CORROSION OF STEEL REINFORCEMENT IN CONCRETE

CTI TECHNICAL NOTE 1

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INTRODUCTION

When steel reinforcement is encased in sound dense concrete, the entire surface of the steel is covered by a stable protective oxide film that forms in the alkaline environment created by the hydration of the cement in the concrete. Under these circumstances no corrosion of the reinforcement can occur.

However, if the protective oxide film is locally destroyed, for example by the ingress of chloride ions, areas of different potential can be set up on the surface. Reference to the galvanic series shown in Table 1 shows that steel encased in concrete with its protective film intact will have a more noble potential than steel without the protection of the alkaline environment.

This difference in potential can result in electrochemical corrosion cells forming between areas on the reinforcement where the protective film has been destroyed and the remainder of the surface where the film is still intact. Such cells create minute electric currents which flow through the reinforcement in one direction and return through the concrete by electrolytic conduction.

The areas where the electrons leave the reinforcement to enter the concrete are called *anodes* and they corrode, whereas the areas where the current re-enters the reinforcement do not corrode and are called *cathodes*. Corrosion takes place at the anode with metal ions going into solution (refer Eqn. 1)

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

No corrosion occurs at the cathode, the cathode simply provides the mechanism for the removal of electrons left in the reinforcement by the corrosion process (refer Eqn. 2).

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

The concrete must be wet enough to provide an electrolytic path for the transport of ions and therefore the corrosion of reinforcement in dry concrete is minimal even if areas of different potential exist.

There are two ways that the protective oxide film that forms on steel reinforcement in sound concrete might be destroyed. These are the reduction of the pH of the concrete by carbonation, and the ingress of chloride ions.

REDUCTION OF pH OF CONCRETE BY CARBONATION

In chloride-free concrete, corrosion will not take place unless the pH drops below 11. The hydrolysis of cement during the curing of concrete splits off calcium hydroxide from the calcium silicates creating an alkaline environment.

Atmospheric carbon dioxide can penetrate concrete and react with calcium hydroxide in the cement paste to form calcium carbonate and this reaction reduces the pH of the concrete to around 9.

Carbonation of concrete in the atmosphere is represented by the following simplified equation (Equation 3).

$$Ca(OH)_2 + CO_2 \xrightarrow{(H_2O)} CaCO_3 + H_2O \quad (3)$$
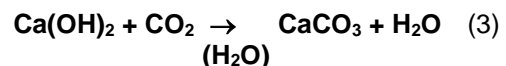
The hydrated calcium silicates in set Portland cement are stable only in contact with an alkaline solution, and if the alkalinity is destroyed by carbonation, they tend to decompose with the liberation of calcium hydroxide which in turn will react with carbon dioxide to form calcium carbonate.

The ingress of carbon dioxide will therefore eventually destroy the alkalinity in the concrete upon which the steel reinforcement depends on for prevention of corrosion.

Carbonation occurs progressively from the outside surface of the concrete exposed to atmospheric CO_2, but does so at a decreasing rate because the CO_2 has to diffuse through the pore system, including the already carbonated surface zone of concrete. If the pores of the hydrated cement paste are filled with water, the diffusion of CO_2 is further slowed because its diffusion through water is 4 orders of magnitude slower than in air.

Reference to Equation 3 shows that water is required for the reaction to proceed. If there is insufficient water in the pores, the CO_2 remains in gaseous form and does not react with the hydrated cement. The carbonation reaction is therefore dependent on the moisture content of the concrete, which varies with the distance from the surface. In practice it has been found that the highest rate of carbonation occurs at a relative humidity of between 50 and 70%.

Under steady hygrometric conditions, the depth of carbonation increases in proportion to the square root of time, as indicated by the following formula:

$$D = K\sqrt{t}$$

where

K = the carbonation coefficient that depends on the quality of the concrete, concentration of CO_2 and its diffusivity through the concrete.

t = exposure time

Carbonation reactions take place over a range of depths forming a carbonation front rather than a specific line. At a given point in time, the concrete would be completely carbonated to a certain depth (pH ~ 8.3) and partially carbonated further in (pH 8.3 to 12.5).

CHLORIDE INDUCED CORROSION

Chloride ions can break down the protective oxide film by a mechanism thought to be due to the chloride ion converting the insoluble gamma iron oxide to soluble iron chloride. For initiation of corrosion of reinforcing steel, chloride ions in the pore solution of the surrounding concrete must exceed a threshold concentration.

This threshold value is not a fixed value and is related to the alkalinity of the pore solution. Technical Note 57 *Durable Concrete Structures*

prepared by the Cement & Concrete Association of Australia, states that corrosion damage is likely to occur if the total chloride content is in excess of 0.4% by weight of cement (bwoc). The threshold level of chlorides for chloride-induced corrosion in prestressed beams is reported as being between 0.11 and 0.17% (bwoc).

AS 2758.1-1985, *Concrete Aggregates,* provided chloride limits of 0.1% (bwoc) for prestressed concrete, 0.2% for reinforced concrete in severe exposures, and 0.4% for mild exposures. The 1998 revision of this standard does not contain these thresholds.

In the USA, chloride contents up to 0.15% by weight of cement are not considered dangerous. Levels in the range 0.35 to 1% chloride ions by weight of cement are known to cause corrosion problems, especially if the concrete is moist enough to allow the flow of the corrosion cell currents.

A fuller discussion of chlorides in concrete is given in CTI Technical Note C2, "Chlorides in Concrete".

MECHANISMS OF CORROSION OF STEEL IN CONCRETE

From the above discussions, it is apparent that three conditions have to be present to allow significant corrosion of steel reinforcement in a concrete structure, namely:

(i)   disruption of the protective iron oxide film to form an anodic site

(ii)   a supply of oxygen to remove electrons remaining from the anodic reaction, and

(iii)   the concrete being conductive enough to allow corrosion currents to flow.

Disruption of the protective oxide film can be caused by the ingress of chloride ions and/or loss of alkalinity due to carbonation. Areas without the protective oxide film will corrode and the rate of corrosion in most cases will be governed either by the diffusion of oxygen to the cathode areas or the resistivity (dryness) of the concrete.

There are three broad types of corrosion experienced by reinforcing bars namely, **Pitting**, **General** and **Macro-cell** corrosion. The factors governing these types of corrosion are discussed below.

PITTING CORROSION

Pitting corrosion is most likely to occur in concrete with good conductivity, a high content of alkali (i.e. non-carbonated) and a moderate level of chloride (or chloride reaching only isolated areas of the reinforcement). The chloride ion breaks down the passive film locally in those areas where the concentration is high or the passive film is weak.

A localized corrosion cell is formed with adjacent areas of passive steel acting as a cathode, where oxygen is reduced, and the anodic dissolution of iron taking place only at the small central anode.

Several factors then maintain or aggravate the development of the existing pit rather than to spread the corrosion or nucleate new pits. Acid is produced at the anode (pit site) due to hydrolysis reactions and alkali at the cathode due to the reduction of oxygen. Under the acid conditions present, the corrosion products formed are soluble. Therefore, considerable amounts of corrosion can occur without spalling of the concrete.

In pitting corrosion access of oxygen is the major factor in determining the total amount of corrosion. However, with the large cathode/anode area ratio, intense pitting can result even with limited oxygen supply.

GENERAL CORROSION

General corrosion may result from carbonation or due to the presence of large amounts of chlorides, so a large number of closely situated pits are formed. Both anodic and cathodic processes take place everywhere on the surface, and the pH shifts associated with each of these processes cancel each other.

This means that the anodic dissolution takes place in a near neutral or alkaline environment, where oxygen has access. The corrosion product, in this case, is solid rust, which occupies about 4 times the volume of the metal that has been corroded.

The build up of corrosion products on the steel reinforcing bars exerts tensile forces on the concrete cover resulting in cracking and spalling.

In practice, general corrosion caused by carbonation or by chlorides have different characteristics.
In cases, where carbonation has penetrated deeply, the concrete is likely to be rather permeable and semi-dry, and the rate of corrosion, once its starts, is probably controlled by the relatively high resistivity and lack of water rather than the diffusion of oxygen. The 'time-of-wetness', known to be an important factor in atmospheric corrosion, is an appropriate measure of corrosion rate under these conditions.

Conversely, corrosion in chloride-rich concrete is more often found where water is abundant and resistivity of the concrete is low. Under these conditions the diffusion of oxygen through the water-filled pores is the rate determining factor.

MACRO-CELL CORROSION

Under certain conditions, it is possible for the anodic and cathodic sites to be significantly remote from each other so that the reaction products from the anode and cathode reactions do not interact.

Such conditions can exist if some of the steel is in anaerobic conditions and if the concrete is sufficiently conductive (ie. low resistivity, 12 kΩcm or less) to carry the macro-cell corrosion current. Typically this occurs in a concrete member with its lower parts permanently immersed in sea-water and extending upwards through the tidal and splash zones. This may include bridge and wharf piles, and skirting panels for wharves or promenades.

Under conditions of macro-cell corrosion, the cathode reaction (Eqn 2) occurs in the oxygen-rich tidal or splash zones, with no noticeable effect on the concrete.

The steel, however, dissolves at the anode (Eqn 1) which will be the immersed lower part of the member, saturated with sea-water but with little or no available oxygen. The ferrous ions react with anions present in sea-water (chlorides, sulphates, hydroxides) to produce ionic compounds which form a sticky black/green colloidal paste within the concrete, often referred to as "black rust".

Since this is not an expansive reaction, the colloidal corrosion products will opportunistically occupy available spaces such as voids and pores, or fracture planes if cracking is present from other causes. The colloid can slowly migrate to the surface where, if oxygen is more abundant, it may form conventional brown/orange rust stains, or it may simply be lost in the sea-water.

Since there are few outward signs of this mechanism, and although this process is generally slow, significant loss of metal can occur over time with subsequent loss of structural integrity and possible sudden, catastrophic failure. Even concrete of high quality and density can corrode by this mechanism.

Table 1   Practical Galvanic Series
(From NACE)

Practical values of half-cell potentials in neutral soils or water, with respect to $Cu/CuSO_4$ reference electrode.

Metal	Potential (volts)
Magnesium (Commercially Pure)	-1.175
Magnesium (6% Al, 3% Zn, 0.15% Mn)	-1.6
Zinc	-1.1
Aluminium Alloy (5% Zn)	-1.05
Aluminium (Commercially Pure)	-0.8
Mild Steel (clean and shiny)	-0.5 to -0.8
Mild Steel (Rusted)	-0.2 to -0.5
Cast Iron (not graphitised)	-0.5
Lead	-0.5
Mild Steel in Concrete	-0.2
Copper, Brass, Bronze	-0.2
High silicon cast iron	-0.2
Mill scale on steel	-0.2
Carbon, graphite, coke	+0.3

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