars

Fibre Reinforced Plastics (FRP) are composite materials consisting of a matrix phase and a fibre phase. They have high corrosion resistance, light weight and high tensile strength [50]. Generally, they are of 4 types: aramid fibre (AFRP), glass fibre (GFRP), carbon fibre (CFRP) and basalt fibre (BFRP). Aramid fibres are sensitive to environmental degradation and glass fibres degrade with time when exposed to alkaline or acidic environments. Carbon and basalt fibre are highly resistant to both alkaline and acidic environments.

Waldron et al. (2001) studied the effect of chloride on durability of FRP [51]. They observed that CFRP bars exposed to combined chloride/moisture attack in concrete show very little degradation with time, with aggressive exposure or temperature. However, AFRP and GFRP bars showed up to 50% loss of strength. Suh

et al. (2007) evaluated the effectiveness of FRP wrapping in slowing down corrosion in heavily contaminated concrete incorporating carbon and glass fibre in a marine environment, by monitoring the corrosion rate and also studying the role of fibre layers. They observed no difference in potential readings in any of the CFRP and GFRP wrapped specimens. Additionally, the number of FRP layers had a relatively minor effect on the potential reading [52]. Thus, the difference between corrosion rates in the CFRP and GFRP wrapped specimens is very minor. However, ACI 440.2R-08 (2008) [53] recommends not to use FRP reinforcement without arresting the ongoing corrosion and repairing any degradation to the substrate, if steel in concrete is corroding or the concrete substrate is degrading, as FRP is not going to stop ongoing corrosion to the existing reinforcement.

Hence, it is clear that CFRP provides more corrosion resistance than GFRP or AFRP bars for concrete exposed to marine environments. However, CFRP bars have a very high cost. As an alternative, BFRP bars shows good corrosion resistance and are cheaper as compared to CFRP [54]. BFRP bars could be an economical solution compared to other FRP bars and SS bars. Moreover, basalt fiber has much higher thermal stability as compared to other fibers, having a melting point near 1400ºC. Thus, it can also provide resistance against fire. However, there has been limited study of it. In practice, a coupled application of CFRP and cathodic protection is recommended. More research is needed into these areas.

3.3 Steel Coating

Coatings act as a physical barrier to corrosion. Coatings should have high adhesion and their protection depends on their porosity and permeability [4]. Coatings suitable for rebar protection in concrete can be metallic, organic or cementitious. These coatings are non-reactive in a corrosive environment and protect steel from mechanical damages.

Metallic coatings for steel reinforcement are of two types: Sacrificial and noble coating. Sacrificial coatings are made up of less noble metals such as zinc and cadmium and provide protection to steel by sacrificing themselves compared to the underlying cathode i.e. parent metal [55]. Unlike, non-sacrificial coatings, even if they break during fabrication, transportation or during service, the parent metal remains protected [55]. They can be applied by dipping, electroplating, spraying, cementation, and diffusion [56]. The most commonly used metallic coating is using zinc metal and is called galvanizing. Galvanized reinforcement can withstand higher exposure to chloride environments, compared to carbon steel and can even provide protection against carbonation in concrete [57]. However, the useful life of zinc coating depends upon coating thickness. A large amount of zinc can be lost before the parent metal is attacked owing to its sacrificial properties. It is mostly suitable for concrete exposed to carbonation [36]. However, the main problem with galvanizing is the formation of hydrogen gas leading to a loss of bond between the coating and the cement paste [58]. One way to protect this is by increasing the passivation time of zinc by adding soluble inhibitors such as chromates. However, due to its toxic and carcinogenic nature, EU limits its use. Bellezze et al. 2018 [58] studied various soluble inhibitors to reduce hydrogen evolution of galvanized steel when embedded in concrete and discovered nitrites suitable to decrease H_2 evolution by shifting the potential to a more positive value. However, a non-toxic solution for this remains to be discovered. Moreover, the risk of stress corrosion cracking in galvanised bars under high stress is high.

Non- sacrificial coatings include Ag, Ti, Ni, and Cr which provide barrier protection to steel i.e. protect the steel by forming a passive layer on it. In this, the parent metal acts as an anode compared to the cathodic passive film. It may lead to localized

attack, if broken during fabrication or transport.

Organic coatings include epoxy coating, polyvinyl chloride, poly-propylene, phenolic nitrite, polyurethane etc. and isolate steel from aggressive agents, oxygen and moisture. Most widely used, bonded epoxy bars have electrostatically applied epoxy powder on thoroughly cleaned and heated bar [4]. They provide excellent corrosion protection without a significant increase in material cost and are not consumed during their operational life. However, the major difficulty is protecting them from abrasion and mechanical damage during transportation and handling and thus becoming ineffective in corrosion protection [55, 59, 60]. Hence, frequent patch-ups are required. Moreover, the bars are not electrically continuous due to the epoxy and thus CP systems are not cost-effective. There is also a risk of significant pitting because the small defects in coating give a small surface area of an anode and a high corrosion current density. Ali et al. (2015) reported that that epoxy bars are not efficient for long term corrosion protection due to their porous and hydrophilic nature [61, 62]. In practice, the durability of epoxy coated reinforcement is of great concern due to its failure record in high chloride environments and localized corrosion conditions.

3.4 Concrete Coating

The application of surface coatings and treatment on a reinforced concrete surface provides a cost-effective and relatively simple approach for protection. The main objective of surface treatment is to provide a barrier between concrete surface and environment, thus make it less permeable to ingress of aggressive substances and moisture and also increasing the concrete resistivity [10]. Hence, sometimes they are also referred as sealers. They are most beneficial if corrosion is due to carbonation. Chloride induced corrosion attracts a lot of moisture, and surface treatment may not be able to stop it [10]. They can be divided into 3 classes: organic coatings, hydrophobic

impregnation, and cementitious coatings [10].

Organic coatings form a continuous polymeric film on the concrete surface, thus blocking penetration of carbon dioxide and chloride ions. Coating thickness ranges from 100-300 μm [10]. Organic coatings can be dense or vapour permeable coatings. Dense coatings are based on epoxy, polyurethane or chlorinated rubber polymer and do not allow the moisture inside concrete at time of application to evaporate, which may lead to a loss of adhesion and hence coating failure [10]. Vapour permeable coatings are generally acrylates and allow the concrete to dry out, reducing risk of degradation or blistering from trapped moisture. In case of carbonation, they will not remove already present contamination, but prevent further ingress of carbon dioxide. In case of heavily contaminated concrete, the coating may fail due to the formation of salt crystals [63].

Coating breathability is important, all anti-carbonation and chloride coatings must be breathable. Non-breathable coating can only be used if only part of the surface area is coated allowing for moisture to escape from the exposed faces.

Hydrophobic Impregnation materials include silanes, siloxanes and silicate-based compounds. They penetrate into the concrete surface and form a water repellent lining on the pore walls, hence preventing the penetration of chloride ions and other aggressive agents. Since pores are left open, this is also vapour permeable in nature [10]. They are not effective against standing water and are most suitable on vertical surfaces where the water can run off [63]. Although, silane and siloxane polymers have shown promise as corrosion protection treatments, there has been limited study on use of silanes as an additive to polymer concrete. Liu et al., 2018 [64]studied the effect of silanes as an additive in concrete and observed silanes showing excellent resistance to corrosion, freeze thaw and carbonation

Cementitious Coatings can be true cement based coatings (<10 mm thick) applied by brushing or in form of overlays (few centimetres thick) applied by plastering or spraying, such as shotcrete [10]. Polymer modified cementitious coatings are easier to apply than coatings requiring a dry substrate and overcome most of the problems with coating concrete [63]. They have good carbonation and chloride penetration resistance [10]. A few millimetres of these coating is equivalent to almost 100 mm of normal cover, but the major issue is its long term bond. Cementitious coatings have been used in combination with an epoxy coated glass scrim to provide restraint to concrete that has a risk of delamination [63].

Surface treatment is affected by many parameters such as air permeability, bond strength, substrate properties and application methods [65]. Goyal et al. 2018 [66] studied the bond behaviour of zinc rich paint coating and observed that substrate roughness affects the bond behaviour of concrete the most. The higher the exposure of aggregate on the concrete surface, the lesser the bond strength. In practice, grit blasting has proven to be the best method of preparation to achieve highest bond. Rotary water jets have also been used successfully.

The application of a coating will affect future inspection and testing of structures. For example, half-cell mapping cannot be done easily and impregnating a coating also affect the reading of half-cell mapping. Pan et al. 2018 [65] reviewed various concrete coatings and suggested some future research such as: the use of polymer/clay nanocomposite as organic coatings and the effect of cement type on the selection of surface treatment for various coatings.

3.5 Cathodic Protection (CP) or Cathodic Prevention (CPre)

These are electrochemical techniques used for preventing corrosion initiation in reinforced concrete structures subjected to chloride penetration [30, 67, 68]. U.S. Federal Highway Administration memorandum in 1982, stated that ‘CP is the

only rehabilitation technique that was able to stop corrosion in salt-contaminated bridge decks irrespective of level of chloride in concrete' [69]. CP can be applied to control corrosion in chloride contaminated structures or to prevent corrosion in new structures [68]. The latter technique is referred as cathodic prevention [70]. CPre requires approximately one-tenth of the energy of CP. Thus, cathodic protection systems for new structures present lower installation and operational costs, use less material due to lower current demand and are more environmentally friendly when compared with concrete patch repairs and retrofitted cathodic protection during the operational life of a structure [71]

When compared to conventional methods of protection, cathodic protection is cheaper, easier, can treat a larger area simultaneously and most importantly does not give rise to incipient anode problems. Therefore, it is most suitable repair technique to be employed in chloride contaminated structures [31].

3.5.1 Types of CP

Cathodic protection is applied in two ways: Sacrificial Anode Cathodic Protection (Passive system) and Impressed Current Cathodic Protection (driven by an external power supply), and more recently a new system with the properties of both methods has been introduced and is called a hybrid system.

Sacrificial Anode Cathodic Protection (SACP)

Sacrificial cathodic protection is generally used for the protection of underground pipelines and submerged structures. In SACP less noble metals than steel like zinc or aluminium are connected with the steel bar and the dissolution of this anode metal provides current instead of an external power supply (**Fig. 8**) [72, 73]. DC current is generated due to the potential difference between the steel to be protected (cathode) and the sacrificed metal (anode) [67, 74]. Its

advantages are simplicity, cost of monitoring and maintenance, and the availability of wide range of anodes [74, 75]. Disadvantages with the SACP are a requirement for the periodic replacement of anodic metal due to its dissolution in the process, limited control over the system and the low driving voltage which may be inadequate to provide full cathodic protection in all situations [74].

Alloys made from zinc, aluminium and magnesium which are less noble (higher electrical potential) with respect to carbon steel reinforcement are generally used as sacrificial anodes [74, 76, 77]. However, during use, Al and Mg oxides can attack concrete [78]. SACP is more effective for CPre than for protection. SACP is limited to small targeted repairs with short life-times [67, 79]. Kean and Davues (1981) stated that SACP is less liable to cause interactions with adjacent structures and unconnected metal parts in the same structures [67]. According to Byrne et al 2016, SACP is a safer option for pre-stressed structures as there is less risk of hydrogen embrittlement.

Common anodes used for SACP include metallic coating anodes (zinc or aluminium-zinc-indium thermally sprayed onto the concrete), anode jackets, adhesive zinc sheet and discrete repair anodes [67, 77, 80]. The application of these anodes is limited, as they need to be replaced after 0.3-0.5 m maximum depending on the amount of steel.

There has been a lot of research carried out on the use of SACP for corrosion mitigation, but there is still concern about the use of SACP for corrosion control in already contaminated concrete., Galvanic anodes are extensively used along with patch repair to prevent the incipient anode affect, however their service life is not long enough (currently 10-15 years). In order to protect them, coating patch repaired concrete with embeddable galvanic anodes should be considered. Experience suggests that galvanic anodes should not be used in tidal zone unless protected with jackets.

Impressed Current Cathodic Protection (ICCP)

In this method, a small direct current (DC) is supplied from a permanent anode (which can be fixed at the surface or into the concrete) through the concrete electrolyte to the steel bars. It uses a permanent, external power source; such as a rectifier powered from the main supply, solar cells, batteries, fuel cells or other means to deliver protective current to the steel reinforcement [77]. The current passed should be sufficient enough to halt the anodic reactions and cathodic reactions can occur at steel surface to produce hydroxyl ions. The production of hydroxyl ions will increase the alkalinity and repassivation of the steel bar and strengthening of passive layer will take place [70]. The potential of steel is brought to a value more negative than the corrosion potential and thus steel bars become a cathode. A schematic diagram of ICCP systems is shown in **Fig. 9**.

The ICCP system is much more commonly used in reinforced concrete than SACP as it can address significant corrosion issues in large structures with longer life expectancies [67]. The current density applied varies from 1 – 2 mA/m^2 for cathodic prevention and 5 – 20 mA/m^2 for CP with respect to steel surface area.

The beneficial effects of ICCP include [32, 81]:

PRIMARY

- Potential of reinforcement is made more negative
- All locally generated corrosion cells are overcome

SECONDARY

- Aggressive chloride ion removal via ionic migration
- Rise in the concentration of hydroxyl ions at the steel reinforcement

After application of CP or CPre on a structure, it should be operated throughout

the service life of the structure [10]. The anode system should be able to perform according to the design parameters and should not result in performance degradation either of concrete-anode interface or the anode itself during the design life. The ICCP system is preferred in dry areas, due to high concrete resistivity in a dry environment. The flow of current can be regulated depending on the resistivity [74].

Anodes for ICCP need to be good electrical conductors, have low corrosion rates and be able to tolerate high currents without forming resistive oxide layers. Common anodes used for ICCP include activated coated titanium wire, ribbon or mesh, organic coating such as polymer or coke and conductive cementitious anodes [67, 80, 82]. **Table 2** gives a comparison between SACP and ICCP systems.

The cause of failure of ICCP is normally early problems or end of component life. The contractor deals with early problems as part of defects liability period, normally 1 or 2 years. Later problems should be dealt with when the ICCP elements reach the end of their design lives. Early issues can include failures of reference electrodes (usually due to lack of contact to the concrete due to grout shrinkage), instability of reference electrodes due to leaching out the solution, debonding of the overlay on MMO/Ti mesh systems, localised high current and consumption of the anode, loss of connection at the interface of conductive coating and concrete due to drying out of concrete when electro-osmosis occurs and water entering junction boxes. However, anode failure does not cause immediate loss of protection, steel will remain in a passive state for few years [83].

The installation of pseudo reference electrodes (MMO/Ti, graphite or stainless steel) together with true reference

electrodes, gives an alternative monitoring means with long life but are less accurate.

During the service life there could be other problems like the client failing to pay the electricity bill, or transferring the data SIM card and therefore operation and monitoring are interrupted. Thus, having a maintenance contract in place is equally important.

Polder (2011) conducted a survival analysis on 105 structures and stated that mean service life of any CP system is 15 years without intervention. There is a 10% probability that a CP system needs maintenance at an age of about 7 years or less and 50% probability that maintenance is needed at an age of 15 years or less [83].

Hybrid Cathodic Protection

A recent advancement in CP systems is hybrid CP. In hybrid system, a temporary impressed current is used in combination with a low maintenance galvanic system to restore and maintain alkalinity [84]. The anodes mainly used with this system are discrete anodes connected to titanium wire for impressing the current [67]. The same anode is used for both impressed and sacrificial systems [84]. Typically, the system involves supplying a very high current for one week and then running the system galvanically [84]. The potential is mainly achieved by realkaization of acidic sites, maintaining high pH and hence restoring steel passivity [84]. This is a new concept and has not yet been significantly explored. Glass et al. 2008 developed a hybrid electrochemical treatment consisting of a pit re-alkalisation process and supplementary galvanic protection to induce and maintain a high pH at the steel. The treatment was able to reduce extreme corrosion and requires low maintenance [85].

Vector Corrosion Technologies, United Kingdom recently developed a fusion hybrid anode with a battery inside a casing. The anode initially operates in ICCP mode and after an impressed current phase, switches over to galvanic mode

automatically without external human intervention. The anode is claimed to be effective for a service life of approximately 30 years. Hybrid cathodic protection has the potential to be the future of CP systems, but requires further development in terms of type of anode, installation and operation.

Table 3 summarizes some of the existing anode types and their performance characteristics suitable for different types of CP system.

3.6 Electrochemical Realkalisation

The purpose of this technique is to provide long term corrosion protection to steel in carbonated concrete [86]. However, the carbonation must be confirmed as the cause of the corrosion before it is applied. In this case, for a short period, a small electric field is applied between steel in concrete and an alkaline electrolyte solution containing carbonate or hydroxyl ions and a temporary external anode (**Fig. 10)** [87–89]. It requires a charge 50 to 500 times greater than CP i.e. up to 0.5-1 A/m^2 of steel area and thus the initial cost is higher than CP. Typical treatment time is 6-8 days [86].

During the realkalisation process, oxygen is reduced at steel and even hydrogen can be generated if very negative potentials are reached [10]. These reactions create hydroxyl ions on the steel surface and help the steel to achieve its passivity. The alkalinity of carbonated concrete is raised and the pH is maintained above 10.5 to restore and maintain a passive protective layer around the reinforcing steel and hence it is called electrochemical realkalisation [28, 90, 91]. Electrolyte solutions of sodium, potassium and lithium may be used [88]

Platinised titanium mesh and steel mesh anodes in the alkaline electrolyte are conventionally used for the realkalisation process in structures [90]. Sodium carbonate solution is generally used as an electrolyte [9, 32]. High current densities and voltages can cause some side effects, such as the possibility of hydrogen embrittlement in case of high strength

prestressing steel when the potential becomes more negative than -1000 mV vs SCE and the risk of alkali-aggregate reaction, bond degradation and anodic acidification [9, 10, 32, 86, 89].

3.7 Electrochemical Chloride Extraction (ECE)

This technique is suitable for treating heavily chloride contaminated and corroded structures. It is a non-destructive, temporary and cost effective rehabilitation technique [29]. The application of an electric field for a short period of time between the steel bar and the externally deposited anode surrounded by alkaline electrolyte solution removes the negatively charged chloride ions present at the steel surface (**Fig. 11**) [92]. These ions migrate towards the external anode layer and thereby reduce the chances for corrosion initiation [91, 93]. Moreover, hydroxyl ions are also produced by the reduction of oxygen and water due to reaction at steel surface, providing alkalinity to concrete in vicinity of the rebar [92]. It requires charge 50 to 500 times higher than CP i.e. up to 1-2 A/m^2 of steel area and thus the initial cost is higher than CP. A typical treatment time is 6-8 weeks [20, 26, 32, 59].

Catalyzed titanium mesh and steel mesh are most commonly used as anodes in the chloride removal process [10]. The most commonly used electrolytes are water, calcium hydroxide solution and lithium borate solution. It is not recommended to use this technique with prestressing wires due to the risk of hydrogen embrittlement and it may also create a risk of alkali silica reaction due to increased hydroxyl ion concentrations near the steel surface during the protection process [10, 26, 86, 89].

Table 4 summarizes advantages and limitations of different corrosion protection techniques.

4 Conclusion

From the review, it is evident that corrosion of reinforcement in concrete is a major issue and needs to be considered when designing concrete structures exposed to aggressive environments. Understanding

the corrosion process and its thermodynamic and kinetic nature is important for designing a suitable protection strategy. There are various protection techniques available such as corrosion inhibitors, alternative reinforcement, steel and concrete coating and electrochemical techniques. However, electrochemical techniques are generally more effective than conventional methods. The suitability of any mitigation technique varies from structure to structure depending upon value engineered, practicality and economic considerations. There is no single best solution for every structure and each one needs to be evaluated on case to case basis. In practice, sometimes, cost pressue based upon client's requirements leads to the adoption of a particular solution.

Table 1 Corrosion state at different pH levels [11]

pH	State of reinforcement corrosion
<9.5	Corrosion initiation
8.0	Passive layer disappears
<7.0	Catastrophic corrosion occurs

Table 2 Comparison of galvanic and impressed current cathodic protection system

Technique	Advantages	Disadvantages	References
SACP	• Simpler installation, design and low maintenance • No external power source required • Less liable to cause interaction • No control system • Low risk of hydrogen embrittlement • Can be applied to prestressed structures	• Less experience in reinforced concrete • Unable to control current • Unknown degree of protection • Additional anode required if current demand changes • Limited service life • Not adequate in high resistance environment • Low driving voltage, thus can be used only in less resistive concrete • Monitoring need to be considered at the design stage. • Anodes can be large and intrusive compared to ICCP • Non-uniform anode consumption	[9, 32, 67, 74, 77, 94]
ICCP	• Commonly used in reinforced concrete • Controllable current • Adequate in high resistance environment • Higher life span • Minimal effects on concrete • Monitoring shows it is effective	• Need permanent external power source and continuous monitoring • Greater risk of interaction • External power source and monitoring system vulnerable to damage and atmospheric corrosion • Service life of control equipment, cabling and silver/chloride electrodes will be around 20 years. Control equipment may also need maintenance in between. Cable routing could be difficult and require expensive access • Greater risk of hydrogen embrittlement • Specialist expertise required • Vandalism of the equipment is also a major factor to be considered especially in remote and secluded areas.	[9, 32, 67, 74, 77, 94]

Table 3 Different anodes and their properties used for CP system

Anode Type	Expected Service Life (years)	Required Current Density (mA/m^2)	Estimated installation cost of anode (£/m^2)	Suitable Environment	Other Performance Characteristics
Conductive Organic Coatings (ICCP)	5-15	2-20	100-300	• Not suitable for wet or structures • Not suitable for running surface	• A series of conductors fixed to concrete surface or integrated into the coating. • Optimum dry film thickness of coating is 0.25-0.5mm • Shortest life of anode systems and are rarely applied in the UK any more. However, some of the earliest conductive coating anodes are more than 20 years old i.e. exceeding their design lives.
Metallic Coatings (ICCP/ SACP)	10-25	2-20	200-400	• May be suitable for wet structures • Not suitable for running surface	• Zinc for SACP and ICCP; Al-Zn-In for SACP; Ti for ICCP • Primary anodes feed connections from Ti, stainless steel or brass plates fixed to concrete surface • Thermally sprayed Zinc applied by arc or flame spraying having optimum thickness of 0.1-0.4 mm • One anode per $10m^2$ is typical
Discrete Anodes (SACP, Hybrid)	25-50	----	160-400	• Suitable for wet structures • Suitable for running surface	• Prevents the repaired area from causing new anodic corrosion nearby. • Similar discrete anodes can be installed in holes cored or cut into the concrete and wired together
Conductive Cement Overlay (ICCP)	25	2-20	150-350	• Suitable for wet (not tidal) structures • Suitable for running surface	• Contains granular carbon or carbon fibres with metallic coating as the conductive medium.
Adhesive Zinc Sheet (SACP)	25-50	---	----	• May be suitable for wet structures • Not suitable for running surface	• Rolls of Zn foil, typically 0.25mm thick coated on one side with ionic conductive adhesive gel (hydrogel)
Anode Jackets (ICCP/SA CP)	120	110	200-400	• Suitable for wet structures • Suitable for running surface	• Expanded anode mesh in permanent glass-reinforced form, grouted to concrete piers, piles or columns • Ti mesh for ICCP, Zn mesh for SACP • High initial cost
Activated Titanium (ICCP)	25-100	110	200-400	• Suitable for wet structures • Suitable for running surface	• Mesh, strip, wire or tube activated Ti anodes, coated with mixed metal oxides with an overlay or cast into slots or drilled holes or fixed to surface under GRP casings

					• High initial cost

Table 4 Comparison of different corrosion prevention techniques

Repair Technique	Applications	Advantages	Service Life	Estimated cost (£/m^2)	Limitations	Reference(s)
Corrosion Inhibitors	• Mixed with fresh concrete for new structures • Penetrated into hardened concrete for repair • Used as a surface treatment on bars	• Easy to handle • Compatible with CP • Low Cost • Limits amount of concrete needed to be removed • Delay initiation of corrosion in concrete exposed to chloride attack and carbonation.	10-15 years or less	20-50	• Shorter long-term performance • Toxic in nature • Less significant effect after corrosion initiation • Issues in uniform and effective spread along reinforcement • Unknown level of protection	[35, 59, 62]
Alternative Reinforcement	• Alternative to carbon or mild steel	• Higher corrosion resistance than conventional steel • FRP bars highly resistant to both alkaline and acidic environment • Less prone to damage during handling compared to coated reinforcement • Can be used with electrochemical techniques	• Long term solution • Needs consideration to not use in the whole structure because of cost	SS-Almost 10 times than mild steel bar	• Expensive • Risk of galvanic corrosion in carbon steel when coupled with SS	[10, 47, 51, 59]
Steel Coating	• Applied on steel reinforcement and acts as a protective barrier	• Available in numerous formulations • Highly corrosion resistant • Protects steel from mechanical damage • Protects steel from chloride attack and carbonation • Cost-effective	Max 15 Years	20-50	• Damage during fabrication or handling may lead to its failure • Epoxy coating not compatible with CP due electrical discontinuity. • Epoxy bars not suitable for long term protection	[4, 20, 55, 59–61]
Concrete Coating	• Applied on concrete surface and acts as a barrier between concrete surface and environment	• Available in numerous formulations • Cost- effective • Simple application • Increase concrete resistivity • Compatible with CP	Max 15 years	20-50 depending on the coating type	• Not suitable for heavily contaminated concrete • Do not remove already present contamination in case of carbonation • Hydrophobic Impregnation are not suitable for standing work and water	[10, 59, 63]

					• Should be defect free • Failure difficult to measure as can occur in different areas	
Cathodic Protection (CP)/ Cathodic Prevention (CPre)	• Applied to new or old structures affected by chlorides. • Also effective in carbonated concrete	• For ICCP, low current density required: CP- 5-20 mA/m^2; CPre- 1-2 mA/m^2 • ICCP lasts for 20-50 years or more • Minimal effects on concrete • Adequacy can easily be checked through monitoring	Depends upon anode type (refer Table 3)	• Approx. 500 £/m^2 • Depends upon anode • Installation cost is higher, however economical long term cost	• Permanent Technique • ICCP requires permanent power supply • Require regular maintenance and monitoring • The effect of permanent anodes needs to be considered at the design stage • CP not advisable for prestressed structures • ICCP system can cause Stray current corrosion	[9, 10, 32, 59, 67, 95]
Electrochemical chloride removal	Applied to structures in which corrosion has not already initiated.	• Less intrusive- power supply and anodes required temporarily • No long-term effect on appearance • Increase passivation of reinforcing steel • Increase pH of concrete. • Completed within 6-8 weeks • No further maintenance required • Temporary Technique (polarization period: 2-6 weeks)	Depends on environmental conditions, like shorter life in high chloride environment and may require to install again	• Approx. 500 £/m^2 • Depends upon anode • May require to operate again in future which increases cost	• Requires charge of 50 to 500 times compared to CP i.e. up to 1-2 A/m^2 • Structures should use conventional reinforcement • Remaining service life must be 5 to 10 years • Length of treatment can create logistical problems • Initial cost higher than CP • Additional monitoring is required to ensure that protection is maintained • Can affect concrete • Potentially serious effects if electrical continuity of all steel is not established • Only effective in cover zone of concrete • Not recommended to use with prestressed wires and risk of alkali aggregate reaction	[9, 10, 26, 29, 32, 59, 95]
Electrochemical Realkalization	• Applied to structures in which corrosion has not already initiated. • Only for carbonated concrete	• Less intrusive- power supply and anodes required temporarily • No long-term effect on appearance • No further maintenance required • Temporary technique (polarization period: 3-10 days)	Rarely applied as chance of carbonated concrete is far less as compared to chlorinated concrete	• Approx. 500 £/m^2 • Depends upon anode • May require to operate again in future which increases cost	• Requires charge of 50 to 500 times compared to CP i.e. up to 0.5-1 A/m^2 • Limited life of treatment • Initial cost higher than CP • Can affect concrete • Potentially serious effects if electrical continuity of all steel is not established • Carbonation must be confirmed as corrosion cause before treatment • Not recommended to use with prestressed wires and risk of	[9, 10, 28, 32, 86, 95]

					alkali aggregate reaction	

Note: - Cost of access and traffic management are not included, which in turn effects the economic benefits of different repair techniques.

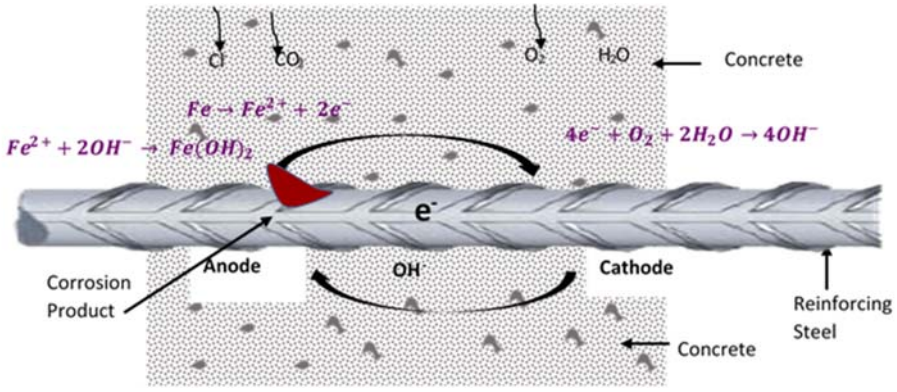

Fig. 1 Schematics of corrosion process in concrete

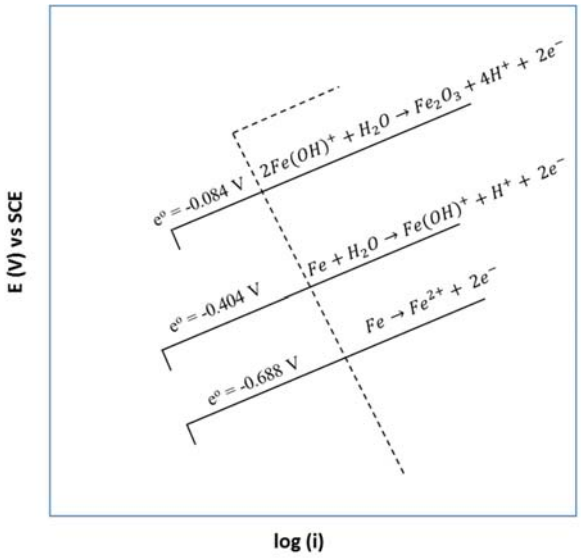

Fig. 2 Corrosion reaction mechanism adopted from [1]

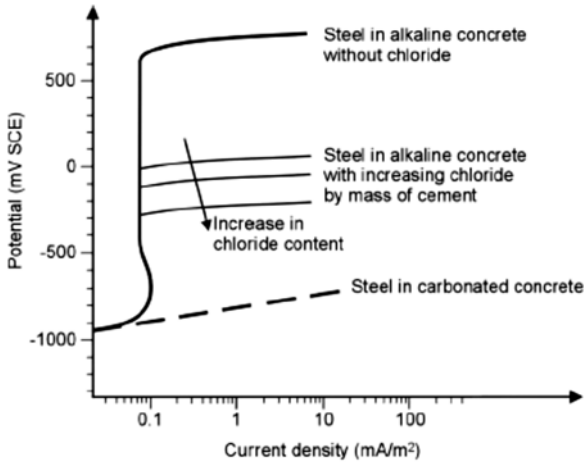

Fig. 3 Schematic diagram of steel anodic behaviour in concrete chlorides presence [55]

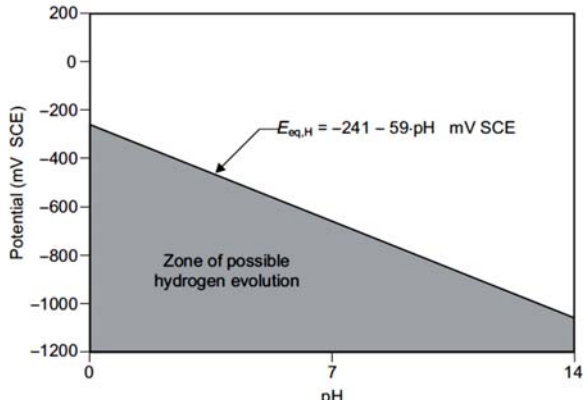

Fig. 4 Potential –pH zone for Hydrogen Embrittlement [10]

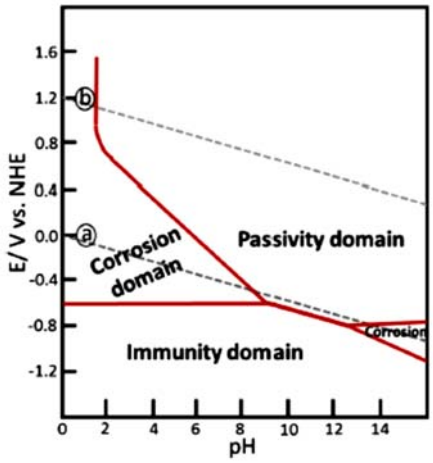

Fig. 5 Pourbaix diagram for iron in chloride solution [15]

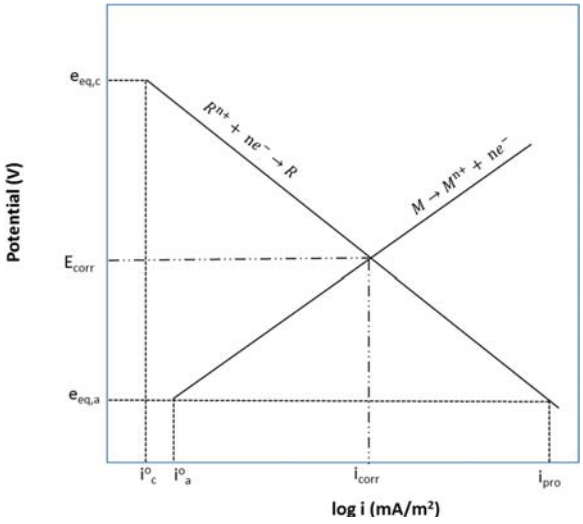

Fig. 6 Evan's diagram showing corrosion process kinetics adopted from [1]

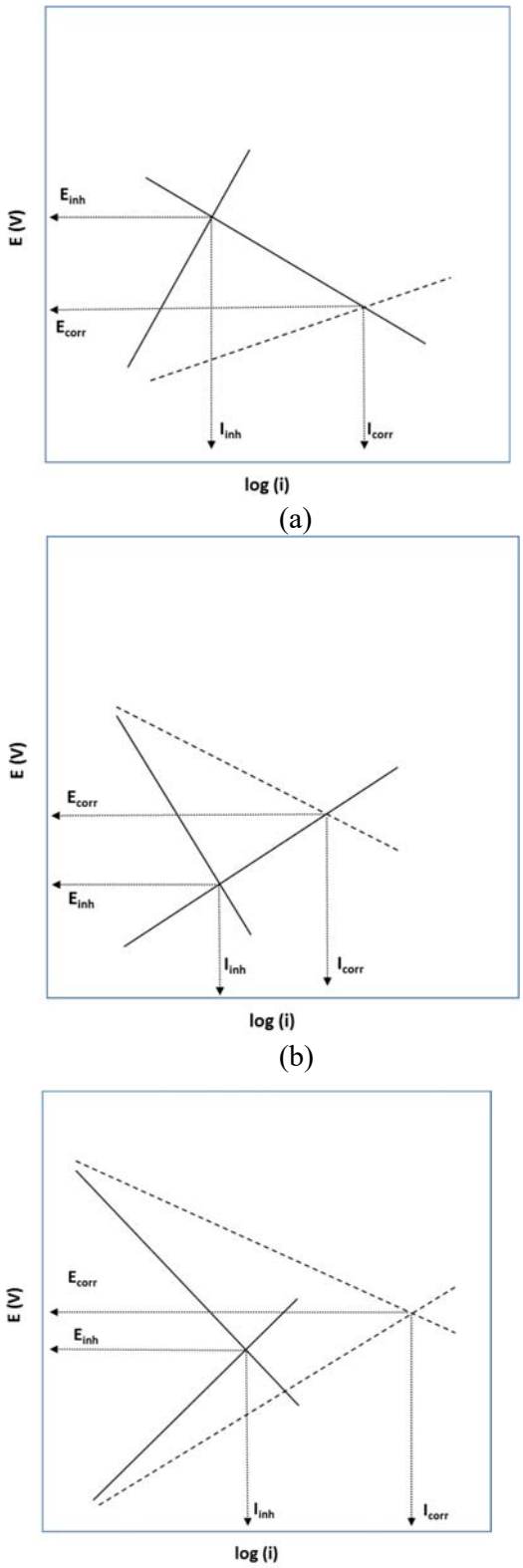

Fig. 7 Corrosion protection mechanism for (a) Anodic (b) Cathodic (c) Mixed Inhibitor, adopted from [1]

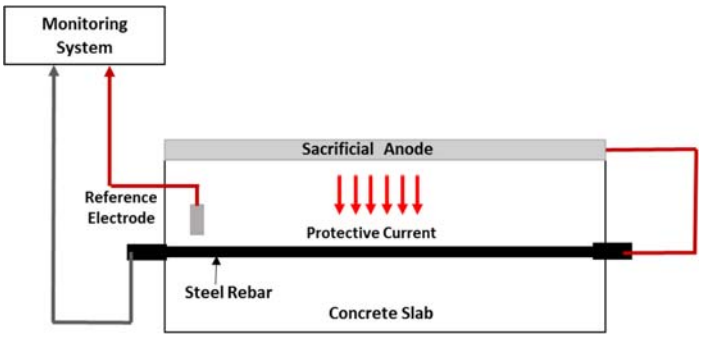

Fig. 8 Schematic of Sacrificial Anodic Cathodic Protection System

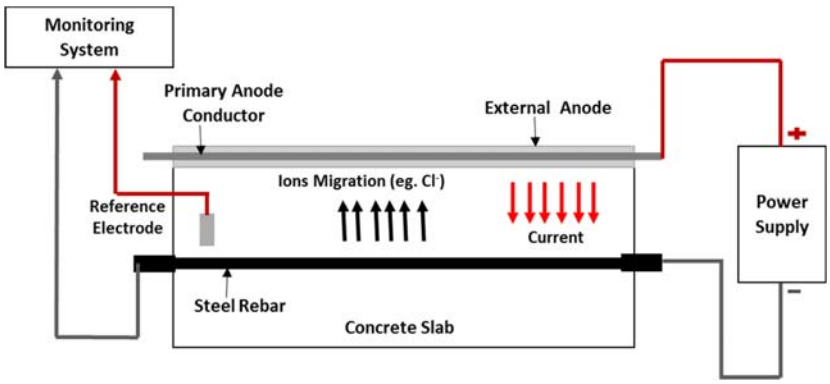

Fig. 9 Schematic of Impressed Current Cathodic Protection System

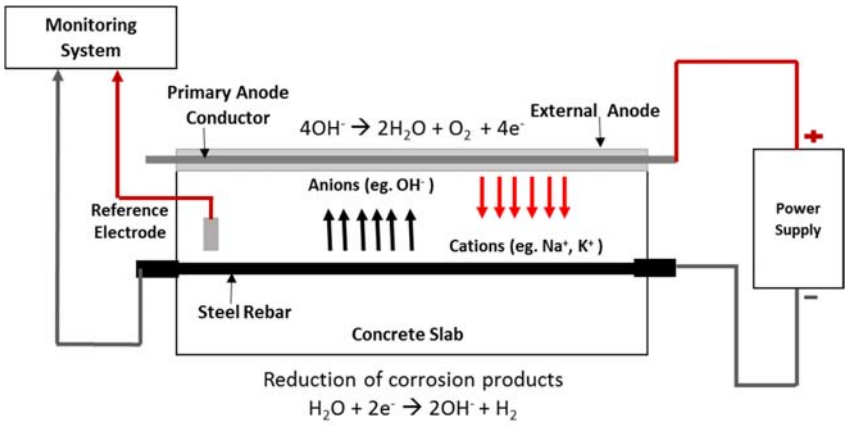

Fig. 10 Schematic of Electrochemical Realkalization

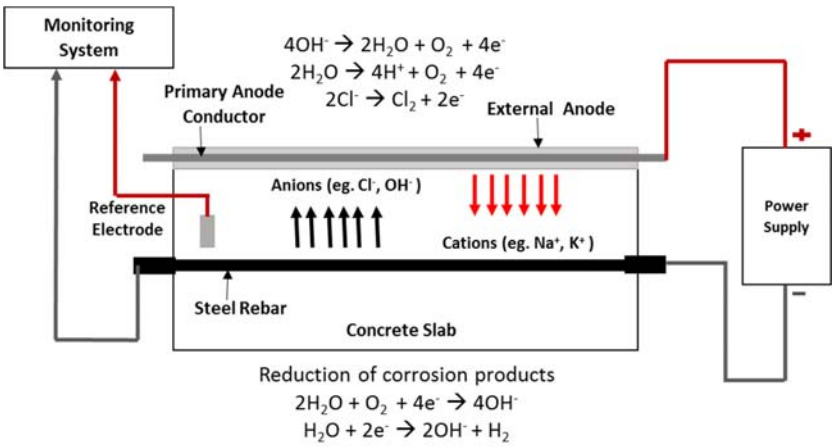

Fig. 11 Schematic of Electrochemical Chloride Removal

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