

# Corrosion of Reinforcing Bars in Concrete

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The causes and mechanisms of corrosion of reinforcing bars in concrete are described in terms of the practical issues as well as the electrochemistry. The parameters affecting corrosion are (i) the ingress of aggressive species, such as chlorides, which break down the protective film on the reinforcing bar and (ii) the amount of those species necessary to do so. The former is largely controlled by the concrete properties while the latter is a function of the type and condition of the reinforcing bar. Thus, the influence of the cementitious components of concrete, the water/cementitious materials ratio and the presence of cracks in the concrete cover, on the ingress of aggressive species is considered and the various currently available reinforcing bar materials and their merits are reviewed.

## Background

Although corrosion of reinforcing steel is now recognized as the major cause of degradation of concrete structures in many parts of the world, it should be understood that this is not due to any intrinsic property or limitation of the concrete itself whether it be normal quality portland cement concrete (OPCC) or high performance concrete (HPC). In fact, all sound portland cement concretes provide an ideal environment for corrosion protection of even the poorest quality steel such as has sometimes been used for reinforcement.

Steel is thermodynamically unstable in the earth's atmosphere and will always tend to revert to a lower energy state such as an oxide or hydroxide by reaction with oxygen and water. The question of interest in the use of steel is not whether this process will occur (it will!) but how fast it will occur in practice. Fortunately, only the surface atoms of the steel are exposed to the atmosphere and, therefore, are available to react. In the case of a 15 mm diameter bar, this amounts to only about 1 in every 40 million atoms. Any coating on the steel will reduce this number even further. For steel embedded in concrete, the concrete itself

provides a coating limiting the access of water and oxygen to the steel surface. A second beneficial aspect of concrete is that the solution in the pores of the cement paste has a very high alkalinity and, as indicated in the Pourbaix diagram in Figure 1, at the pH levels typical of concrete, the corrosion products which do form are insoluble. They produce a very thin (~ few nm) protective coating on the steel (a passive film) which limits the metal loss from the steel surface due to corrosion to about 0.1 - 1.0  $\mu\text{m}/\text{year}$  [1-3]. It is generally considered that, at these passive corrosion rates, the steel embedded in concrete would not be noticeably degraded within a 75 year lifetime and the volume of corrosion products would not be sufficient to cause any damaging stresses within the concrete. The passive film does not form immediately but starts as soon as the pH of the mixing water rises in the concrete when the cement begins to hydrate and stabilizes over the first week to protect the steel from active corrosion [4].

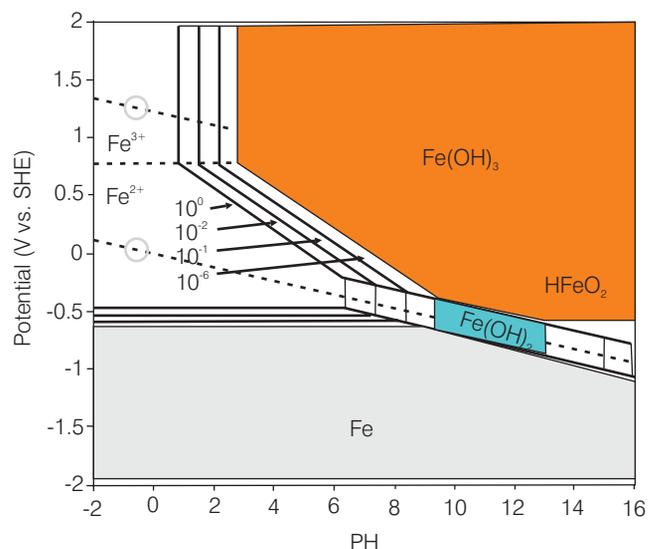


Figure 1. The Pourbaix diagram for iron showing regions of electrochemical potential and pH where metallic iron is stable (grey region); where active corrosion occurs (white areas) and where the metal is passivated (green and orange areas) [5].

Unfortunately, however, the passive film is not stable in solutions containing chloride ions or at pH levels below about 9, as indicated in Figure. 1 [6]. Also unfortunately, concrete is both permeable, allowing the ingress of chlorides from de-icing salts or marine atmospheres, and reactive, allowing acidic gases, particularly CO<sub>2</sub>, to neutralize the pore solution. When the passive film is broken down either by chlorides or by carbonation of the concrete, active corrosion occurs at rates as high as several mm/year and it is this process which is responsible for much of the structural degradation occurring in reinforced concrete, such as that illustrated in Figure 2.



Figure 2. (a) Retaining wall of bridge and (b) underside of bridge deck.

Corrosion, whether at the negligible passive rate or the damaging active rate, is an electrochemical process, involving the establishment of anodic and cathodic half-cell reactions on the microscopic and/or macroscopic levels. In high pH solutions and in the absence of chloride ions, the anodic dissolution reaction of iron:



is balanced by the cathodic reaction:



and the Fe<sup>2+</sup> ions combine with the OH<sup>-</sup> ions to produce the stable passive film. The electrochemical process is illustrated schematically in Figure 3(a).

### Chloride-Induced Corrosion

The mechanism by which chloride ions break down the passive film is not fully understood [1], largely because the film is too thin to be examined and because the events occur inside the concrete. One hypothesis is that the chloride ions become incorporated into the passive film and reduce its resistance. This incorporation is not uniform and, where it occurs, it allows a more rapid reaction and the establishment of an anodic area where corrosion continues while the remaining steel remains passive, Figure 3(b).

A second hypothesis is that the Cl<sup>-</sup> ions “compete” with the OH<sup>-</sup> anions for combining with Fe<sup>2+</sup> cations and, because the Cl<sup>-</sup> ions form soluble complexes with the Fe<sup>2+</sup> ions, a passive film is not formed and the process stimulates further metal dissolution. The soluble iron-chloride complexes diffuse away from the steel and subsequently break

down, resulting in the formation of expansive corrosion products and, simultaneously freeing the Cl<sup>-</sup> ions, which are then able to migrate back to the anode and react further with the steel. In this overall process, hydroxyl ions are continuously consumed, locally decreasing the pH (i.e. making the solution acidic in that localized region) and, thereby, enhancing further metal dissolution. The Cl<sup>-</sup> ions, on the other hand, are not consumed and the attack then becomes “autocatalytic”. Ultimately, the reinforcement cross-section and its structural resistance are seriously compromised.

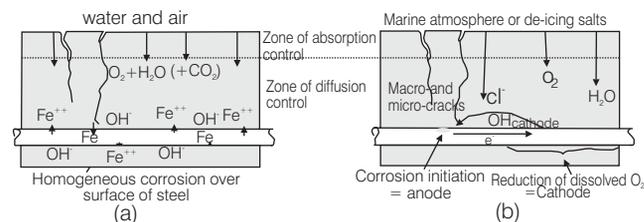


Figure 3. Schematic representation of (a) passive corrosion and (b) chloride-induced active corrosion of steel in concrete.

Either of these hypothesized mechanisms would explain the local nature of the attack often observed. The local actively corroding areas behave as anodes while the remaining passive areas become cathodes where reduction of dissolved oxygen takes place. The galvanic cells may be “macro” or “micro” in scale depending on a number of factors, as described below. Thus, the anode and cathode may be widely separated or they may be adjacent on an atomic scale.

### Chloride threshold concentration for corrosion initiation

Many studies [7-11] have been made to determine the threshold or critical value of chloride concentration below which active corrosion will not occur. The interest in knowing this value is twofold: (i) to specify limits of chloride contamination in aggregates or water used in the concrete mixture and (ii) to permit prediction of the incubation period between first exposure to chlorides and the onset of active corrosion and, thereby, allow for scheduled maintenance and rehabilitation. Unfortunately, the idea of a universal value applicable to all structures is not realistic because it will be a function of many variables including:

- mixture proportions of the concrete;
- type and specific surface area of the cement;
- use of any supplementary cementing materials (SCMs)
- w/c ratio;
- sulfate content;
- curing conditions, age and environmental history of the concrete;
- degree of carbonation of the concrete;

- temperature and relative humidity of the environment;
- roughness and cleanliness of the reinforcement.

An illustrative representation of the interrelation of some of these factors is given by CEB (Comité Euro-International du Béton) [12] and is shown in Figure 4. Different national standards consider different limits for chlorides depending on the experience within that country but a value of 0.4% Cl by weight of the dry cement is the most common value.

In the United States, the Federal Highway Administration (FHWA) has stated that a chloride ion concentration of 0.15% by weight of the cement can be tolerated but that 0.3% is considered dangerous [13]. More recently, McDonald et al. [14] have determined a value of 0.2%. However, when chlorides diffuse into concrete, some react with the aluminate phases and become chemically bound and some may become physically trapped in closed pores or in the hydrate phases. Only the free chlorides will be available to attack the passive film on the steel and, therefore, the use of total chloride content as measured per ASTM C 1152 [15] as a measure of the threshold value for corrosion can be misleading.

The limits on chloride content of constituents have recently been questioned in view of the increasing use of supplementary cementing materials and their effect on the pH of the pore solution. For example, the maximum chloride content at the reinforcement level for steel which did not exhibit any active corrosion after exposure to natural sea water is given in Table 1. for steel in concretes with different fly ash contents [16]. The threshold for steel in mortar with

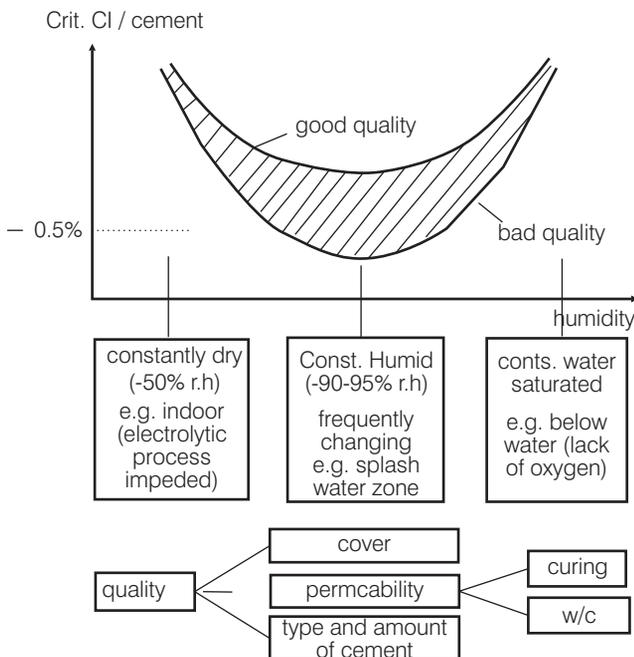


Figure 4. The critical chloride content of concrete of reinforcing steel according to CEB recommendations [12].

either fly ash or silica fume was also found to be lower than that of steel in mortars without supplementary cementitious materials [8].

Two factors should be noted. First, that this is a potential problem only for chloride contamination of the constituents; chlorides penetrating into hardened concretes with SCMs exhibit lower diffusion rates and lower active corrosion rates, which are believed to more than offset the lower chloride threshold value. Second, that, in both of these investigations, the chloride thresholds were significantly higher than those recommended by the FHWA, suggesting that the latter are conservative relative to those measured in laboratory experiments. Nevertheless, suppliers of potentially contaminated materials should be cognizant of the effects of pozzolans on the amount of chloride needed to initiate active corrosion.

Fly-Ash content (% replacement of cement)	Chloride threshold concentration (% by mass of dry cement)
0	0.70
15	0.65
30	0.50
50	0.20

Table 1. Effect of Fly Ash Replacement on the Chloride Threshold Concentration for Corrosion [16].

Very high levels of chlorides can accumulate in concrete, particularly in the splash zone of marine structures or, for example, in columns embedded in ground which are exposed to de-icing salt run off or the substructure of bridges exposed to either runoff from above or splash from the roadway below. As moisture evaporates from the exposed surface of the concrete, the salts remain behind. The subsequent “wicking” of the saline solution from the sea or soil by capillary suction into the dry concrete replenishes the water and builds up the chloride levels and the process repeats itself.

There is little field information on the effect of temperature and relative humidity on the rate of chloride-induced corrosion but laboratory tests have shown that, if the internal humidity in concrete is less than ~85%, high active corrosion rates cannot be sustained [17].

**Carbonation-Induced Corrosion**

Carbon dioxide from the atmosphere reacts with the calcium hydroxide (and other hydroxides) in the cement paste by the following reaction:



effectively neutralizing the pore solution.

Carbonation is detected as a reduction in the pH of the pore solution in the surface regions of the concrete and appears as a fairly sharp front, parallel to the surface. Behind the front, the  $\text{Ca(OH)}_2$  has completely reacted and the pH is  $\sim 8$  whereas ahead of the front, the pH is  $> 12.5$ . The depth of carbonation increases with time and the rate at which it advances is a function of relative humidity (RH): the penetration of the  $\text{CO}_2$  into the concrete is highest at low RH but the reaction with the  $\text{Ca(OH)}_2$  takes place in solution and is, therefore, highest in saturated concrete. The net result of these two factors is that carbonation is most rapid in the 50% - 70% RH range, Figure 5 [7, 18]. The carbonation front penetrates the concrete at an ever decreasing rate because of three factors. Firstly, the gas has to penetrate further into the concrete and, secondly, the concrete continues to hydrate and becomes more impermeable as it ages. Finally, the carbonation itself decreases the permeability both by the precipitation of the carbonate in the existing pores and because the reaction releases water, which could result in increased hydration [19].

When the carbonation front reaches the reinforcement, the passive film is no longer stable and active corrosion initiates. Unlike chloride-induced corrosion, the corrosion process is generalised and relatively homogeneous. Moreover, the corrosion products tend to be more soluble in the neutral carbonated concrete and may diffuse to the surface appearing as rust stains on the concrete, rather than precipitating in the concrete cover and causing stresses and cracking. The corrosion rates are lower than those caused by chlorides but, over a long period, the cross-section of the reinforcement can be reduced significantly while there

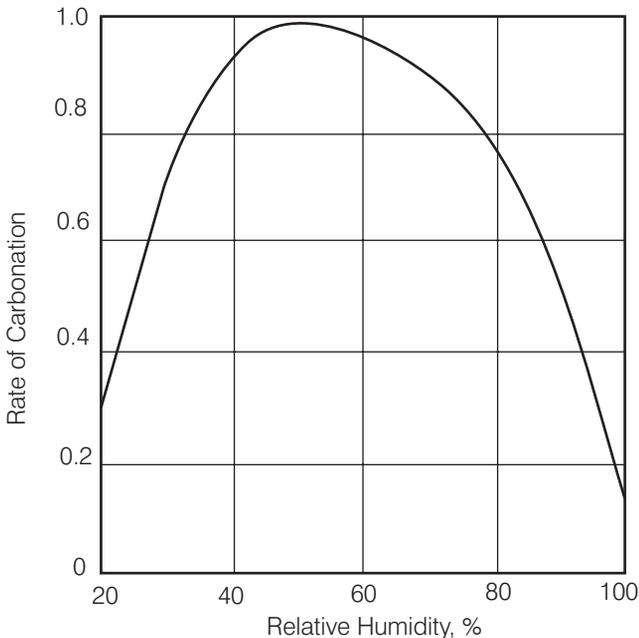


Figure 5. The influence of relative humidity on the rate of carbonation of concrete [18].

is little visible damage to the concrete. The active corrosion process is described schematically by Fig. 3(a) but with a much higher rate than the passive corrosion.

Although an intermediate RH provides the highest rate of carbonation, active corrosion of any significance does not occur in that humidity range [1]. Consequently, the most aggressive environment for carbonation-induced corrosion is alternate semi-dry and wet cycles [18]. Carbonation can, therefore, be a major factor in the durability of concrete in hot climates where the concrete is easily dried out and periodically subjected to saturation by rainstorms. Chloride attack and carbonation can act synergistically and are responsible for major problems in hot coastal areas. Carbonation-induced corrosion is not found to be a major problem in northern North America where adequate concrete cover over steel is used.

**Corrosion Products**

The most detrimental consequence of chloride-induced reinforcement corrosion is the build-up of voluminous, insoluble corrosion products in the concrete which leads to internal stresses and, eventually, to cracking and spalling of the concrete cover. Obviously once such damage is visually apparent, the reinforcement is prone to very rapid further corrosive attack because access to oxygen and moisture is no longer limited by diffusion through the concrete cover.

All forms of iron oxide and hydroxide have specific volumes

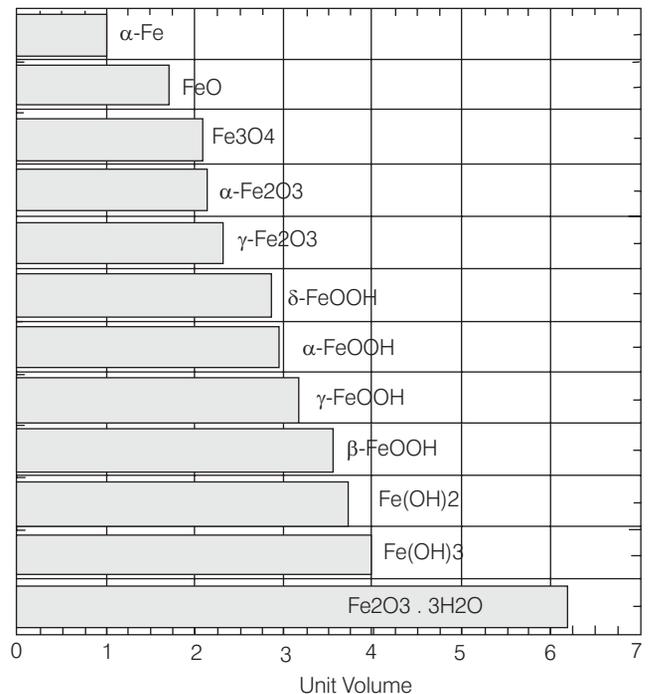


Figure 6. Specific volume of the corrosion products from iron [19].

greater than that of steel but their volumes vary by a factor of more than five as indicated in Figure 6 [19].

Thus, the degree of damage to the concrete produced by a certain amount of corrosion will depend on the specific corrosion products formed and their distribution within the concrete cover as well as on the porosity and strength of the concrete itself.

In many reports it is assumed that the corrosion products are rust, i.e.  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  because this is the orange colored product observed on damaged concrete. Consequently, in models, it is also assumed that the corrosion products are more than six times as voluminous as the steel from which they are formed and the predicted stresses in the concrete are based on this conclusion. In fact, analysis of the products formed indicates that they are  $\text{Fe}_3\text{O}_4$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\gamma\text{-Fe}_2\text{O}_3$ ,  $\alpha\text{-FeOOH}$  and  $\gamma\text{-FeOOH}$  and have a specific volume between 2.2 and 3.3 times that of the steel. It is only after cracking and spalling and, thus, exposure to the atmosphere, that these products convert to the familiar rust. Moreover, results which have been obtained to date [20, 21] suggest the quality of the concrete, the use of supplementary cementing materials and the presence of macrocracks do have an influence of the specific corrosion products and on the corrosion-induced deterioration of the cover once active corrosion has been initiated.

Theoretical models of the quantity of corrosion [22] needed to cause cracking of the concrete cover assume the corrosion products are (a) of a uniform specific volume and (b) all form at the interface between the reinforcement and the concrete. Observations [20, 21] of the products formed during the active corrosion in real concrete with normal shrinkage and loading cracks shows that this is not the case. The corrosion products vary in composition within the same concrete and they precipitate within the cover, as illustrated in Figure 7 not just at the steel/concrete interface.

### Microcell and Macrocell / Galvanic Corrosion

Microcell corrosion is the term given to the situation where active dissolution and the corresponding cathodic half-cell

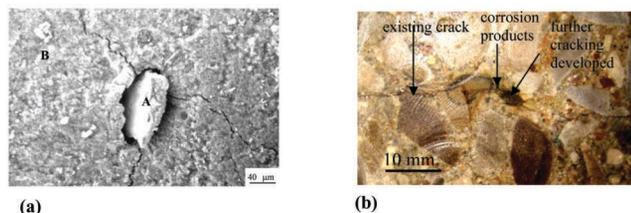


Figure 7. (a) Precipitate of magnetite in the concrete cover of HPC. "A" is a particle of Akaganeite ( $\beta\text{-FeOOH}$ ) containing approx. 40% Fe in HPC. The surrounding material labelled "B" contains approximately 18% Fe as corrosion product intimately embedded in the cement [20]; (b) corrosion products in a crack penetrate into the concrete causing further cracking [23].

reaction (the reduction of dissolved oxygen) take place at adjacent parts of the same bar, as illustrated in Figure 8 (a). This process always occurs in practice and, in most cases, is the dominant corrosion process. Macrocell or galvanic corrosion can occur when the actively corroding bar is coupled to another bar, which is passive, either because of its different composition or different environment. For example, the former situation might occur when black steel is in contact with stainless steel and the latter situation when a top mat in chloride-contaminated concrete is coupled to a bottom mat in chloride-free concrete, as in Figure 8 (b). Macrocells can also form on a single bar exposed to different environments within the concrete or where part of the bar extends outside the concrete. The process is the same in all cases and, in all cases, the corrosive action of the macrocell is added to that of the microcells.

It should be emphasized that the simplified view of the "active steel becoming the anode and the passive steel becoming the cathode" is not actually correct. In each of these cases, the anodic and cathodic reactions occur on both metal surfaces; when the two metals are coupled, the anodic corrosion of the active metal increases and the anodic corrosion of the passive metal decreases.

While macrocell corrosion can be measured directly, the same is not true of microcell corrosion and most investigators choose to neglect the microcell component. This has led to the general assumption that macrocell corrosion is always the dominant component. On the other hand, Trejo and Monteiro [24] concluded that the difference between the corrosion mass loss measured gravimetrically and that calculated from macrocell corrosion rate measurements must be due to the microcell corrosion. Andrade et al. [25] have analyzed the relative contributions of microcells and macrocells and concluded that: (i) the

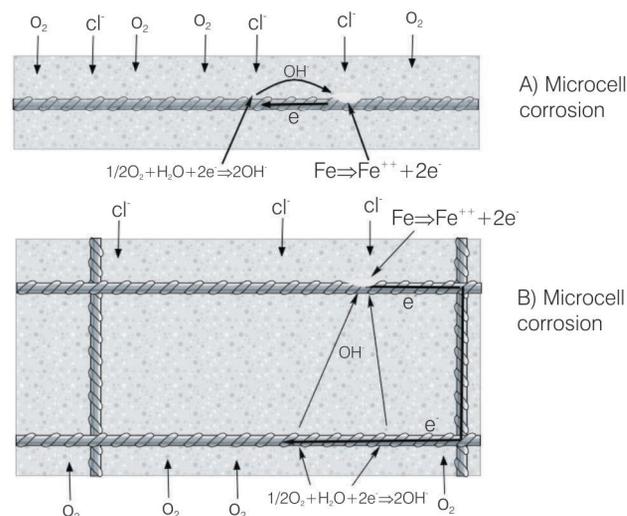


Figure 8. Schematic illustration of (a) microcell corrosion and (b) macrocell corrosion [26].

influence of the latter only becomes significant, i.e. of the same order as the microcell corrosion, when the ratio of surface areas of the passive:active regions is greater than approximately 50:1 and (ii) the theoretical maximum effect (with an infinitely large cathode and infinitely small anode) would be an increase in active corrosion rate of only 2 - 5 times that of the microcells alone. This has been confirmed in laboratory studies [26]. Suzuki et al. [27] concluded that the maximum anodic dissolution rate of the steel in concrete was the limiting rate controlling factor not the anode/cathode area ratio.

## The Influence of Concrete Parameters on Corrosion of Reinforcement

### Concrete Mixture Design

Chloride ions from de-icing salts and/or marine environments penetrate the concrete cover depth to reach the surface of the reinforcing steel by a number of mechanisms. As illustrated in Figure 9, the surface of the concrete may be dry, allowing the dissolved chlorides to be absorbed by capillary action together with moisture through the interconnected pores in the cement paste. At deeper levels, concrete rarely dries out in the atmosphere [28] and so continued penetration of the chlorides is by diffusion through the pores, which is a much slower process than absorption. A third mechanism is via cracks in the concrete cover, which is discussed below.

Porosity in cement paste consists of capillary pores, gel pores and calcium silicate hydrate (C-S-H) interlayers [29]. Capillary pores are the remains of originally water-containing spaces between cement particles that have not been filled up by products of hydration [30]. They are the largest (diameter > 5 nm [31]), and their number and interconnectivity control the ingress of chloride ions, oxygen and moisture into concrete [32]. Gel pores and interlayer spaces are believed to be too small and disconnected to contribute to transport.

Two factors that significantly influence capillary porosity in concrete are the water to cementitious materials (w/cm) ratio [33] and the use of supplementary cementing materials (SCMs) [34]. Theoretically, a w/cm ratio of 0.42 is required for the complete hydration of cement. However, hydration is a gradual process and the unused mixing water is retained in the capillary pores [22]. Higher w/cm ratios, traditionally used to give a workable mixture, increase the amount and interconnectivity of capillary porosity in the cement paste allowing greater diffusion. With the advent of high range water reducing agents, much lower w/cm ratios are now possible and significantly limit the penetration of chloride ions.

SCMs, such as fly ash (FA) silica fume (SF) and ground

granulated blast furnace slag (GGBFS) react with the potassium, sodium and calcium hydroxides in the pore solution of the cement paste, thereby reducing the pH of the solution. As has been shown above, this can reduce the amount of chlorides necessary to initiate active corrosion. On the other hand, the additional C-S-H produced as a result of the pozzolanic reactions between the SCMs and  $\text{Ca}(\text{OH})_2$  can block the capillary pores. Because of its small particle size ( $<0.1\mu\text{m}$ ), un-reacted SF also reduces the capillary porosity. This retards the ingress of chloride ions, thereby increasing the initiation time for corrosion. It also decreases the corrosion rate, once initiated, by decreasing the mobility of  $\text{OH}^-$ , which is required to complete the macrocell and microcell corrosion circuits, as shown in Figure 8.

Concrete with low w/cm ratios ( $\leq 0.35$ ) and incorporated SCMs provide high strength and low permeability. It should be noted here that these mixtures must be accompanied by adequate curing to prevent the concrete from cracking due to self-desiccation or autogenous shrinkage. These concretes, exhibit long reinforcement corrosion initiation times [26, 31] and low corrosion rates [35]

### The Influence of Cracks in the Concrete on the Corrosion of Embedded Steel

While interconnected capillary porosity provides a tortuous path for the ingress of chloride ions, oxygen and moisture into concrete, cracks provide a more direct path. Cracks in concrete can be classified as macrocracks and microcracks or, from the viewpoint of their effects on corrosion as those transverse to the reinforcement and those parallel to the bar (longitudinal cracks). The sources of cracks in concrete include shrinkage [22], chemical reactions (e.g. alkali aggregate reaction, [31]), weathering processes (e.g. freezing and thawing [36]), reinforcement corrosion [37] and mechanical loading.

Concrete always contains cracks and codes on concrete structural design such as ACI 318 [38] take this into account and relate permissible crack widths to exposure conditions. However, an understanding of the effects of cracks on corrosion is limited [39-41]. For concrete with multiple cracks, corrosion at one crack appears to protect

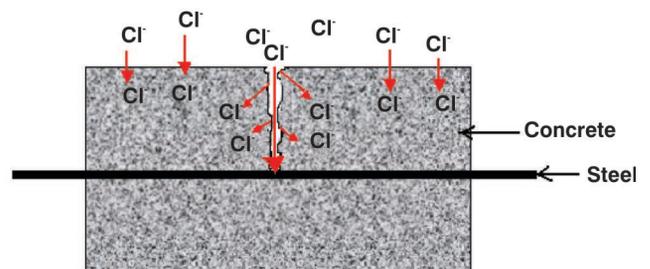


Figure 9. Schematic illustration of chloride diffusion in cracked concrete.

the steel at the other cracks by forming a galvanic cell or there is a low corrosion rate at all the cracks [42]. Chloride ingress is significantly enhanced by cracks because the ions penetrate the concrete cover from the walls of the crack as well as from the outer surface of the concrete [43], as illustrated schematically in Figure 9. Thus, while the chlorides reach the steel very rapidly directly through the crack, they also reach adjacent areas of steel more rapidly than in uncracked concrete.

Low w/cm ratio concrete containing SCMs has been found to provide good protection for steel exposed to transverse cracks, in large part because of its resistance to chloride penetration from the walls of the crack. However, the benefits are not as great as they are for sound (uncracked) concrete [40]. Moreover, the higher the quality of the concrete, the more spatially localized the corrosion along the reinforcement. Unfortunately, however, this can be accompanied by a greater depth of corrosion, leading to the possibility of the bar being severed [21].

In the case of cracks parallel to the reinforcement, low w/cm ratio concrete containing SCMs does not appear to have any beneficial influence on the corrosion of bars [44], which is not surprising in view of the fact that the whole length of the bar is directly exposed to the environment via the crack.

### Alternative Reinforcing Materials

#### Epoxy coated reinforcing bars

Epoxy provides a barrier coating to the steel and, thereby, prevents the chlorides from breaking down the passive layer on the steel providing a longer service life. While many structures with epoxy-coated steel have performed well, some have not. The latter cases have been attributed either to flaws in the coating, most likely due to defects introduced during construction, or to absorption of moisture by the epoxy leading to swelling and debonding from the steel [45, 46]. It is generally concluded that good quality epoxy coatings will increase the time to initiate corrosion but, once initiated, the corrosion rate will be about the same as that of uncoated black steel.

#### Stainless steel reinforcing bars

With increasing service life requirements, stainless steel is being regarded as a viable alternative reinforcement despite its higher cost. The most common grades of stainless steel for reinforcement are 316LN and 2205, both of which have excellent corrosion resistance [47, 48] and are commercially available. They should provide service lives well in excess of 100 years. Research shows that grade 304 is less corrosion resistant than the other two grades [49] but, in fact has the longest successful field

record of any stainless steel [50]. The cost of the stainless steels is more than five times that of black steel [51] but, on a life cycle cost basis, they are considered to be cost-effective [52].

#### Corrosion resistant reinforcing bars – MMFX and 2201LDX

In order to provide better corrosion resistance than black steel but at lower cost than the traditional stainless steels, efforts have been made in recent years to develop corrosion resistant alloys for reinforcement. Three examples of these steels are (i) a “low carbon, low chromium microcomposite steel” designated as MMFX-2 (ASTM A615 Grade 75) [53], (ii) a 1.5% Ni 21% Cr alloy designated 2101LDX (ASTM A955-98) [51], and (iii) a 3% Ni, 12% Cr alloy designated 3Cr12 [53]. In macrocell corrosion tests [54], the corrosion initiation times for these alloys were measured to be 2, 7 and 1.6 times that of black steel, whereas the 304 and 316LN grades had initiation times in excess of 12 times that of the black steel (i.e. they had not begun to corrode during the period of the research). The corrosion rates of the MMFX and 2102LDX after initiation were less than half of that exhibited by the black steel. Their cost is between 2 and 4 times that of black steel, whereas the cost of the stainless steels is more than five times that of black steel [55].

Other investigators [56] have concluded that “...high performance alloys outperformed black steel from a corrosion resistance standpoint”. Unlike the various grades of black steel however, a relatively wide range of corrosion performance was apparent for the high performance counterparts depending on the alloy and surface condition.”

#### Galvanized steel reinforcing bars

Galvanized steel reinforcement has been used in reinforced concrete structures since 1930s [57]. The advantages of hot-dipped galvanizing are two-fold: unlike most other forms of coatings, a metallurgical bond is formed between the steel and the zinc which means that the coating is not susceptible to flaking or other forms of separation from the substrate. Secondly, zinc not only forms a barrier coating but acts as a sacrificial anode. Thus, any scratches or other flaws in the coating are not critical and do not lead to active corrosion of the underlying steel. Zinc has the advantage over black steel that it can tolerate more chlorides (approx 2.5 times [58-60] and lower pH levels [pH~8] before significant active corrosion is initiated. Thus, it would provide better protection than black steel to both chloride-induced and carbonation-induced corrosion.

The galvanized layer has the disadvantage that it corrodes very rapidly in the wet cement but this reaction rate ceases once the concrete hardens [61, 62]. While chromating

the galvanized bars has been performed to minimize this initial corrosion, the use of chromates is not recommended because of adverse health effects of the hexavalent chromate ions. However, recent research has indicated the effect of chromating is minimal at best [62]. Because of its passivation in neutral solutions and its sacrificial anode role when in contact with steel, galvanized steel is ideally suited for parts which are to be partially embedded in concrete and partially exposed to the atmosphere.

### Non-metallic reinforcement

The carbon-fiber reinforcements currently being marketed [63] do not suffer from corrosion and will not be discussed here. The long term performance of these materials in concrete has not yet been evaluated. Whether the epoxy matrix for these bars will suffer the moisture absorption that was observed in epoxy coatings is not yet known.

### The Corrosion Behavior of Other Metals in Concrete

#### Aluminum and its alloys

Aluminum develops a passivating layer on its surface at pH 4-9 [6] which protects it from further corrosion. However, the passive layer is unstable in alkaline environments and aluminum reacts with sodium and potassium hydroxides in concrete, a reaction which is accompanied by the evolution of hydrogen gas. This reaction occurs at high rates in wet concrete causing plastic concrete to develop a very porous structure as it hardens. This may affect the bond between aluminum and concrete, as well as, increase the ingress of chloride ions into concrete which exacerbates the corrosion of aluminum. The use of chloride admixtures also greatly increases aluminum corrosion and spalling. The corrosion products of aluminum are extremely expansive and cause cracking and spalling of the surrounding concrete [64, 65].

Aluminum elements should never be embedded in concrete exposed to moist service environments, unless the aluminum is prevented from direct contact through use of a protective barrier.

#### Lead

Although lead is deemed to have superior corrosion properties to those of steel and aluminium under atmospheric conditions, it reacts with calcium hydroxide in concrete to form soluble lead oxides and hydroxides, which do not protect the metal from further corrosion. As with aluminium, the reaction occurs at high rates in wet concrete which decrease as concrete hardens. If lead is to be placed in wet concrete, it should be protected using bituminous or plastic coatings [64, 65].

#### Copper and its alloys

Copper and its alloys do not corrode in non-chloride

contaminated concrete provided it does not contain ammonia and nitrates, which can induce stress corrosion cracking in the metal. The copper oxide formed in alkaline environments such as concrete is not soluble and, hence, forms a protective layer that limits further corrosion. However, the presence of chlorides in concrete perforates copper [64, 65]. Macdonald et al. [14] tested copperclad reinforcement and found it to have significantly higher resistance to chloride-induced corrosion than did black steel.

### Service Life of Reinforced Concrete Exposed to Chlorides

The service life of black steel reinforcement in OPC concrete is often depicted as consisting of two phases: an incubation period during which chlorides or carbonation penetrates the cover, and a propagation period where active corrosion causes degradation of the concrete. However, it is illustrative to assess the behavior of the reinforcement independently of that of the concrete, as has been shown schematically Figure 10.

The blue curve in Figure 10 represents the steel corrosion and shows an initial, relatively high, corrosion rate until the

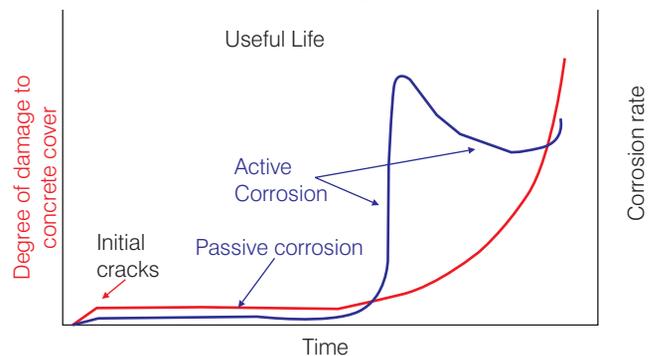


Figure 10. Schematic representation of the variation of corrosion rate of the reinforcement as a function of time (shown in blue) and the corresponding damage produced in the concrete cover (shown in red) [18].

passive film on the steel is developed (a matter of several days to a few weeks). Thereafter, the corrosion rate will be low ( $\sim 10^{-4} \text{ A/m}^2 = 0.116 \mu\text{m/yr}$ ) until the chlorides reach the steel in sufficient quantities to initiate active corrosion. The corrosion rate will jump very rapidly, possibly by as much as three orders of magnitude, and will remain high until all the dissolved oxygen in the cement paste pores adjacent to the steel has been consumed by the cathodic half cell reaction:



The corrosion rate will then drop to a level determined by the diffusion/permeation of oxygen from the environment. The specific corrosion products formed during these processes and their distribution within the concrete cover will be

determined by: (i) the porosity and the density of micro- and macro-cracks in the concrete, i.e. the available space for precipitation of the products and (ii) the availability of oxygen and moisture, and the concentration of chlorides. Once the volume of corrosion products causes stresses in excess of the tensile strength of the concrete, cracks will develop and propagate out to the surface. At this point, oxygen is made readily available at the reinforcement and the corrosion rate increases as shown.

Simultaneously, the damage in the cover can be described by the red curve in Figure 10. There will be some initial damage as the structure comes into service and loading and settling cracks develop but do not propagate further. After initiation of active corrosion and the precipitation of corrosion products, cracks will begin to develop around the corrosion products, as illustrated in Figure 10. As these grow, they will intersect and eventually propagate to the surface, causing spalling. For the purposes of this report, this is considered the "end of service life".

Many models [66-72], based on Fick's Second Law, have been developed to predict the length of the "incubation period" under different circumstances. Only a few attempts [37, 73] have been made, however, to model the propagation phases of the deterioration process including the cracking.

### Corrosion Monitoring Techniques

One of the major problems associated with reinforcement corrosion is that its initiation and early stages of propagation cannot be detected visibly. Yet early detection of corrosion in a reinforced concrete structures can provide the opportunity to schedule appropriate maintenance procedures, thereby ensuring the safety of the structure. If corrosion remains undetected until cracking and spalling occur, then the costs of repair are significantly higher because all of the concrete cover and much of the reinforcement must be replaced. Moreover, patch repair at this time can enhance active corrosion in the surrounding original reinforcement and lead to a continuous cycle of repairs.

The most commonly used techniques for evaluating the condition of embedded reinforcement are based on the electrochemical nature of the process. The electrons released by the iron as it corrodes (Equation 1) and consumed by the dissolved oxygen (Equation 2) constitute a current, illustrated in Figure 3, which can be indirectly measured. This current, representing dissolution of one iron atom for each two electrons in the current, can be converted to thickness of steel dissolved by the equation:

$$1\text{mA/m}^2 = 1.16 \text{ mm/year} = 0.0456 \text{ mils/year (mpy)} \quad (\text{Eq. 3})$$

The currently available electrochemical monitoring

techniques are described below. Unfortunately only a few of these can be readily used in the field.

### Half-cell potential mapping

Half-cell potential measurements are the most widely used method of detection of corrosion of steel reinforcement in concrete. The method was introduced in the 1970s by Richard F. Stratfull in North America [74, 75] and by the Danish Corrosion Centre in Europe [75-77] and was approved in 1980 as a standard by ASTM [78]. ASTM C 876 involves measuring the electrochemical potential of the steel reinforcement with respect to a copper/copper sulfate reference electrode by connecting one wire of a high impedance voltmeter to the reinforcement and the other to the reference electrode placed on the surface of the concrete. The voltage can provide an indication of the probability of active corrosion of the steel. The recommended ASTM interpretation of the measurements is as follows:

Half-cell potential reading vs. Cu/CuSO4	Corrosion activity
More positive than -200 mV	90% probability of no corrosion
Between -200 and -350 mV	An increased probability of corrosion
More negative than -350 mV	90% probability of corrosion

Table 2. Probability of Corrosion of Carbon Steel According to Half-Cell Potential Reading [78].

It is important to note that the interpretations are of probabilities of corrosion only and that there are other possible causes of high negative potentials. For example, in deaerated concrete, such as that submerged in deep water, potentials as low as -700 mV are normal despite the fact that the steel remains passive. It should also be noted that half-cell potentials give no indication of the rate of corrosion, nor of how long the steel has been corroding.

### Linear Polarization Resistance (LPR)

When a very small electrical potential (of the order of 10 mV) is applied to the corroding steel, the relationship between potential and current is linear. The polarization resistance,  $R_p$ , is the ratio of the applied potential to resulting current and is inversely proportional to the corrosion rate [79, 80]. In order to calculate a corrosion rate with the LPR technique, the following fundamental assumptions must be made [5]:

- uniform corrosion damage;
- the rate controlling step in corrosion is activation polarization (i.e. the ease of stripping electrons from the iron);
- there is a single anodic and a single cathodic reaction;

- the proportionality constant between corrosion rate and  $R_p$  must be known;
- the electrical resistance of the solution (i.e. the concrete) is negligible;
- the half-cell potential is stable.

In fact, of these assumptions, only the third one is applicable to the case of chloride-induced corrosion of embedded reinforcement. Despite this, the LPR technique has become increasingly popular for measuring corrosion in the field because: (i) it is a nondestructive technique; (ii) it is simple to apply and (iii) it usually needs only a few minutes for corrosion rate determination [81].

Consequently, an increasing number of commercial instruments are available for field measurements of LPR. Measurements are performed by applying a potential in the range of  $\pm 10$  to 20 mV about the  $E_{corr}$ , either as a constant pulse (potentiostatic), or a potential sweep (potentiodynamic), and measuring the current response. Alternatively, a current pulse (galvanostatic) or a current sweep (galvanodynamic) can be applied, and potential response is measured. The RP and, in turn, the corrosion rate is calculated by the instrument.

In addition to the assumptions mentioned above, the major limitation of these techniques is that it is impossible to know the area of steel which is being polarized by the applied potential, or the area which is actively corroding. Therefore, the corrosion is generally considered to be uniform over the polarized area and the measured corrosion current is divided by a "guesstimated" polarized area to give an average corrosion rate. An additional limitation is that this is an instantaneous corrosion rate and (a) gives no indication of how long corrosion has been going on or (b) how the corrosion rate varies with time and ambient conditions. An example of how much corrosion rates vary is given in Figure 11 together with the corresponding temperature and relative humidity variations inside the concrete over the same time period. It should be noted corrosion rate increases or decrease with increasing or decreasing temperature, as expected. The relative humidity, on the other hand, remains approximately constant, at  $\sim 100\%$ , over this period, despite significant changes in the external temperature and relative humidity. This illustrates that the concrete is not dried out at all at depths of approximately 25 mm, and that only the surface layers are affected by drying.

Attempts to overcome the uncertainty in the polarized area have resulted in the development of the "guard ring". The objective of the guard ring is to concentrate the polarization to within a specified length of the steel reinforcement. Guard ring electrodes have been incorporated in several commercial corrosion measurement instruments [82, 83].

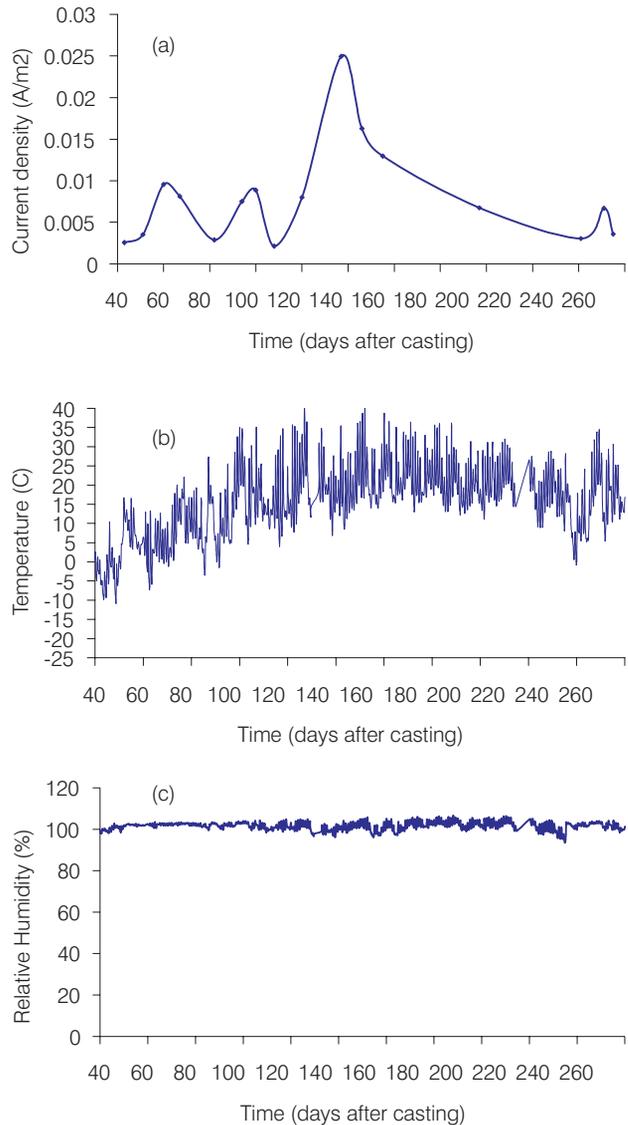


Figure 11. (a) Corrosion rate of steel, (b) internal temperature and (c) internal relative humidity variations in OPC concrete [41].

Studies have shown, however, that all of instruments have some limitations [84-86] and that the use of a guard ring does not solve all of the deficiencies of the technique..

### Cyclic potentiodynamic polarization

Cyclic polarization is relatively non-destructive technique that provides the corrosion rate, corrosion potential and susceptibility to pitting corrosion of the metal in the test environment, as well as giving information about the expected behavior of the steel should its potential be changed by, for example, exposure to stray currents, coupling with other metals or the surrounding concrete becoming anaerobic. Like most electrochemical techniques, cyclic polarization is carried out with three electrodes: a working electrode (the reinforcing steel), a

counter electrode and a reference electrode. The potential of the specimen is changed continuously or in steps, while the resulting current is monitored. From a plot of the applied potential versus the logarithm of the resulting current density, the condition of the steel in the present environmental, as well as its potential behavior under other conditions, can be assessed. Cyclic polarization is most useful in the laboratory, for example, to evaluate the behavior of steel in new concrete mixes or the behavior of alternative reinforcing materials in normal concrete. While such tests have been successfully performed in the field by the authors, they suffer the same limitation of LPR that of knowing the polarized area of the steel, as well as taking a longer time to perform.

**Electrochemical Impedance Spectroscopy (EIS)**

Analyzing the response of corroding electrodes to small-amplitude alternating potential signals of widely varying frequency is the basis of EIS [81]. EIS has become popular as a tool of corrosion measurement and monitoring applications for which traditional DC techniques have been unsuitable. It has been used extensively for coated and painted materials to detect the impact of holidays (flaws) in the coating. Thus it is a useful technique for evaluating epoxy-coated reinforcement [87]. It has also been employed to evaluate the effectiveness of cathodic protection [86] and corrosion inhibitors [88] as well as chloride diffusivity in concrete [89] and electrical resistance of concrete. Most of these studies have been carried out in the laboratory and, based on the authors' experience, this technique is unsuitable for field measurements because the measurements take too long and because the system is susceptible to electrical interference.

**Prevention and Protection Methods**

**Cathodic Protection (CP)**

The first example of cathodic protection applied to concrete structures was reported in 1957 [90] and widespread use of the technique for protecting bridge decks contaminated by deicing salts began in 1973 in North America [91, 92].

Cathodic protection is based on changing the potential of the steel to more negative values. This potential change can be obtained by connecting an external anode to the steel and impressing an electrical DC current through the reinforcement using a rectified power supply. Activated titanium expanded mesh with a surface coating of titanium oxide is the most widely used anode in practice. This external anode is mounted on the surface of concrete. The positive terminal of low voltage DC current source is connected to the mesh and the negative terminal is connected to the steel bars. In order to halt corrosion of the reinforcement completely, the potential would have

to be lowered to values more negative than ~ -1200 mV CSE (immunity region in Pourbaix diagram for iron) [6]. However, at those values, the cathodic reaction would result in hydrogen evolution which could cause hydrogen embrittlement of any prestressed steel in the structure. Consequently, the potential is carefully controlled to a level (typically -1000 mV CSE) at which the corrosion is negligible but not actually stopped.

Alternatively, the process can rely on the galvanic effect and a less noble metal can be used as sacrificial anodes. In this case, metals such as zinc and zinc-aluminium alloys, are applied to the concrete surface by flame spray, as a mesh or sheet adhered via a conductive gel [93].

CP must be applied for the remaining lifetime of the structure and must be monitored regularly. For this purpose, the potential of the steel should be monitored with respect to a reference electrode before and after disconnecting the system to make sure that the system is depressing the potential from the open-circuit potential. The limits and standard practices are outlined in [94]. Resistance of the concrete should be considered.

**Electrochemical Chloride Extraction (ECE)**

The goal is to repel the (negatively charged) chloride ions from the reinforcement and out of the surface of the concrete by applying a negative charge to the reinforcement, as illustrated schematically in Figure 12. ECE is similar to CP but a higher current is applied for a short period of time (a matter of weeks). During the treatment, any corrosion products are electrochemically reduced at the reinforcing steel [95].

ECE is being applied successfully in North America but the long term effects of such treatment have not yet been evaluated. In laboratory tests on steel in mortar, it has been

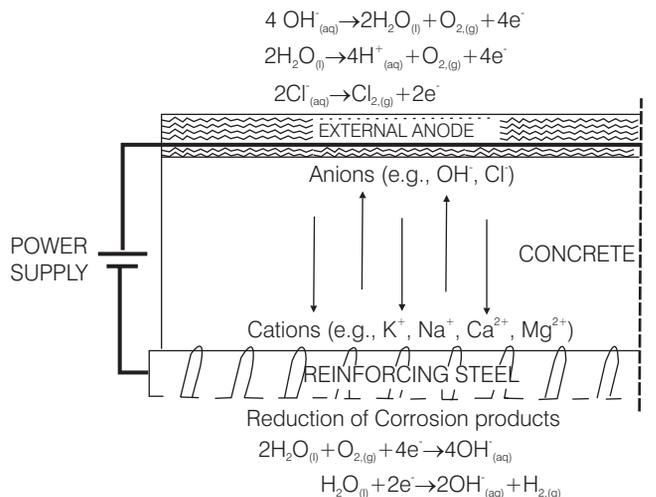


Figure 12. Schematic illustration of the application of the electrochemical chloride extraction treatment to a corroding reinforced concrete structure [95].

shown that the applied current can significantly alter the composition and morphology of the mortar at the steel/mortar interface and the steel/concrete bond strength [96, 97]. ECE is best applied when the chlorides are almost reaching the reinforcing steel but have not yet initiated active corrosion. It cannot stop the damage if the process of deterioration is advanced. Therefore, the extraction treatment may be considered an appropriate preventive method but, strictly speaking, not a rehabilitation method [98]. Thus, while the electrochemical extraction process is obviously successful in removing the chlorides, it should be used with caution and practical limits of current density should be established to minimize the harmful effects [97].

### Inhibitors

Corrosion inhibitors are defined as chemical compounds that reduce the corrosion rate by affecting the anodic or cathodic half-cell reactions or both. It should be noted that the materials which affect the transportation mechanism of the aggressive species to the reinforcing steel bars are not considered inhibitors [99].

A corrosion inhibiting admixture to concrete can function by [100]:

- Increasing the resistance of the passive film on the steel to breakdown by chlorides
- Creating a barrier film on the steel;
- Increasing the degree of chloride binding in the concrete;
- Scavenging the oxygen dissolved in the pore solution; and
- Blocking the ingress of oxygen.

Numerous compounds have been investigated in the laboratory as potential corrosion inhibiting admixtures to concrete and the most widely used ones are summarized in Table 3.

The efficiency of the inhibitors in steel reinforced concrete structures has not yet been proved and there are many discussions in this area. Lack of understanding the mechanism, environmental and safety aspects are some of the major limitations of using inhibitors in reinforced concrete structures properly [99, 101]. Consequently, while calcium nitrite is used in many jurisdictions and is required in some, it is not permitted in others. Corrosion inhibitors should conform to ASTM C 1582.

### Non-chloride de-icing agents

Sodium chloride, calcium chloride and magnesium chloride have traditionally been used for snow and ice removal operations. However, these de-icers cause durability problems in concrete structures. Environmental concerns

Inhibitor	Application	Mechanism
Calcium nitrite	Added to the mixing water of concrete	Due to the negative charge of nitride, it migrated into the pit and enhance passivation by its oxidative properties [3, 101]
Calcium nitrate	Added to the mixing water of concrete	In the presence of corrosion products, nitrate is reduced to nitrite. This reaction in alkaline environment is fast enough to provide required nitrite to inhibit corrosion [99]
Sodium monofluorophosphate (MFP)	Added to the mix or applied to the surface	None of the studies on MFP determined the mechanism by which MFP inhibits the corrosion of steel in concrete (anodic, cathodic or mixed) [102-104].
Hydroxyalkylamines	Added to the mix or applied to the surface	Generally, is produced in a gas phase and migrate relatively fast to the surface of concrete and reduces the corrosion rate. No detailed information available regards to protection mechanism [99].

Table 3. The Most Widely used Inhibitors for Applying in Steel Reinforced Concretes.

are also involved. In this regard, several non-chloride de-icers have been used in recent years. De-icers based on potassium acetate, sodium acetate, sodium formate, calcium magnesium acetate (CMA), urea, ammonium nitrate and ammonium sulfate are the most common ones. None of these compounds contains chlorides and so they are not expected to corrode the embedded steel. However, there are reports of deterioration of concrete due to application of some non-chloride de-icers. The cement matrix of concrete is reported to be severely attacked by CMA solutions [105]; potassium acetate is found to exacerbate alkali aggregate reactions [106]; ammonium nitrate and ammonium sulfate rapidly attack and disintegrate concrete [107] and urea decreases the resistance of concrete to freezing and thawing [108] and salt scaling [109].

## Summary and Conclusion

Portland cement concretes provide excellent protection for embedded steel in the absence of chloride contamination or carbonation by (a) acting as a physical barrier and (b) by chemically passivating the steel surface. Nevertheless, reinforcing bar corrosion is a major cause of the degradation of reinforced concrete structures particularly in northern North America, because of the high quantities of chloride de-icing salts used. In addition the increase in construction near coastal marine environments may increase the potential for corrosion deterioration in these areas. As a result, some structures of ordinary portland cement concrete with black steel reinforcement are requiring repair and remediation long before their current specified service lives (typically 40 – 50 years) are reached. Therefore, easier, faster and more reliable condition analysis techniques are required than those currently available, and described above, to allow corrosion detection at an earlier stage and, thus, permit remedial action to be taken before major repairs are required.

At the same time, with the current emphasis on sustainability, building codes are now requiring longer service lives, of the order of 75 to 100 years. Consequently, for new structures, there must be a greater understanding of the reinforcement corrosion process and of materials and structural designs aimed at minimizing the risk of corrosion.

A two-fold approach to corrosion resistant structures should include:

- The use of high performance concrete (HPC) to lower concrete's permeability and reduce the rate of ingress of chlorides or carbonation and, thereby, increase the effectiveness of the physical barrier.
- The use of more resistant reinforcing bar materials to provide better chemical resistance. In those parts of structures exposed to very severe chloride environments, stainless steel is recommended. Despite the initial expense, it is a cost effective solution in these circumstances when both direct and indirect costs (such as user costs) are taken into account. In the somewhat less severe chloride environments, corrosion resistant alloys such as MMFX or 2101LDX, which are more resistant to chlorides than black steel - but less corrosion resistant and much less costly than stainless steel - should be considered. Galvanized reinforcement is recognized as having greater resistance to chlorides than black steel and is significantly more resistant to carbonation-induced corrosion or combinations of chlorides and carbonation than black steel.

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