CHAPTER - I

REINFORCEMENT CORROSION - MECHANISM
TECHNIQUES OF STUDY AND CORROSION CONTROL

1.1 INTRODUCTION TO REINFORCEMENT CORROSION

Reinforced concrete has now become one of the most widely used materials of construction. According to the design engineer, concrete is primarily a structural material and will offer barrier protection to steel rebars even under aggressive conditions. In general concrete is providing a passivating protective coating for rebars. It is a fact that, the high alkalinity and fairly high electrical resistance of concrete can very effectively protect the steel rebars under all conditions.

In India alone, about 700 bridges especially in the coastal regions are said to be under distress. The 740 metres long Princess street fly over, the biggest in Mumbai, India located very near to the sea was badly cracked within 9 years due to saline environment [1]. A reinforced concrete pier at Trivandrum, India extending 72.75 metres into the sea suffered deterioration within 7 years of construction. The Highway Research Station, Madras surveyed 80 concrete bridges along the coast of State of Tamil Nadu and brought out many instances of spalling and cracking together with extensive corrosion of reinforcement [2].

In the United States, majority of the structures showed evidence of deterioration within 10 years [3]. In the Union of South Africa, it has been observed that reinforced concrete structures exposed to marine atmospheres deteriorated in relatively shorter period [4]. From the above failures, it can be realized that, within 10-20 years, the durability of concrete structures exposed to marine condition is affected even though they have been designed for a minimum life of 60 years. To increase the life of the structures, effective additional measures must be undertaken at the initial stage itself [5].
In the present era, when bridge construction work is growing fast in almost all parts of the country, it is of paramount importance in the design stage itself to consider the factors which affect their durability. Structures suffer distress from deterioration of the concrete as well as from corrosion of the rebars and both cannot be fully separated.

The following are the main factors to be considered in the design stage itself.

a) proper mix design
b) type of cement
c) curing period
d) concrete cover thickness
e) porosity / voids in the concrete
f) moisture content of the concrete

a. PROPER MIX DESIGN

Poor concreting practice produces micro and macro cracks in the concrete. The aggregate-cement ratio, water cement ratio, the maximum size of aggregate and its grading, the method of compaction of concrete, its curing etc. are the parameters to be considered in the design stage itself. Low cement content and high water cement ratio produce a readily permeable concrete [6-8]. As a result, concrete allows oxygen, water and salts to pass through it facilitating corrosion of the rebar, ultimately the load bearing capacity is affected.

b. TYPE OF CEMENT

Pozzolana Portland Cement (PPC) which contains sulphides initiates rebar corrosion and concrete deterioration [9]. It was reported that the corrosion rate with ordinary Portland cement (OPC) was about five times lower than that with pozzolana cements like fly ash and slag cements [10]. It is found that the concrete with Portland cement has got a higher pH value than
that with pozzolana cement. Hence the former has a better passivating capacity.

c. CURING PERIOD

During the curing period, the hydration reaction which is mainly responsible for strength of the concrete, proceeds at a slow rate [11]. Longer duration of curing favours complete gel formations and decreases the permeability of the concrete cover. The curing period should not be less than 72 hours [7,12]. As the curing time increases, the strength of the concrete also increased. Inadequate curing causes shrinkage cracking and earlier spalling of concrete structures [13].

d. CONCRETE COVER THICKNESS

Provision of adequate concrete cover is essential. Investigations carried out at the Central Electrochemical Research Institute, Karaikudi have revealed that a minimum cover of 40 mm is necessary for marine exposure and a 50 mm cover will be the optimum [14]. However, cover thicknesses of 70 mm and 100 mm have also been recommended for structures exposed to marine environment [15-17]. Clear [18] showed very clearly the importance of concrete quality and adequate cover in combating corrosion. They recommended a clear cover thickness of 250 mm with concrete having a water/cement ratio of 0.40 and 75 mm cover with concrete having a water/cement ratio of 0.50. Cover is an important factor that preserves the electrochemical stability of steel in chloride-contaminated concrete. The minimum cover requirements for reinforcing bars exposed to submerged zones, splash zones and atmospheric zones as per various standards are reported in Table - I. The cover thickness in these cases varies from 50 mm to 75 mm.
TABLE - I
COMPARISON OF COVER THICKNESS

<table>
<thead>
<tr>
<th>Zones</th>
<th>Nominal cover to reinforcement (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Submerged</td>
<td>60</td>
</tr>
<tr>
<td>Splash</td>
<td>75</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>75</td>
</tr>
</tbody>
</table>

However, the quality of concrete cover is more important than its thickness. If the recommended cover thickness is not applied, in due course, the steel rebars will be directly exposed to the aggressive environment and acceleration of rebar corrosion might occur. As a result, the diameter of the rebars will decrease leading to structural failures.

e. POROSITY OF CONCRETE

Concrete is naturally a porous material. The porosity, in other words, the permeability of the concrete to liquids is a strong function of water/cement ratio [7,19]. As the water / cement ratio increases, the porosity will also increase [8]. Concrete capillaries vary from approximately 15-1000 Å in diameter. Chloride ions are less than 2 Å in diameter [20] with the result, faster penetration of aggressive chloride ion occurs causing reinforcement corrosion.

f. MOISTURE CONTENT OF CONCRETE

Moisture content of the concrete is an important factor in controlling the rate of rebar corrosion. The conductivity of the concrete determines the magnitude of any corrosion current set up by areas of varying potentials. In concrete, the moisture content is usually expressed by means of relative humidity (RH) in the pore system. Thus at 100 % R.H. the corrosion rate is very low. In this highly moist state, the corrosion process is probably cathodically controlled as a result of a low oxygen diffusion to the cathodic areas.
1.1.1 FACTORS RESPONSIBLE FOR CONCRETE DETERIORATION

The factors mainly responsible for concrete deterioration during prolonged exposure are:

a) carbonation

b) sulphate attack on concrete

c) reduction in alkalinity by leaching action and reaction with concrete

a. CARBONATION

Fresh concrete has a pH value of > 12.6. The moist carbon-di-dioxide present in the atmosphere reacts with alkaline material present in concrete as follows.

\[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \ (\text{pH} = 7) \] ... (1)

This neutralization is a continuous process [21]. Hence the pH value near the rebar drops to 8-9, which leads to corrosion of rebars with the formation of different complex iron oxides. Moreover, the carbonated concrete does not have the same capacity for binding chlorides as does non-carbonated concrete. This increases the free chloride content in concrete.

b. SULPHATE ATTACK ON CONCRETE

It is caused by the following chemical reactions between concrete and sulphate present in underground soil and sea water.

i) formation of gypsum

\[ 4\text{CaO.Al}_2\text{O}_3.19\text{H}_2\text{O}+3\text{CaSO}_4.2\text{H}_2\text{O}+16\text{H}_2\text{O} \rightarrow 3\text{CaO.Al}_2\text{O}_3.3\text{CaSO}_4.31\text{H}_2\text{O}+\text{Ca(OH)}_2 \] ... (3)

\[ 3\text{CaO.}2\text{SiO}_2 + 3\text{MgSO}_4.7\text{H}_2\text{O} \rightarrow \text{CaSO}_4.2\text{H}_2\text{O} + 3\text{Mg(OH)}_2 + 2\text{SiO}_2 \] ... (4)

Thus the conversion of Ca(OH)$_2$ and calcium aluminate to gypsum and ettringite more than doubles the solid volume. These reactions account for the expansion and cracking of concrete structures [22].
c. REDUCTION IN ALKALINITY BY LEACHING ACTION AND REACTION WITH CONCRETE

For structures completely submerged in water, the leaching of lime is a major weakening factor [20,21]. During leaching process, hydroxide ion is always diffused outwards. If extensive leaching of lime takes place it will increase the porosity and decrease the strength and durability of concrete structures. The presence of chemicals like ammonium chlorides, ammonium sulphate and acids like hydrochloric acid, sulphuric acid, phosphoric acid etc., in the environment bring about accelerated deterioration of the concrete.

1.1.2 FACTORS RESPONSIBLE FOR REINFORCEMENT CORROSION

The most important factors mainly responsible for rebar corrosion are as follows:

a. non-homogeneity of the concrete matrix
b. applied stress
c. depassivation of rebars by chloride ions.

a. NON-HOMOGENITY OF THE CONCRETE MATRIX

The most important factor in influencing the rebar corrosion is the inherent heterogeneity of the concrete matrix. Steel in contact with contaminated concrete becomes anodic (contact with chloride, oxygen and water) with respect to that in uncontaminated concrete, initiating active rebar corrosion.

b. APPLIED STRESS

Concrete structures have to perform under a variety of complex environmental conditions. Bridge structures have to function under dynamic loading conditions in aggressive environments where safety and durability are of paramount importance. These environments favour stress corrosion cracking of steel.
It is generally known that the high strength steels are susceptible to stress corrosion cracking in a variety of environments [23-26]. Particularly steel with bainitic structures are more susceptible than those with pearlitic or sorbitic structures [27]. Oil tempered wires fail much more readily under stress corrosion than do hard drawn stress relieved wires [28]. Stress corrosion failures, during service, have occurred particularly in sulphide, nitrate and chloride environments.

c. **DEPASIVATION OF REBARS BY CHLORIDE IONS**

Of the various anions encountered in corrosive environments, chloride has acquired a significant reputation as the most aggressive ion [29]. Earlier study revealed that chloride ions have the very high penetrating power in the passive oxide films on metals. This effect is considered to be associated with its smaller size in comparison to other ions [30].

In reinforced concrete structures, the pore solutions surrounding the reinforcement attains a pH of 12.5 after the completion of hydration reaction. The high alkalinity is buffered at this pH by calcium hydroxide in a lime rich layer in intimate contact with the surface of the reinforcement. As long as the pH remains in the passive region, the rebar also remains free from corrosion [31].

The most common cause of rebar corrosion problem stems from the introduction of chloride ions. The contamination of chloride in concrete structures by chloride occurs due to (i) their use as accelerator in the mix, (ii) the presence of a marine atmosphere and (iii) the use of deicing salts. Chloride occurs in concrete in three forms [32].

a) chemically bound
b) physically adsorbed and
c) free chlorides
Among all, only the free chlorides are mainly responsible for rebar corrosion. If the free chloride to hydroxide ratio (Cl\(^{-}/\) OH\(^{-}\)) exceeds 0.6, loss of passivity occurs and pitting progresses. The free chloride not only alters the Pourbaix equilibrium diagram (Fig. 1.1), it reduces the area of the passive region, but also transfers the rebar from the passive to the active region [33].

![Pourbaix diagram](image)

**FIG. 1.1: Influence of chloride on corrosion and passivation of iron**

The corrosion reactions that occur can be represented as follows [34, 35].

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{2+} + 2 \text{e}^- & \text{(5)} \\
O_2 + 2H_2O + 4 \text{ e}^- & \rightarrow 4 \text{ OH}^- & \text{(6)} \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2 \rightarrow \text{White corrosion product} & \text{(7)} \\
4 \text{Fe(OH)}_2 + 2H_2O + O_2 & \rightarrow 4 \text{ Fe(OH)}_3 \rightarrow \text{Red rust} & \text{(8)} \\
3 \text{Fe} + 8 \text{OH}^- & \rightarrow \text{Fe}_3\text{O}_4 + 4 \text{H}_2\text{O} + 8 \text{e}^- \rightarrow \text{Black rust} & \text{(9)}
\end{align*}
\]
At high chloride concentrations

\[ \text{Fe} + 2 \text{Cl}^- \rightarrow \text{FeCl}_2 \rightarrow \text{Fe}^{2+} + 2 \text{Cl}^- + 2e^- \]  ... (10)

Yellowish green

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \]  ... (6)

\[ 6\text{FeCl}_2 + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 2 \text{Fe}_3\text{O}_4 + 12 \text{H}^+ + 12 \text{Cl}^- \]  ... (11)

The iron-free chloride reaction is self-perpetuating in that, the free chloride originally responsible for the reaction is released for reuse when iron hydroxide is formed as shown in Fig. 1.2. In fact, the free chloride acts as a reaction catalyst [29].

\[ \text{Cl}^- \quad \text{O}_2 \quad \text{H}_2\text{O} \]

\[ \text{H}_2\text{O} \]

\[ \text{H}^+ + \text{Fe(OH)}_2 + \text{Cl}^- \]

\[ \text{FeCl}_2 \]

\[ \text{O}_2 + \text{H}_2\text{O} \]

\[ \text{Cathode} \]

\[ \text{Concrete} \]

\[ \text{O}_2 + \text{H}_2\text{O} \]

\[ \text{Cathode} \]

\[ \text{Anode} \]

FIG.1.2 : THE CORROSION PROCESS FOR STEEL IN CONCRETE

Even though a high level of alkalinity remains around the steel embedded in concrete, the chloride ions can locally depassivate the steel and promote rebar corrosion problem.
Usually concrete and reinforced steel do not deteriorate at the same rate. The reason for this is that the conditions leading to the deterioration of the concrete do not necessarily corrode the steel rebar or at least not to the same extent and vice versa. It is true however, that the deterioration of the concrete usually accelerates the corrosion of the steel rebars and vice versa.

1.2 MONITORING METHODS FOR CONCRETE DETERIORATION AND REINFORCEMENT CORROSION

Corrosion monitoring is defined as the systematic measurement of corrosion rate for examining the health of the structures and equipments periodically. The In situ corrosion monitoring techniques provide information on the state of condition of reinforcement bars and concretes in the case of concrete structures. They also interrelate the corrosion processes with the concrete variables.

The losses due to rebar corrosion run into several crores of rupees due to reduced life of reinforcements. So measurement of the extent of deterioration of concrete and the corrosion rate of rebars are very essential for adopting suitable preventive measures of structures at the right time.

1.2.1 TECHNIQUES FOR MONITORING CONCRETE DETERIORATION

Concrete contains substances such as CaO, Na₂O and K₂O which provide an alkaline environment. As the concrete is highly alkaline in nature, the acidic materials present in the atmosphere like SO₂, H₂S and CO₂ easily attack the concrete structures and cause deterioration.

Field inspection and visual observation directly indicate the following defects in the deteriorated concrete structures [36-40].

1. scaling
2. efflorescence
3. rust stains
4. exudation
5. incrustation
6. popouts  
7. dampness  
8. discolouration  
9. honey combing and air pockets  
10. longitudinal, transverse, diagonal and random cracks

Insitu strength determination is used for finding out the deteriorated areas [41-45]. Core sample analysis for strength [46,47], alkalinity, free chloride and free sulphate [48-50]. Petrography analysis [51-54] indicates the areas of leaching and sulphate attack. If the free chloride and free sulphate content exceed the threshold value then the corrosion at the rebars is quite possible. The tolerable limit for chloride is 0.1% by weight of concrete [49].

On the basis of surveys made on concrete structures in Britain, the BRE [55] proposed the following classification for assessing the risk of corrosion in terms of acid soluble chloride contents by weight of cement.

Low risk = < 0.4%  
Medium risk = 0.4% -1%  
High risk = > 1%

When struck with suitable hammer, the areas which give off a hallow sound indicate the dummy areas in the existing concrete structures [56].

1.2.2 IDENTIFICATION OF CARBONATED CONCRETE

In the existing structures, the carbonated portions are identified using Bromo-cresol purple indicator [49] or with phenolphthalein indicator [50].

The Bromocresol purple indicator when sprayed on existing concrete structures produces an yellow colour in the carbonated areas and a violet colour in the uncarboanted areas.

The phenolphthalein indicator, when sprayed on the existing concrete structures produces a purple colour on the uncarboanted areas, while the carbonated areas remain colourless.
1.2.3 IDENTIFICATION OF ALKALI - SILICA REACTIVITY

To identify the alkali silica reaction in the existing concrete structures, a 5% solution of uranyl acetate is applied on to the concrete surface and allowed to react for about 5 minutes. An ultraviolet light is then made incident on it. If alkali-silica reactivity is present, it will reveal a greenish yellow glow [57-59].

1.2.4 IDENTIFICATION OF SULPHATE ATTACK ON CONCRETE STRUCTURES

When quinalizarin reagent is sprayed on the existing concrete structures, the sulphate attacked portions become crimson in colour in contact with gypsum [60-62].

1.2.5 NON DESTRUCTIVE TESTING TECHNIQUES

The most important non-destructive testing techniques used to assess the concrete deterioration are as follows:

i. resistivity measurements using four probe resistivity meter
ii. ultrasonic pulse velocity (UPV) technique
iii. radiography technique
iv. infrared thermography technique

i. RESISTIVITY MEASUREMENT

The method essentially consists of using a four probe technique in which a known current is applied between two outer probes and the voltage drop between the inner two elements is measured in terms of resistance (R). The equation relating resistivity to measured resistance has been derived from the four probe method.

\[ \rho = \frac{2 \pi a R}{2} \]

Where, \( a \) = inter electrode distance in cm.
\( R \) = measured resistance in ohm

The factors which govern the resistivity values are:
- constituents of concrete
- chemical contents of concrete such as moisture, chloride level and other ions regardless of whether or not these were introduced by formulation, atmospheric or sea water penetration.
- type of pore structure of concrete.

It is possible that resistivity values will vary quite significantly over a structure. The following indicates the general guidelines of resistivity values based on which having probable corrosion risk can be identified in concrete structures.

**CORROSION RISK FROM RESISTIVITY**

<table>
<thead>
<tr>
<th>Resistivity (Ω.cm)</th>
<th>Corrosion Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greater than 20,000</td>
<td>Negligible</td>
</tr>
<tr>
<td>10,000 - 20,000</td>
<td>Low</td>
</tr>
<tr>
<td>5,000 - 10,000</td>
<td>High</td>
</tr>
<tr>
<td>Less than 5,000</td>
<td>Very high</td>
</tr>
</tbody>
</table>

**ULTRASONIC PULSE VELOCITY TECHNIQUE**

This technique is more helpful in locating the defects and cracks in concrete structures [63-65]. The interpretation of data is very difficult as a large number of factors affect the pulse velocity [66]. The relationship between ultrasonic pulse velocity and the quality of concrete is given as follows.

<table>
<thead>
<tr>
<th>Longitudinal pulse velocity (km/sec)</th>
<th>Approximate compressive strength (N/mm²)</th>
<th>Quality of concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Below 2.0</td>
<td>---</td>
<td>Very Poor</td>
</tr>
<tr>
<td>2.0 - 3.0</td>
<td>4.0</td>
<td>Poor</td>
</tr>
<tr>
<td>3.0 - 3.5</td>
<td>Upto 10</td>
<td>Fairly good</td>
</tr>
<tr>
<td>3.5 - 4.0</td>
<td>Upto 25</td>
<td>Good</td>
</tr>
<tr>
<td>4.0 - 4.5</td>
<td>Upto 40</td>
<td>very good</td>
</tr>
<tr>
<td>above 4.5</td>
<td>Upto 40</td>
<td>Excellent</td>
</tr>
</tbody>
</table>
iii. RADIOGRAPHY

In gamma radiography studies, Gamma and X-rays have been widely used to examine concrete testing have been used [67]. Gamma ray transmission has been used to measure the thickness of the concrete slab [68]. Voids in concrete as small as 5mm in 130mm thick beams have been detected using gamma rays [69]. Arrangements of aggregate particles, air voids, paste film thickness, segregation and location of cracks have been evaluated in concrete using X-rays [70]. X-rays also have been used to detect the amount of corrosion of rebar in chloride contaminated concretes, and to evaluate corrosion products on rebar embedded in concrete [71,72]. Defects in post-tensioned concrete beams were studied using X-rays and gamma rays [73]. The Swathyling bridge, Southampton, UK, was investigated using high energy X-rays to assess radiation hazards and establish the usefulness of this technique for in-situ examination of reinforced concrete structures [74]. The concrete quality is assessed as follows:

<table>
<thead>
<tr>
<th>Back Scatter Steel Reading (mm)</th>
<th>Density</th>
<th>Concrete Quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>&gt;2300</td>
<td>Good</td>
</tr>
<tr>
<td>7.8 - 8.5</td>
<td>2000 - 2300</td>
<td>Below average</td>
</tr>
<tr>
<td>7.5</td>
<td>&lt;2000</td>
<td>Poor</td>
</tr>
</tbody>
</table>

CECRI has made use of portable high energy (6Mev) Betatron radiographic equipment for carrying out the condition survey of concrete bridges especially in girders and beams. CECRI has been carried out the radiographic examination in one of the bridges, for the first time in India [75]. The study gave information on the quality of the concrete, grouted and ungrouted portions, tensioned and untensioned steels.

iv. INFRA - RED THERMOGRAPHY TECHNIQUE

This technique identifies the areas of delamination in existing concrete structures [76-78]. Delamination occurs due to corrosion of reinforcing steel [79].
1.3 TECHNIQUES FOR MONITORING REINFORCEMENT CORROSION

As the corrosion process is an electrochemical phenomenon, electrochemical techniques have been found to be useful for studying corrosion of rebars in concrete structures. The advantage of electrochemical techniques is their simplicity and quickness. They can be easily implemented both in laboratory and field conditions.

The most important techniques used for monitoring reinforcement corrosion are:

a. Gravimetric weight loss method
b. Open circuit potential (OCP) measurements
c. Surface potential (SP) measurements
d. Polarisation resistance method
e. Impedance technique
f. Harmonic analysis
g. Noise analysis

a. GRAVIMETRIC WEIGHT LOSS METHOD

A comprehensive guidance for the preparation of specimens for gravimetric method is given in ASTM G4-68. Weighed metal specimens [W1] are embedded in concrete for a specified period. At the end of the exposure period, the rebar specimens are removed from concrete, cleaned in Clarke's solution and weighed again [W2]. The difference between weight (W1-W2) will give the actual loss of metal. From the weight loss, the corrosion rate in mmpy is determined from the following formula:

\[
87.6 \times \text{loss in weight (mg)}
\]

Corrosion rate (mmpy) = \[
\frac{\text{density (g/cm}^3\text{)} \times \text{area (cm}^2\text{)} \times \text{time (hrs)}}{\text{loss in weight (mg)}}
\]
b. OPEN CIRCUIT POTENTIAL MEASUREMENTS

The tendency of the 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 nature of the concrete environment which may vary from place to place. The electrical circuit for open circuit potential measurements is shown in Fig.1.3.

![Electrical Circuit for Open Circuit Potential Measurements](image)

**FIG 1.3 : ELECTRICAL CIRCUIT FOR OPEN CIRCUIT POTENTIAL MEASUREMENTS**

As per ASTM C876 - 98 the probability of reinforcement corrosion is as follows:

<table>
<thead>
<tr>
<th>Open circuit potential</th>
<th>Probability of corrosion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mV vs SCE</td>
<td>mV vs CSE</td>
</tr>
<tr>
<td>More -ve than -275</td>
<td>more -ve than -350</td>
</tr>
<tr>
<td>between -275 &amp; -125</td>
<td>between -350 &amp; -200</td>
</tr>
<tr>
<td>more +ve than -125</td>
<td>more +ve than -200</td>
</tr>
</tbody>
</table>
c. **SURFACE POTENTIAL MEASUREMENTS**

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 structures and indirectly detecting the probability of corrosion of rebar in concrete. The electrical circuit for this system is shown in Fig.4. Electrical connection to the rebar is not necessary in this technique.

![Electrical Circuit Showing Surface Potential Measurements](image)

**FIG 1.4 : ELECTRICAL CIRCUIT SHOWING SURFACE POTENTIAL MEASUREMENTS**

d. **POLARISATION RESISTANCE TECHNIQUE**

Among the various electrochemical techniques the best known technique for evaluation of instantaneous corrosion rate in the laboratory is the polarisation resistance method. This technique was developed by Stern and Geary in 1957 [80]. The principle involved in this technique is that a linear relationship exists between potential and applied current. Based on the kinetics of electrochemical reactions and the concept of mixed potential
theory postulated by Wagner and Traud an equation was derived, which relates quantitatively the slope of the polarization curve in the vicinity of the corrosion potential to the corrosion current density ($i_{corr}$) as follows:

$$i_{corr} = \frac{1}{k} \times b_\text{a} \times b_\text{c}\times \frac{1}{2.303 (b_\text{a} + b_\text{c}) R_p R_p}$$

where,

$b_\text{a}$ = Anodic Tafel slope
$b_\text{c}$ = Cathodic Tafel slope
$R_p = \frac{\Delta E}{\Delta I}$ = Polarization resistance

This principle can be applied for estimating the corrosion rate ($i_{corr}$) of rebars 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. potentiodynamic 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 potentiodynamic 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 mV/min.
Polarisation can be carried out by any one of the above methods and $E$ vs. $I$ plot can be obtained. From this plot, $R_p$ value can be calculated.

The value of $b$ lies between 13 and 52 mV depending on the passive and active corroding conditions.

e. IMPEDANCE TECHNIQUE

In recent years, A.C. impedance spectroscopy is being experimented as a useful non-destructive technique for quantifying corrosion of steel rebars embedded 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

$$\frac{|Z|}{\omega} = R_s + \frac{1}{1 + j\omega C_{dl} R_t}$$

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

As $\omega \rightarrow 0$, the cell impedance $|Z/\omega| = R_s + R_t$ and

$|Z/\omega| \rightarrow \alpha$, 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, $i_{corr}$ can be calculated from $R_t$ using well known Stern-Geary equation.

$$i_{corr} = \frac{b_a \times b_c}{2.303 (b_a + b_c)} \times \frac{1}{R_t}$$
where, $b_a$ the anodic Tafel slope and $b_c$ the cathodic Tafel slope are to be determined experimentally.

f. HARMONIC ANALYSIS

The harmonic analysis method is an extension of the impedance method. It is a relatively new technique, that is quicker to carryout and leads to results which are more straightforward than those of the electrochemical impedance method. A simple amplitude sinusoidal voltage of 10 mV is applied to perturbate the working electrode in the same manner as the electrochemical impedance method. However only a single frequency is employed and the current response is measured in terms of the fundamental, first and second harmonics.

This technique is quick and has the advantage over other electrochemical techniques in that it enables the calculation of the Tafel slopes ($b_a$ and $b_c$) directly from the system under test. However, this technique is still in an experimental stage.

g. ELECTROCHEMICAL NOISE ANALYSIS

Electrochemical noise technique is an emerging technique for monitoring corrosion of reinforced concrete structures. This technique enables information on the mechanism and rate of corrosion processes at areas identified in concrete structures. A low amplitude variation of the corrosion potential of steel in concrete is measured to obtain a noise data as a record of potential fluctuations in the form of power spectra.

A noise source is located within the probable corroding area. A time record of sufficient interval is monitored over the frequency range (10 $\mu$Hz to 1 Hz) noise data as a record of potential fluctuation is obtained. Noise signal is transformed from time domain to frequency domain displayed in the form of amplitude and frequency based on either fast fourier transform or maximum
entropy method of spectral analysis. The measurement interval is usually between 2-10 seconds depending upon the frequency range.

1.3.1 CORROSION PROTECTION METHODS

Detailed analysis of the factors which influence corrosion mechanisms and process, indicates that corrosion protection requires a multiple approach. There are many possible approaches as listed below:

1. Coating to reinforcement
2. Galvanized reinforcement
3. Using stainless steel rebars
4. Coating to concrete surface
5. Using chemical admixtures
6. Cathodic protection
7. Electrochemical removal of chloride
8. Realkalization
9. Using blended cements

1. COATING TO REINFORCEMENT

This is an effective essential means to compact corrosion in such environment where ordinary concrete with surface coating is not able to protect the reinforcement against corrosion. There are several methods of providing protective coatings to the reinforcement. The important coatings are

- Inhibited and sealed cement slurry coating [81-84]
- Cement polymer composite coating [85-86]
- Epoxy coating [87]

2. GALVANIZED REINFORCEMENT

Galvanized reinforcement consists of standard black bar, hot dipped in molten zinc [88]. This process forms a coating which is metallurgically bonded to the surface of the parent metal. The surface of the zinc reacts with calcium hydroxide in the concrete to form a passive layer, preventing corrosion. It has
been used in bridges and similar high value structures for the last 20 years or so in the United States and parts of Europe and in some buildings in India.

3. STAINLESS STEEL REINFORCEMENT

Stainless steel is the name given to a family of corrosion resistant steels containing a minimum of 12 % chromium. On contact with air, chromium forms a thin oxide layer on the surface of steel, this is passive and resists corrosion. The addition of other elements such as nickel and molybdenum enhances the passivity and thus improves the corrosion resistance. As the oxide layer is formed by the elements in the stainless steel rather than being an applied coating, it is in fact self - repairing. Thus if damage does occur during handling and fixing, the passive oxide layer rapidly reforms and the corrosion resistance is not affected.

4. COATING TO CONCRETE SURFACE

Concrete is permeable to water and solutions of chlorides and sulphates [79]. The penetration of aggressive salts accelerate rebar corrosion and failure of concrete structures. In order to prevent the penetration of aggressive salts, the concrete surface must be provided with surface coatings. The surface coatings serve as an effective barrier against ingress of salts, gases and moisture and extend the life of the structure. Types of coatings normally used were based on silicates, latexes, acrylics, siloxanes, chlorinated rubber, polyvinyl chloride etc.

5. USING CHEMICAL ADMIXTURES

It has already been stated that to protect concrete against corrosion the concrete should be impermeable i.e. concrete should be produced at very low water / cement ratio. This can be achieved by using high range water reducing plasticisers (HRWR) or superplasticizers (SP). Now -a- days it is possible to produce concrete at as low as 0.28-water -cement ratio having workable concrete (slump = 0.5 mm). Air entraining admixture also helps in reducing the
permeability of concrete thereby reducing the sulphate, chloride attack and reduces the diffusion rate of CO₂.

6. CATHODIC PROTECTION

The corrosion of reinforcement in concrete is an electrochemical process. Cathodic protection is a technique by which electrical potential of the steel is increased to a level at which corrosion cannot take place. It is widely used for both steel and concrete offshore structures, while on land it has been used for the protection of pipelines and similar structures. Two different methods are employed, an impressed current and the use of sacrificial anodes.

6a. SACRIFICIAL CATHODIC PROTECTION

In this protection method the metallic structures to be protected, is connected by a wire to a more anodic metal so that the corrosion by a wire to the more anodic metal that all corrosion is concentrated at this more active metal. The more metal itself get corroded slowly, while the parent structure, which becomes cathode is protected. The more active metal as employed is called “sacrificial anode”. The corroded sacrificial anode block is replaced by a fresh one, which consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Important applications of sacrificial anodic method include protection of buried pipe line, underground cables, marine structure, ship hulls, water tanks, piers etc.

6b. IMPRESSED CURRENT CATHODIC PROTECTION

In this method an impressed current is applied in opposite direction to nullify corrosion and convert the corroding metal from anode to cathode. Usually the impressed current is delivered from a direct current source like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually a sufficient D.C current is applied to an insoluble anode, buried in the soil impressed in the corroding medium and connected to the metallic structure to be protected. The anode is usually in backfill (composed of coke breeze or
gypsum), so as to increase the electrical contact with the surrounding soil. This type of cathodic protection has to be applied to water pins, condensers etc. This kind of protection technique is particularly useful for large structure for long term operation.

7. **ELECTROCHEMICAL REMOVAL OF CHLORIDE (ECR)**

This is another emerging area with lot of potentialities. This is akin to cathodic protection but unlike cathodic protection which requires a permanent installation, this technique needs only a temporary installation lasting few days. 20 to 50% of the chloride present in concrete can be removed. An electrical current in the range of 1 to 5 A/m$^2$ is needed.

8. **REALKALIZATION**

Realkalization can be described as the equivalent of ECR for corroding steel in carbonated concrete structures. It is a short term treatment (days instead of weeks) and the proprietary system was a sodium carbonate electrolyte as an aid to regenerating the alkalinity in the concrete and around the rebar. The same anode systems are used as for ECR. The treatment is most commonly applied to buildings with carbonation damage, but with atleast moderate cover of the reinforcing steel ($\geq 10$ mm). The literature is still contradictory about the use of the sodium carbonate electrolyte to maintain alkalinity after treatment and the extent to which it migrates into the concrete. The pH of sodium carbonate is not far above the pH corrosion threshold use of phenolphthalein indicator causes colour change at pH 9.5 [89].

9. **USING BLENDED CEMENTS**

Blended cements are produced by the additions of supplementary cementitious materials such as fly ash, slag, silica fume, rice husk ash, metakaolin etc. to ordinary Portland cement. This technology is well established globally to produce blended cements with ensured quality
standards. Recently several important and major structures have been constructed with blended cements.

These supplementary cementitious materials possess properties which impart certain desirable characteristics to the concrete mix which can enhance the strength and durability of concrete. Of course, a number of tests and a lot of processing of these materials have to be carried out before they can be suitably blended with cement.
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