DURABILITY OF CONCRETE STRUCTURES

CHAPTER - 2

Mechanism Of Corrosion

2.1 Steel is used in concrete principally as reinforcement. Concrete ordinarily provide an almost ideal environment for protecting steel from corrosion. Its high alkalinity causes the formation of a thin invisible protective passive film of Ferric Oxide (Fe_2O_3) on the steel (thickness approx. 10000 A^0). It is expected that when the embedded steel is protected from air by an adequate thick cover of low permeability concrete, the corrosion of steel would not arise. This expectation is not fully met in practice, as is evident from the unusually high frequency with which the RCC & PSC structures suffer damage due to steel corrosion. The magnitude of damage is especially large in structures exposed to marine environments. The damage to concrete, resulting from corrosion of embedded steel, manifests in the form of expansion, cracking and eventually spalling of the cover concrete.

2.2 Mechanisms Involved in Concrete Deterioration by Corrosion of Embedded Steel

2.2.1 Corrosion of steel in concrete is an electrochemical process. The electrochemical potentials, to form the corrosion cells, may be generated in two ways:

(i) Concentration cells may be formed due to differences in concentration of dissolved ions in the vicinity of steel, such as, chlorides and oxygen.

(ii) Composition cells may be formed when two dissimilar metals are embedded in concrete, such as steel rebars and aluminum conduit pipes, or when significant variations exist in surface characteristics of the steel.

2.2.2 As a result, one of the two metals (or some part of the metal when only one metal is present) becomes anodic and the other cathodic. The fundamental chemical changes occurring at the anodic and cathodic areas are as follows:

At anode surface $\qquad$ $Fe \rightarrow 2e^- + Fe^{2+}$
(metallic iron)

At cathode surface $\qquad$ $1/2\, O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$
(air)   (water)

At anode $\qquad$ $Fe^{++} + 2(OH)^- \rightarrow FeO.(H_2O)\, x\ (rust)$
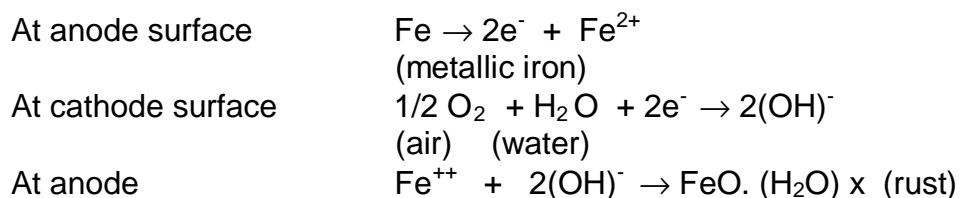
Fig 2.1 illustrate the electro- chemical process of steel corrosion in moist and permeable concrete. The galvanic cell constitutes an anode process and a cathode process.
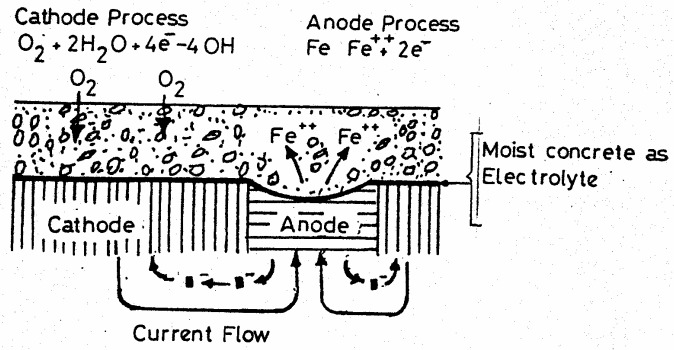
Cathode Process
$O_2^- + 2H_2O + 4e^- - 4\,OH$

Anode Process
$Fe\ Fe^{++} 2e^-$

O_2 O_2

Moist concrete as Electrolyte

Cathode   Anode

Current Flow

Fig. 2.1 : ELECTROCHEMICAL PROCESS OF STEEL CORROSION

Fe

FeO

Fe_3O_4

Fe_2O_3

$Fe(OH)_2$

$Fe(OH)_3$

$Fe(OH)_3\ 3H_2O$
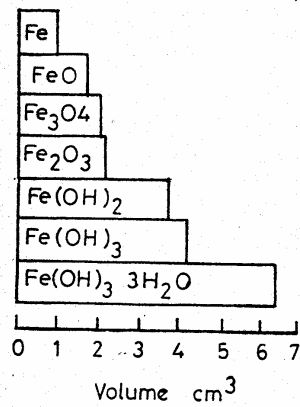
0 1 2 3 4 5 6 7

Volume cm^3

Fig. 2.2 : INCREASE IN VOLUME OF GROSS DUE TO OXIDATION

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2.2.3 The transformation of metallic iron to rust is accompanied by an increase in volume, which depending on the state of oxidation, may be as large as 600 % of the original metal as shown in fig. 2.2. This volume increase is believed to be the principal cause of concrete expansion and cracking. It should be noted that the anodic reaction involving ionization of metallic iron will not progress far unless the electron flow to the cathode is maintained by consumption of the electrons at the cathode; for this the presence of both air and water at the surface of the cathode is absolutely necessary. Also, ordinary iron and steel products are covered by a thin iron-oxide film which becomes impermeable and strongly adherent to the steel surface in alkaline environments, thus making the steel passive to corrosion ; that is, metallic iron will not be available for the anodic reaction until the passivity of steel is destroyed.

2.2.4 The anode process cannot occur until the protective or the passive iron oxide film is either removed in an acidic environment (e.g., carbonation of concrete) or made permeable by the action of Cl^- ions. The cathode process can not occur until a sufficient supply of oxygen and water is available at the steel surface. The electrical resistivity of concrete is also reduced in the presence of moisture and salts.

2.2.5 Carbonation The Carbon-di-oxide gas present in the atmosphere combines with hydrated concrete (alkaline hydroxides) and partly neutralize the alkaline nature of concrete. This process is known as carbonation. Carbonation brings down the pH value of concrete from above 12-13 to less than 9. When depth of carbonation increases and becomes equal or more than the depth of cover of reinforcement, it breaks down passive film surrounding steel and make steel embedded in concrete more active.

2.2.6 Chloride attack Free chloride ions present in concrete, surrounding reinforcement, react with alkaline solution at anode to form hydrochloric acid which destroys the passive protective layer on the reinforcement steel. The surface of steel then becomes activated locally to form the anode, with the passive surface forming the cathode, setting the electrolytic process. Presence of free chloride ions in concrete depends upon total chloride contents of concrete. Chlorides are present in concrete due to ingredients, mixing water and calcium chloride used as accelerating admixtures etc. Chlorides enter concrete due to salt water spray in sea shore or through atmosphere.

2.2.7 In the absence of chloride ions in the solution, the protective film on steel is reported to be stable as long as the pH of the solution stays above 11.5. Since normally hydrated Portland cements contain alkalis approximately 20 percent by weight in the pore fluid, normally there is sufficient alkalinity in the system to maintain the pH above 12. In exceptional conditions (e.g., when concrete has high permeability and alkalis and most of the hydroxide are either carbonated or neutralized

by an acidic solution), the pH of concrete in the vicinity of steel may be reduced to less than 11.5 , thus, destroying the passivity of steel and setting the stage for the corrosion process.

2.2.8 In the presence of chloride ions, depending on the Cl^- / OH^- ratio, it is reported that the protective film may be destroyed even at pH values considerably above 11.5. When Cl^- / OH^- molecular ratio is higher than 0.6, steel seems to be no longer protected against corrosion, probably because the iron oxide film becomes either permeable or unstable under these conditions. Further more, when large amounts of chloride are present, concrete tends to hold more moisture, which also increases the risk of steel corrosion by lowering the electrical resistivity of concrete. Once the passivity of the embedded steel is destroyed, it is the electrical resistivity and the availability of oxygen that control the rate of corrosion. In fact, significant corrosion is not observed as long as the electrical resistivity of concrete is above 50 to 70 x 10^3 Ω cm. It should be noted that the common sources of chloride in concrete are ingredients, admixtures, penetration of sea water and atmospheric gases.

2.2.9 Due to similar mechanism bimettalic contact increases the risk of corrosion of steel. Thus, bimettalic contact needs to be avoided as far as possible. If, it is unavoidable like in case of buildings, approval should be taken prior to execution of work.