Chapter - 1

INTRODUCTION
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1.1 Corrosion as a phenomenon

Mild steel is an alloy of iron, carbon and various additives, all in their elemental forms. The chemistry of iron dictates that the elemental form is not the most thermodynamically stable and that iron tends towards oxidized forms (i.e., tends to revert back to the native ore). Thus in the presence of water (seawater, moisture layers, etc) the iron in steel will oxidize by the process of corrosion.

The electrochemical nature of corrosion may be described in terms of a simple corrosion cell. The essential components of this cell are an anode, a cathode, an electrolyte, and an electronic connection between the two electrodes. The behavior of corroding metal implies the formation of electrolytic cell and consequent current flow and existence of potential difference between local anodic and cathodic sites. The potential drop across the electrical double layer, namely, metal and the solution is known as the electrode potential. In a corrosion couple, the electrode potential is always lower at a local anode than at a cathode. The quantum difference will vary depending upon the spacing of anodes and cathodes and the resistance of the separating medium.

The corroding metal in aqueous medium functions as a mixed electrode on which anodic and cathodic sites are formed and corresponding reactions take place. Corrosion or metal dissolution occurs at anodic sites where the metallic ions released into solution and the free electrons making the reduction process at the cathodic sites.
For the case of iron in aerated water, the anodes and cathodes are generally adjacent metallic grains of differing electrochemical potentials.

The anode is a site for oxidation and for iron the initial reaction is:

\[ \text{Fe(s)} \rightarrow \text{Fe}^{2+} \text{(aq)} + 2e^- \]

The corresponding cathodic reaction is usually the reduction of oxygen, i.e.

\[ \text{O}_2(g) + \text{H}_2\text{O (l)} + 2e^- \rightarrow 2\text{OH}^- \text{(aq)} \]

Under certain conditions, hydrogen reduction occurs, i.e.:

\[ 2\text{H}^+ \text{(aq)} + 2e^- \rightarrow \text{H}_2(g) \]

The electrons liberated at the anode flow through the electronic connection to the cathode where they are consumed. Thus all that is required for the continued aqueous corrosion of iron is a supply of oxygen.

The electrochemical potential of the iron itself governs the nature of the corrosion reaction. The potential is basically a measurement of the degree of interaction between the metal and the environment expressed in terms of electrical / chemical energy.

Consider again the simple oxidation of iron:

\[ \text{Fe(s)} \rightarrow \text{Fe}^{2+} + 2e^- \]

The liberation of electrons during the above process provides the Electrochemical Potential of the corrosion reaction.
1.1.1 pH Effects

The typical cathodic reactions presented indicate a second fundamental parameter governing the corrosion process. This parameter is the pH of the aqueous solution:

\[ \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow 2\text{OH}^- \text{(aq)} \]

\[ 2\text{H}^+ \text{(aq)} + 2\text{e}^- \rightarrow \text{H}_2 \text{(g)} \]

The hydrogen ion and the hydroxide ion are the two species, which will describe the actual solution pH.

Water exists in equilibrium with its dissociation products:

\[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \]

such that

\[ -\log [\text{H}^+] = \text{pH} \]

where \([\text{H}^+]\) = concentration of hydrogen ion (Mol dm\(^{-3}\))

Therefore the pH will have an effect on both cathodic reactions as it governs the quantity of the two species in question, which may be present[1].

1.2 Corrosion of steel in concrete structures

Reinforced and prestressed concrete undergo rapid deterioration, when exposed to aggressive marine and industrial environment. The reduction in durability which is mainly due to the corrosion of reinforcing and prestressing steels have been established as the main cause of deterioration of concrete structure. A number of individual cases exist, however principle agents for
premature deterioration are chloride ion contamination, carbonation of the concrete, prior construction practice, lack of cover, etc.

Corrosion of mild steel reinforcement in concrete has been identified as the main cause of deterioration of concrete structures. Various methods have been suggested to inhibit this corrosion process. Some of which have been successful. Concrete has a highly alkaline environment due to the presence of Ca(OH)$_2$ as the product of hydration. A well-hydrated Portland cement can contain 15-30% of Ca(OH)$_2$ by weight of the original cement [2]. Concrete structures made out of these materials are supposed to have long life requiring negligible maintenance. Protection to the embedded steel against the external environment was believed by the cover thickness and the quality and type of concrete.

The durability of concrete has been an important consideration in aggressive environments in spite of its other advantages like mould ability, low cost etc. The deterioration, in general, may be caused due to physical, chemical or mechanical actions. Particularly the constituents of the cement paste are susceptible to the sulphate ion in the aggressive environments like seawater. The sulphates chemically react with the hydrated C$_3$A (tricalcium aluminate) compounds present in concrete forming Ettringite [C$_3$A$_3$CS$_2$H]. The Ettringite formed in the pores may cause considerable expansion and even cracking. On the other hand, the calcium hydroxide liberated during the hydration of cement react with the sulphate solution to form gypsum [CSH$_2$]. This reaction is due to the acidic nature of sulphate solutions which contrary to the ettringite expansion cracking phenomena results in surface damage of the softening spalling type.

The use of inadequate material specifications and inappropriate construction practices further accentuates the problem. As a result of this aggressive environment, structures that were designed for a service life of 60 to 70 years exhibits science of deterioration with in 10 to 15 years. Reinforcement corrosion associated with cracking and spalling of concrete, are the most severe
form of concrete deterioration. According to the general accounting office of the U S, 162,622 U S bridge decks were damaged due to reinforcement corrosion as a result of the use of deicing salts on the highways in 1981 [3]. Numerous parking garages in cold countries, particularly the United States, have been seriously damaged by reinforcement corrosion [4], [5]. Premature deterioration of many buildings has also been reported due to the corrosive effects of chloride-based accelerating agents added to concrete during construction [6]. The relationship between the magnitude of reinforcement corrosion and the load carrying capacity of a structure has been established by the extent of corrosion.

A typical concrete mixture might consist of 1,420 kg of aggregate (stone and sand), 228 kg of cement, and 114 kg of water in each cubic meter of poured concrete [7]. The water serves as a vehicle for pouring the mixture, it is then partly consumed by the cement hydration reaction, which gives concrete its compressive strength. In hydration, or arising about half the water in the mix becomes part of the concrete. That leaves a roughly equal amount of free water in the pores of the material. Thus, a typical newly cured concrete would have a theoretical residual moisture content of about 3.5 wt % [8].

Principal source of CI⁻ was seawater spray or splash on the concrete. For the structures exposed to seawater are characterized by a sharp drop from the surface concentration of 0.44 to 0.57 wt% of concrete 0.24 to 0.26% at the level of reinforcement and a more gradual decrease to the base level of 0.21 to 0.24% starting at a depth of about 180 mm.

Wind blown marine salts were also a contributor to the presence of CI⁻ in the concrete. In general, the concentration of marine salts in the atmosphere is high about 5 mg/ m³ [9].

If chloride ions are present in the reinforcement zone, protection may be triggered even at higher pH values, the precise value depending on the chloride concentration of this zone. The critical value for corrosion to occur is related to
the chloride hydroxyl ion concentration ratio. Hausmann has shown that when this ratio is higher than 0.6, corrosion of the rebar is possible [10]

The higher the chloride ion concentration, the greater is the probability of corrosion. To predict the probability of corrosion, it is necessary to know the chloride concentration in the concrete next to the reinforcement and the position of the concentration front relative to it [11]

Chlorides penetrate hardened concrete exposed to marine spray, when they reach the rebar, corrosion occurs with a progressive accumulation of rust. The build-up of corrosion products which being more voluminous than the embedded metal, introduce significant tensile and compressive loads on the concrete leading to cracking, disbondment and ultimately, spalling of the concrete cover. Cracking and disbondment leads to further corrosion, which can compromise the life of the entire structure. The problem involves reinforced concrete structures such as bridge decks, parking garages, and certain concrete buildings.

1.2.1 Permeability and reactant transport

The single most important factor influencing the corrosion of steel in concrete, is the inherent heterogeneity of the concrete matrix. Concrete generally consists of aggregate particles of varying size and chemical composition incorporated within a matrix of hydrated Portland cement paste. The cement itself is a composite mixture of bi- and tri-calcium silicates, together with tri-calcium aluminates and an iron-containing phase whose composition approximates to tetra-calcium aluminoferrite. The calcium silicate reacts with the mixing water to form calcium silicate hydrate which undergoes a condensation reaction to yield higher polymeric forms with more ordered structures. The conglomerate of different structures, even under ideal mixing and compaction conditions, forms a composite of areas of differing permeability and resistivity with many interfaces at which these areas adjoin.
This situation will produce preferred pathways for water migration and electrolytic current flow. This will create a large number of localized corrosion cells whose area of influence will be determined by the resistivity of the concrete matrix.

Apart from the heterogeneity's inherent in the nature of the material used, are those introduced on a macro scale by conditions prevailing during construction and the construction methods adopted. These may produce cracking, areas of poor compaction, and the introduction of impurities, etc., all of which will produce further heterogeneity's in the concrete.

The most serious heterogeneity in concrete, from the point of view of corrosion, is the varying degree of permeability of the concrete cover along any given length of steel reinforcement. This allows atmospheric ingress to occur at different rates, thereby causing differential aeration cells to occur.

The rate of oxygen transfer through cements has been found to vary with water/cement ratio and depth of cover, with lower water/cement ratios and greater depths of cover giving reduced rates of oxygen transfer. Additionally, it has been shown that the rate of oxygen transfer through best quality concrete (low water/cement ratio) is significantly greater than through the worst quality cement paste alone. This demonstrates that oxygen travels preferentially either through the aggregate or along the cement paste/aggregate interfaces.

Where concrete is exposed to the atmosphere, it possesses an interfacial film approximately 1mm of laitance. The rate of transfer of oxygen through this film is an order of magnitude lower than the transfer rate through the bulk matrix.

1.2.2 Corrosion of steel reinforcement

Mild steel exposed to the atmosphere will rapidly corrode, with the formation of red rust. When mild steel is applied as the reinforcement in a
concrete structure, then theoretically it should be protected from corrosion due to the highly alkaline nature of concrete

Two major factors however, may drastically change this situation. These are carbonation and chloride ingress

### 1.2.2.1 Carbonation

Initial curing of concrete produces substantial amounts of calcium hydroxide as a by-product. This collects as a highly concentrated solution in cement micro pores, thus giving rise to the highly alkaline conditions

Mild steel in a highly alkaline medium (above pH 10) will naturally form a passive oxide film. This natural oxide film halts further corrosion of the steel rebar. Carbon dioxide (CO₂) in the atmosphere is subject to a slow hydrolysis process in which carbonic acid is produced, i.e.

\[
\text{CO}_2 + \text{H}_2\text{O} \rightarrow (\text{HCO}_3) + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3
\]

This natural atmospheric episode causes carbonic acid to be formed within the reinforced concrete structure. The carbonic acid will react with the calcium hydroxide in the concrete to produce calcium carbonate, this has the effect of decreasing the pH since calcium carbonate is less alkaline than calcium hydroxide

\[
\text{H}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O}
\]

From the Pourbaix Diagram [Fig 1.1] it can be seen that as this process continues the concrete pH drops less than pH 10[12]. In this pH the reinforcement brings down to unprotected regions causing the passive oxide film over the reinforcement to break down such that general corrosion becomes possible
A concurrent effect is the deterioration of the concrete itself due to acidification by the carbonic acid. Thus carbonation can cause corrosion and structural deterioration of the reinforced concrete.

![Potential pH diagram for steel in concrete](image)

**Fig. 1.1: Potential pH diagram for steel in concrete**

### 1.2.2.2 Chloride Ingress

The passive oxide film over reinforcement in fresh, unpolluted concrete occurs as a result of the various thermodynamic parameters in operation. Thus in order for corrosion to occur at the reinforcement surface, this passive oxide film must be broken down.
Chemically, there is an energy barrier to surmount in removing the passive oxide film. In alkaline condition, enough chemical energy cannot be provided to surmount the barrier mentioned, thus the rebar does not corrode.

However, chloride ions migrating into the concrete will catalyze the breakdown of passive oxide. This can be described as the energy barrier mentioned being much reduced in size, such that even though the concrete remains alkaline, corrosion reaction forces may now surmount the very small energy barrier and instigate pitting and eventually general corrosion.

Therefore the greatest danger to reinforcing steel in concrete lies in the ingress of chloride anions. The chlorides in the salt dissolve readily in water and the resultant solution penetrates into the porous concrete matrix. The high ionic mobility of the chloride ions has the effect of markedly reducing the electrolytic resistivity of the pore solution. However, it is the interaction of these ions upon the passivated steel structure, which causes the most serious problems.

Steel in contact with calcium hydroxide solution with a pH of 12.5, as is found in concrete [13], develops a protective film of Fe$_2$O$_3$ which passivates the metal [14]. The chloride ion from deicing salts or sea water contaminates the concrete and initiates the corrosion reaction by destroying the protective film. The corrosion reaction involving reinforcing steel in chloride-contaminated concrete is an electrochemical cell believed to consist of the following:

**Anodic reaction**

\[
\text{Fe} + 2\text{Cl}^- \rightarrow \text{Fe}^{2+} + 2\text{Cl}^- + 2e^-
\]

Followed by

\[
\text{Fe (Cl)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe (OH)}_2 + 2\text{H}^+ + 2\text{Cl}^-
\]
With oxygen present, a secondary reaction occurs at the anode

$$6(\text{Fe}^{2+} + 2 \text{Cl}^{-}) + \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_3\text{O}_4 + 12 \text{H}^{+} + 12 \text{Cl}^{-}$$

Cathodic reaction

$$\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2 \text{e}^{-} \rightarrow 2 \text{OH}^{-}$$

Thus the role of the Cl\(^{-}\) is to promote corrosion at the anode; it is then released for reuse and therefore, the corrosion reaction in concrete bridge decks is an oxygen diffusion limited system. That is the reaction can occur only as fast as oxygen can be supplied to the cathode [15].

Under standard conditions, a passive film consists of a dynamic equilibrium between chemical dissolution of the oxide and its repair at defect sites. These sites are anodic with respect to the bulk of the film and consequently ions migrate to them under the influence of the electric field where they react and form the anodic product Fe(OH)\(_2\). This further reacts to form the passivating oxide layer.

When chloride ions are present, these are also attracted to the anode sites but the anodic product remains Fe(OH)\(_2\). Thus the chloride concentration at the anode increased until the pH has reached sufficiently low value adjacent to the iron surface for the ferrous hydroxide to be soluble. Thus Fe(OH)\(_2\) precipitation occurs at a point remote from the anode.

To make matters worse, the chloride ion has a catalytic effect on the dissolution of Fe(OH)\(_2\) from the passive film. To end result of these two effects is that the steel reinforcement is now covered by a non-protective, defect film.

A further disadvantage of chloride ions is their effect upon relative humidity. The value of relative humidity above which condensation occurs in the presence of sodium chloride is 76%. Thus the inclusion of chlorides into a
Concrete structure will result in the attraction of moisture to the concrete and the subsequent retention of this water by the structure.

The chloride ion does not actually alter the mechanism of iron corrosion in any appreciable manner but it does significantly affect the rate of reaction. The end products of the rusting process vary from $\text{Fe}_3\text{O}_4$ to $\text{FeO OH}$ (dependent upon the oxygen availability) but the crystallographic allotrope of $\text{FeO OH}$ formed is affected by the presence of chloride ions. The levels of chloride required to initiate corrosion are extremely low.

1.2.3 Structural Deterioration

Given that corrosion continues unchecked by either of the two mechanisms described above then the eventual result is complete dissolution of the reinforcement. Thus the concrete is no longer a reinforced structure and in regions where tensile forces act, may fail causing structural collapse.

1.2.4 Effects of corrosion on reinforced concrete

Reinforced concrete is a composite material. With the steel reinforcement in intimate contact with the bulk concrete, the structural properties of both materials are improved, in those undesirable properties for example, brittleness of the concrete, plastic deformation of the steel under load are largely eliminated.

If the concrete and the steel become detached, then the value of reinforced concrete as a composite material is largely undermined.

1.2.5 Cracking

The corrosion products of steel are two to twelve times the volume of the original steel. Therefore since the original steel was in intimate contact with the concrete, then on formation of corrosion products, enormous pressures are exerted outwards on the concrete [Fig 1 2]. The direction of this pressure and
the brittle nature of concrete results in the surface concrete layer becoming cracked, since it does not have the benefit of the internal reinforcement for protection.

Stage 1: Corrosion initiation by Chloride ingress

Stage 2: Creation of pressure and cracking due to accumulation of corrosion product

Stage 3: Spalling of concrete

Fig. 1.2: Sequence of corrosion of steel in concrete

1.2.6 Delamination

As corrosion of reinforcement continues, the concrete surface layer as a whole begins to be pushed away from the reinforcement. This expansive reaction leads to the delamination of the surface concrete. At this point, major damage to the structure is present.

1.2.7 Spalling

As delamination continues unchecked, external effects will cause regions of the delaminated 'floating' surface concrete to be removed.
For example, this can be caused by vehicles passing over a deck surface or even the natural thermal expansion / contraction cycle occurring throughout a day.

The most serious case is in overhanging concrete regions, such as ceilings, where the weight of the delaminated concrete provides enough force for the concrete to fall away. Clearly this constitutes a serious safety hazard.

### 1.2.8 Loss of Structural Strength

As deterioration of the reinforced concrete continues, reinforcement steel is lost and the concrete itself deteriorates. Therefore structural properties of reinforced concrete, such as strength, may be seriously undermined such that the ability of the reinforced concrete to function as a composite material may become seriously compromised.

From the descriptions of early and intermediate stage damage due to corrosion given in this section, it is clear that the inevitable result will be structural failure. This aspect is of most concern in critical load bearing structures.

The structural quality of reinforced concrete is undermined by long-term corrosion of the reinforcement. The point in time when the degraded material can no longer support its design load is unpredictable. Therefore time to failure and therefore collapse of the structure is not known. This point implies that rehabilitation methods need to be employed soon after very early stages of corrosion damage are discovered.

Some of the remedial measures for controlling corrosion of the embedded steel include application of protective coatings and inhibitors on the surface of the embedded steel bars [16]. Many conflicting findings have been reported in the literature on the performance of galvanized embedded bars in a marine environment [17], where as cadmium is reported to be unaffected under high chloride concentrations [18]. Corrosion inhibitors are not widely used in marine
RCC structures, however it is reported that sodium nitrite is being used in Europe [19] for this purpose. Though the development of polymers in other branch of engineering is in vogue for more than a century, their advent in construction has been since 1950. Their utility in construction and maintenance is becoming inevitable [20]

1.3 Use of polymers in concrete construction

Polymer is a substance that is composed of thousands of simple molecules combined into giant molecules. The simple molecules are called monomers, and the reaction that combines them into polymer is termed as polymerization. The polymer can be in a liquid or a powder form. Polymers are introduced in concrete by modification made properly, can improve properties of the fresh and hardened concrete. Such properties are, workability and finishability, cohesion, bleeding and segregation, strength especially flexural and tensile, bond, abrasion resistance, impermeability, physical and chemical durability.

Improvement of properties of concrete by the use of Polymer Concrete and Polymer Portland Cement Concrete has been under consideration for many years. Polymer Impregnated Concrete development on a large scale was undertaken in 1966 as a joint effort between the Bureau of Reclamation and Brookhaven National Laboratory. Such work produced very large improvements in both structural and durability properties of concrete and provided the impetus for the widespread worldwide developments and use of polymers in concrete has come and established [21].

The advantages of polymer Concretes make these materials very attractive building materials and much research concerning them has been carried out recently throughout the world. Thermal incompatibility of most polymer based binders and aggregate must be taken into account before effecting any formulation.
In such cases, the great compressive and tensile strength of many polymers eliminates binder as the cause of deterioration of composite material. The tensile strength of aggregate is rather small, in many cases 1/20 to 1/40 of its compressive strength. For example, for cured epoxies, which promise to be very useful binders for polymer concretes, [22,23] Polyesters are considered recently as prospective binders for polymer concretes [24,25]. Other physical properties of polymers, such as very low modulus of elasticity, lessen the negative influence of thermal incompatibility of polymer binders and aggregate. Polymer modified concretes and mortars have been used successfully in various applications, such as construction of bridge decks, industrial and carriage floors, and pavements. They are also suitable for overlays and other repair and rehabilitation of concrete, floors, pavements and other structures [26].

The main objectives of the polymers in concrete are

a. To improve the mechanical properties of cement concrete such as compressive and tensile strengths, impact toughness etc

b. To impart more chemical, freeze–thaw and corrosion resistance

c. To provide more water proof ness, adhesion, thermal insulation, light weight, abrasion and acid resistance

Polymers are used in different forms such as polymer impregnated concrete, resin concrete, polymer admixed concrete, bonding layer for bonding old to new concrete, polymer mortar and as protective coatings for steel and concrete surfaces.
1.4 Corrosion protective measures in concrete

1.4.1 Construction Practice

The concrete should be adequately workable for achieving sufficient compaction especially in closely spaced reinforcement locations. Adequate moisture curing is a key to achieving good impermeable concrete cover. The required period of curing increases with increasing percentage of pozzolanic materials, decreasing cement content, decreasing environmental humidity and increasing aggressivity of environment. Depending on these parameters, the period of curing may vary from 2 to 14 days.

The decisive parameters with regard to corrosion of steel in concrete are the percentage of free chlorides in pore water, related to the percentage of inhibitive ions, especially (OH) ions. For reinforced concrete a limiting value of 0.4% chloride by weight of cement normally is a good criterion for minimizing the incipient danger of corrosion.

1.4.2 Protective Coatings

Following methods control corrosion of the embedded steel in concrete:

1. By applying protective coatings on the embedded steel surface

2. By applying protective coatings on the concrete
1.4.2.1 Corrosion control by protective coatings on embedded steel

Considerations to be made in selecting an optimum coating system on the embedded steel are as follows

1. The first and the foremost is the durability of the coating against the aggressive chloride ions

2. The degree of surface preparation required providing adequate bond to the steel

3. The coating must withstand mechanical bending and abrasion

4. The coating should dry/cure rapidly

The majority of protective systems provided on the embedded steel are grouped under two categories. They are

- Organic coatings
- Metallic coatings

1.4.2.2 Organic coatings

After many years of use of different organic coating systems on reinforcement, electrostatically applied powdered epoxy coatings have in practice for rebar coating. Adequate care needs to be taken while handling and using epoxy coated rebar’s in construction as a slight damage or local defect in coating may prove to be detrimental in the long run.
1.4.2.3 Metallic coatings

The most common metallic coating would be galvanized zinc coating. But studies indicate that under conditions in which chloride ions are present around the embedded steel, substantial corrosion of zinc occurs. Zinc is passive in pH range of 9 to 11 due to Zn(OH)$_2$ film. In presence of chloride ions, passivation of zinc is adversely affected.

The corrosion rates for zinc do not vary appreciably whether the coats are applied by hot dipping, spraying, etc. Element silicon is known to promote formation of intermetallic compound of iron and zinc.

When the laid concrete is still green, a chemical reaction between zinc and alkaline constituent of concrete will occur. This results in liberation of hydrogen gas and formation of corrosion products on the surface of zinc. The results in loss of bond strength and increases the permeability of the surroundings concrete. This is overcome by chromate treatment to the surface of the zinc coating prior to placing in contact with green concrete.

Cadmium coatings are usually applied by electroplating in cyanide solution. Cadmium reacts with seawater and forms black insoluble cadmium chloride film. The disadvantages of the cadmium coating are its high cost and relatively less sacrificial action compared with zinc.

Inorganic coating systems based on inhibited sealed cement slurry and alkali silicate have been considered for rebar coating. These systems have multifarious sequential operations and hence are laborious and time consuming.

1.4.2.4 Coating on concrete surface

Coatings or impregnation on concrete reduce the chloride ion penetration, gas penetration (to decrease carbonation) or water penetration. Coatings consist...
of continuous film applied on the concrete surface with a thickness in the range of 100 to 300 micrometer. The coatings in the liquid form are sprayed or brushed on the concrete surface. Different coatings/sealing materials are based on Acrylic copolymers, Styrene Butadiene, chlorinated rubber, epoxy resins, polyester resins, polyurethane, vinyl etc. The other types of materials used for treating the concrete surface are pore liners, which impregnate in the concrete pores and line them with water repellent materials. Materials used in this category as hydrophobic liner are silicones, siloxanes and silanes. The third category of sealers is pore blockers, which penetrate into the pores and then react with calcium hydroxide and block the pores. The materials available in this category are liquid silicates and silicofluoride.

1.4.3 Alloy Steel Reinforcement

In most of the investigations on rebar corrosion to date the influence of the steel properties have seldom been considered. Some of the primary factors effecting the rebar corrosion include the type of steel reinforcement (mild steel, high strength deformed bars both cold) twisted and hot rolled, alloy steel, TISCON and metallurgical composition and surface condition. It is probably essential also to consider the effects of mechanical working on the steel during reinforcement cage fabrication leading to additional stresses at specific location apart from welding.

The steel reinforcements bars bearing Cu-W(Copper and WO$_2^+$) developed by Koichi Kishitani et al [27] showed good performance against corrosion. It showed the tendency to delay the occurrence and the growth of concrete cleavage (Spalling) caused by the expansion force of the corrosion products of the embedded reinforcing bars much more than the ordinary steel bars. But investigation by Gjory and Vennesland [28] revealed that the austenitic stainless steel is superior to that of medium carbon steel. Further the experiments conducted by the above investigations also show that the increasing silicon contents in the stainless steel from 0.6 to 3.38 percent distinctly
improvement in the corrosion properties. While corresponding additions of silicon to the carbon steel reduced the corrosion properties, substantially. It was reported that even small variations in the chemical composition of the steel did distinctly affect the breakdown potential of the steel. Hence the above investigations can be noted that the chemical composition of the steel assumes a greater importance in the rebar corrosion studies. It is found that austenitic stainless steels have a very high resistance in concrete containing up to 30% chloride by weight of cement.

1.4.4 Mineral Admixture as Corrosion Inhibitors

The use of fly ash to replace cement is known to have beneficial effect on inhibiting sulphate attack, alkali aggregate reaction, reducing heat of hydration and increasing denseness. However, more data need to be evolved for studying its role in long-term corrosion resistance characteristics of reinforced concrete, especially in view of the concern expressed by some users about the possible negative effect of fly ash addition on corrosion resistance of reinforced concrete.[29]

1.4.5 Cathodic protection

Corrosion of steel in concrete structures is a costly ongoing problem that can be mitigated with cathodic protection.

Cathodic protection is designed as the reduction or elimination by making the potential of the steel more negative, i.e., the potential of the metal is lowered from active corrosion potentials to immunity or passivity potentials. In this way all anodic or corroding areas of the metal are made cathodic, thereby stopping the corrosion process. When the cathodic protection system is energized, the oxygen reaching the steel surface is reduced to hydroxyl ions and the alkalinity generated restores the passive film on the metal. As a consequence of the
current flow, chloride ions are removed from the steel surface, thus eliminating one of the main mechanisms of corrosion [30].

Cathodic protection is achieved by generating a direct current flow from an anode through an electrolyte to the metal (which acts as a cathode) using of an external DC current source (impressed current systems) or connecting the steel to a zinc, magnesium, or aluminum anode (sacrificial anode system). The potential at which the corrosion rate becomes negligible is the protection potential. In the case of steel in concrete, the situation is more complex. Among many values proposed (-0.85 V for some authors –0.77 V for others) [31-35] the protection potential shall be selected such that the reinforcement bars may be maintained in the perfect passive region.

For concrete structures exposed to the atmosphere the high resistivity of the concrete and the low driving voltage available makes a sacrificial anode system generally inadequate to obtain sufficient current flow to make all areas of the reinforcing steel cathodic.

Further more, some sacrificial anodes (e.g. aluminum) have been demonstrated to be in appropriate, because their voluminous corrosion products break the surrounding concrete. Although zinc has been applied as a sacrificial anode for cathodic protection of bridge decks [36] impressed current systems are the most common for cathodic protection in concrete.

### 1.5 Coating options for corrosion protective systems

To prevent the oxidation of mild steel reinforcement, a surface coating capable of interacting / nullifying the released electron should be provided. Further the steels during service are exposed to an alkaline medium and this necessitates additional measures by way of topcoat, which should be compatible to concrete. Suitability of the protective coating system is to be established.
1.5.1 Electro static powder coating

Among organic protective coatings, epoxy coatings were reported to perform satisfactorily as the long term reliable protective coatings on embedded bars under the direct intrusion of sea water [37]. Over the past 20 years, fusion bonded epoxy coated bars have been widely used in the USA and other countries because of its barrier protection. However recent evaluation studies have indicated that this coating may not give satisfactory protection under certain conditions of exposure [38]. Studies have been made in aqueous as well as in concrete environments. Coating disbondment has been observed in many test solutions particularly in the presence of chlorides. Studies carried out by Sagues showed that epoxy coating can undergo considerable pitting corrosion under polarized condition. Patch repaired work may not prove to be effective under all conditions. Vibrating equipment used during concrete compaction may introduce considerable damage in the coating. Even the smallest damage in the coating can initiate corrosion in the severe environment.

1.5.2 Metallic coating

Initially in the US and UK galvanized rebar's were advocated because of the sacrificial protection if offered [39]. However zinc was found to have lower tolerance towards chloride, and its durability was related to the critical alkaline content in cement [40-42]. Sacrificial protection to steel can be made by a range of metal coatings but in respect of rebar's, the use of zinc is widely accepted. Zinc coating can be applied in hot-dip galvanizing, zinc spraying or electrolytic coating. Of these, hot dip galvanizing has gained most widespread use for reinforcing bar. Zinc coating may protect the steel cathodically in the region of small defects of the coating but if zinc coated bar is in contact with uncoated bars, the corrosion rate of zinc locally can be very high.
1.5.3 Inorganic coating

In India, an inhibited and sealed cement slurry coating has been widely used over the past 15 years because of its cost effectiveness and feasibility at the work site [43]. Though it has a desirable minimum durability factor of 25 under accelerated corrosion condition, the process is labor intensive and tedious and can be done only at site. Mechanization of the coating system could not be achieved mainly because of the longer setting time (10 hrs) of cement. This system cannot be applied prior to the cutting and bending operations of rebar, as it cannot withstand plastic yielding through bending of the bars [44].

1.5.4 Thermoplastic powder coatings

Thermoplastic powder coatings have been recommended for coating prefabricated reinforcement bar structures [45]. Typically, the coatings are based on polyolefin resins. Because they are thermoplastic, it is claimed that they are less prone to cracking in service and that bonding, not only to the bars themselves but also to the poured and set concrete, is good.

1.5.5 Liquid protective coatings for reinforcement bars

Reports are also available in which asphalt, chlorinated rubber and vinyl paints have been tried as organic protective coatings on the embedded rebars [46].

Polyvinylbutryal-based coated reinforcement bar (PVBCR). Polyvinylbutryal is a permeable film-forming resin which, when applied to reinforcement bars in concrete structures, still allows the concrete to passivate the steel. Coatings based on this resin have been used in the Middle East, Africa and the Caribbean for twenty years [47].

The PVB-based coating is applied relatively thin and, as a consequence, bonds well to the concrete. Formulations usually contain an anticorrosive...
pigment to improve corrosion protection at points of mechanical damage. To date, no major problems have been reported openly with this coating in service.

### 1.5.5.1 Polyurethane coating for reinforcement bars

Two-pack urethane-acrylic coatings have been developed successfully in India for this application [48]. Formulations are pigmented and contain, inter alia, small amounts of Zinc phosphate and sand. It is claimed that the sand helps the subsequently, applied concrete to bond more firmly. Typical dry film thickness is 80 micrometers, applied in two coats with forced curing at 60°C.

It is also claimed that the tough film stands up well to rough handling on site.

### 1.5.5.2 Water-borne coating for reinforcement bars

Water-borne coatings have been proposed as maintenance coatings for reinforcement bars [49]. Application for two coats after careful and thorough surface preparation is advised. The second coat is usually applied before the first coat has hardened fully. An overcoating interval between 30 and 90 minutes is the norm.

Commercial disclosure on the coating itself has been limited but it is known that one formulation is based on styrene-acrylic latex pigmented with Portland cement, carefully graded filler, and reinforcement fibers.

### 1.5.5.3 Inorganic Silicate – based coating for reinforcement bars

In the US, workers at the University of South Florida have developed a protective coating for reinforcement bars based on alkali silicate binders [50]. The development has been patented. The coating is formulated from a proprietary mixture of inorganic alkali silicates and cross-linked with a novel compound. Freshly blast cleaned reinforcement bars are coated. Heated to approximately 200°C for a short time, and then allowed to cool. The resulting
cured coating is typically 0.1 mm in thickness. It is claimed that concrete, poured over the coated bars in subsequent use (construction), bonds particularly well to the cement-like coating.

1.5.5.4 Cement polymer composite coating for reinforcement bars

Cement polymer composite coating (CPCC) technology has developed for the protection of steel reinforcement rods against corrosion in aggressive marine atmosphere after analyzing the merits and demerits of various protective coatings system currently in operation including FBEC and cement-slurry anticorrosive system [51].

1.5.6 Conductive coating for reinforcement bars

Conductive coatings can be used to protect reinforcement bars from corrosion successfully in conjunction with cathodic protection. Workers in Australia have reported encouraging results with a chlorinated rubber-based coating pigmented with graphite [52]. Used as the secondary anode, the coating still performs well after six years in service. No significant reduction in either adhesion or conductivity is claimed.

1.5.7 Coating to prestressing steel

Prestressing steel, since it is being held under permanent tension is vulnerable to more dangerous forms of corrosion such as pitting corrosion, stress corrosion, hydrogen embrittlement etc. Failure of Berlin Assembly hall is well known [53] because of the strategic importance of prestressing wires in a structure, research in the recent years has been directed towards development of compatible coating system for prestressing steel.
1.6 Methodologies of corrosion evaluation of steel in concrete structures

Reinforced concrete structures are often exposed to marine environments when degradation by corrosion occurs frequently [54,55]. Chlorides and sulfates, oxygen and other deleterious agents in seawater damage concrete and corrode rebar. Several techniques can characterize corrosion processes in real concrete structures: Half cell potential mapping, electrical resistivity measurement, determination of profiles and critical content of chlorides, carbonation depth measurement, ultrasonic pulse velocity and hammer impact measurements, visual examination and delamination detection [56,57].

Concrete is a heterogeneous material composed of cement, sand and stone aggregate. Concrete behaves like an unpredictable electrolyte and the active metal reinforcement lying encased by this unpredictable electrolyte is inaccessible during service. Since a network of reinforcement is generally used, there are hidden and shielded areas. Electrochemical techniques are being experimented for measuring the status of corrosion in concrete.

1.6.1 Open circuit potential measurements [OCP]

1.6.1.1 Principle

The tendency of any metal to react with an environment is indicated by the potential it develops on contact with that environment. In reinforced concrete structures, concrete acts as an electrolyte and the reinforcement will develop a potential depending on the concrete environment, which may vary from place to place. The principle involved in this technique is essentially measurement of corrosion potential of rebar with respect to a standard reference electrode, such as saturated calomel electrode, copper-copper-sulfate electrode, silver-silver chloride electrode and others. Because of its good stability, calomel electrodes...
are widely used in reinforced concrete structures. The electrical circuit for open circuit potential measurement is shown in figure [1 3].

The steel rebar in concrete structure should be accessible in a few locations for giving electrical connections. The positive terminal of high impedance voltmeter is connected to exposed rebar and negative terminal (common) to referenced half cell. The surface of concrete is divided into a number of grids. The reference electrode is moved along the nodal points and the corresponding potentials are recorded.

These are referred to as either open circuit potential or corrosion potential. As per ASTM Standards, the probability of reinforcement corrosion is as follows:

<table>
<thead>
<tr>
<th>OCP values in terms of mV Vs.SCE</th>
<th>Probability of corrosion</th>
<th>OCP values in terms of MV Vs CSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>More -ve than -275</td>
<td>More -ve than -350</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Between -275 &amp; -125</td>
<td>Between -350 &amp; -200</td>
<td>Uncertain</td>
</tr>
<tr>
<td>More +ve than -125</td>
<td>More +ve than -200</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>
Fig. 1.3: Schematic for OCP measurement

Half-cell potential measurements in concrete approximately indicate the corrosion condition of rebar. They are performed frequently on real concrete structures because they identify zones with different corrosion probability. The general test method is described in the ASTM C876-87 Standard [58]. The standard states that at potentials above -200 mV Vs. CSE (Copper / Copper Sulfate Electrode) the probability for corrosion is very low (less than 5%) while below -350 mV, corrosion is very probable (greater than 95%) [59].

Stratfull first investigated the utility of OCP measurements for reinforcement corrosion monitoring in 1957 on San Mateo Hayward Bridge [60]. In 1973, the probability of reinforcement corrosion was also assessed by OCP measurements. Potential studies were carried out by the California division of highways on three different bridges in USA [61]. As the deck slab was covered with asphaltic concrete overlay, it was attempted whether there will be a correlation between potential measurements on sealed deck and the actual probability of corrosion. Open circuit potential measurements obtained on the deck were subject to much uncertainty and a definite relationship between the
top deck surface and soffit potential could not be established. Potential studies made on asphaltic concrete overlay, on bridge deck showed that potential values varied with time, leading to large errors.

Extensive cracking in floors of a seven storied parking garage constructed in 1971 in North America was showed heavy deterioration due to reinforcing bar corrosion. About 5.9% of floor area showed potentials between −200 mV and −350 mV vs CSE indicating that corrosion activity had initiated. Only 0.2% of floor area showed potentials greater than −350 mV vs CSE indicating more than 90% probability of corrosion [62].

Marison investigated the corrosion of rebar in concrete columns and balconies using this technique [63]. Corroded reinforcing steel was identified in the 12th and 20th floor of the building, using open circuit potential measurements. Potential survey technique has also been employed in a chimney structure for assessing the condition of reinforcing rods in concrete [64]. CECRI, Karaikudi, has also done extensive work using open circuit potential measurement. Potential studies in the case of a bridge structure, which was under distress, indicated more than 50% probability of corrosion [65]. Similar potential measurements made on a bridge structure, which was in good condition showed values in the range −26 to −40 mV vs SCE indicating less than 10% probability of corrosion. This agreed with the visual observation made on the structure, which revealed steel rebar’s in rusted condition.

Extensive studies carried out on different members of various bridges indicated 60-80% probability of corrosion in one bridge, while in another bridge, deck slab showed 70-90% probability of corrosion. A third bridge structure, showing advance stage of reinforcement corrosion gave a potential value as high as −100 mV. Potential measurements made on various members such as roof slab, sunshades, beams of a multi storied residential building revealed that in many places, OCP measurement indicated 90% probability of severe corrosion.
1.6.2 Surface potential measurements [SP]

1.6.2.1 Principle

During corrosion process, an electric current flows between the cathodic and anodic sites through the concrete and this flow can be detected by measurement of potential drop in the concrete. Hence, surface potential measurement is used as a non-destructive testing for identifying anodic and cathodic regions in concrete structure and indirectly detecting the probability of corrosion of rebar in concrete. Two reference electrodes are used for surface potential measurements. The electrical circuit for this system is shown in figure.[1.4]. No electrical connection to the rebar is necessary in this technique.

![Electrical Circuit Diagram](image)

**SCE** - Saturated Calomel Electrode  
**R** - Rebar Connection  
**V** - High Impedance Volt meter

**Fig.1.4 Schematic for SP measurement**

In this measurement, one electrode is kept fixed on the structure on a symmetrical point. The other electrode called moving electrode is moved along the structure on the nodal points of the grid as mentioned in OCP measurements.
The potential of movable electrode, when placed at nodal points, is measured against the fixed electrode using a high impedance volt meter. A more positive potential reading represents anodic area where corrosion is possible. The greater the potential difference between anodic and cathodic areas, greater is the probability of corrosion.

1.6.3. Polarization resistance technique

1.6.3.1 Principle

Among the various electrochemical techniques, the best-known technique for evaluation of instantaneous corrosion rate in the laboratory is the polarization resistance method. Stern and Geary developed this technique in 1957 [66]. The principle involved in these techniques is that a linear relationship exists between potential and applied current, at potentials only slightly shifted from the corrosion potential. Based on the kinetics of electrochemical reactions and the concept of mixed potential theory postulated by Wagner and Traud, an equation was derived, which related quantitatively the slope of the polarization curve in the vicinity of the corrosion potential to the corrosion current density \( I_{corr} \) as follows:

\[
I_{corr} = \frac{b_a \times b_c}{2 \times 303 (b_a + b_c)} \cdot \frac{1}{R_p} = \frac{k}{R_p}
\]

Where

\[
k = \frac{b_a \times b_c}{2 \times 303 (b_a + b_c)}
\]

\( b_a \) = Anodic tafel slope constant

\( b_c \) = Cathodic tafel slope constant

\( R_p = \frac{\Delta E}{\Delta I} \) = Polarization resistance
This principle can be applied for estimating the corrosion rate \( (I_{\text{corr}}) \) of rebar's embedded in concrete. In this technique, a small amount of D.C current \( (\Delta I) \) is applied to the embedded rebar and the corresponding potential \( (\Delta E) \) is monitored. This polarization can be carried out from \(-10\) mV to \(+10\) mV in the vicinity of open circuit potential (OCP). There are three methods to carry out this polarization:

(i) Galvanostatic method

(ii) Potentiostatic method and

(iii) Potentio Dynamic method

In the Galvanostatic Method a small increment of current is applied and the change in potential is monitored. For each increment of current a waiting time of 10 minutes is necessary, in order to obtain corresponding stabilized \( E \) values.

In the potentiostatic Method, for each increment of potential \( (\Delta E) \), the current value \( (\Delta I) \) is recorded after 30-60 seconds.

In the potentio-dynamic method, the potentiostat is coupled with a voltage scan generator and the polarization is carried out at a particular sweep rate. Reliable results have been obtained at a scan rate of 5-10 m V/min.

Polarization can be carried out by any one of the above methods and \( E \) vs \( I \) plot obtained. From this plot, \( R_p \) value can be calculated. This is nothing but slope of the curve near zero current.

1.6.3 Guard ring technique

1.6.4.1 Principle

While attempting to estimate the corrosion rate of reinforcing steel in large concrete structures using polarization resistance technique, some special
problems arise, which are not found with small test specimens in the laboratory. The main difficulty is the non-uniform distribution of the electrical signal applied to the reinforcement via counter electrode, whose surface area is much smaller than that of the reinforced concrete structure to be tested. The degree of polarization gradually decreases with the distance from the position of the counter electrode and so the true $R_p$ value cannot be estimated accurately along each position of rebar.

This problem can be eliminated by the Guard Ring Technique[67]. According to this, the use of a second electrode located concentrically around the central counter electrode confines the electrical signal to a defined region of the reinforced concrete structure. Both the counter electrodes (central and ring) are maintained at the same electrical potential with regard to the working electrode (the rebar) and the current, which flows from the central electrode, is measured. Therefore, the central electrode locally polarizes the bar, another auxiliary electrode, concentric with the former provides polarization to the rest of the rebar around the area affected by the central electrode. Since the central electrode's current and the area of the reinforcement influenced by it are known, determination of the $R(p)$ value can be made accurately. In practice, the two counter electrodes are controlled separately by a potentiostat and a current followed for the same applied signal.

1.6.4 Impedance technique

1.6.5.1 Principle

In recent years, A.C. impedance spectroscopy is being experimented as a useful non-destructive technique for quantifying corrosion of steel rebar's embedded in concrete. In this technique an A.C. signal is applied to the embedded rebar and the response is monitored in terms of the phase shift of the current and voltage components and their amplitude. This is done in the time or frequency domain using a spectrum or frequency response analyzer.
equivalent circuit of a corroding reinforcing bar embedded in concrete can be represented as shown in figure [1.6]. The Nyquist plot for steel in concrete is shown in figure [1.7].

![Diagram of an equivalent circuit for corrosion of steel in concrete](image)

**Fig. 1.6:** Equivalent Circuit for corrosion of steel in concrete
Impedance $z$ is the ratio of A.C Voltage to A.C current. An alternating voltage of about 10 to 20 mV is applied to the rebar and the resultant current and phase angle are measured for various frequencies.

As per the circuit, cell impedance:

$$|z| = R_s + \frac{R_t}{1 + j \omega C_{di} R_t}$$

where $\omega = 2\pi f$, $j = \sqrt{-1}$, $R_s$ is the resistance of concrete, $C_{di}$ is double layer capacitance and $R_t$ is the charge transfer resistance.

As $\omega \to 0$, the cell impedance $|z| = R_s + R_t$

and as $\omega \to \infty$
the cell impedance $z = R_s$

Hence subtraction of cell impedance $z$ at high frequency from that at low frequency gives $R_t$

Corrosion current $I_{corr}$ be calculated from $R_t$ using well-known Stern Geary equation

$$I_{corr} = \frac{b_a \times b_c}{2 303 (b_a + b_c) R_t}$$

Here 'b_a' the anodic tafel slope and 'b_c', the cathodic tafel slopes are to be determined experimentally. In practice, it may be possible to get $R_t$ from just two measurements, one at high frequency and another at low frequency.

As is seen in proceeding sections, corrosion, an electrochemical phenomenon, is inherent to metallic substrates and found to cause serious repercussion in the service of metallic based structure. Concrete, having accepted mild steel, as its integral component, the problem of corrosion due to embedded steel is to be address and nursed. These features have also been highlighted in this section to provide the necessary understanding of the ongoing issues concerned with concrete structures. To supplement this issue, methods of measuring and controlling the corrosion phenomenon, has been documented to provide logic for the issues being addressed in this thesis. Of all the protective measures suggested in the construction industry, the use of protective coating to the embedded steel prior to evolution of concrete structure in the most promising and successful approach. Hence the study on the use of protective coating for embedded steel has been chosen as the major concern of this thesis.