# PART - A

# CHAPTER - I

# INTRODUCTION

## 1.1 Corrosion – A metal dissolution

Corrosion is the gradual destruction of properties of material when exposed to the environment due to irreversible chemical and electrochemical reactions. Corrosion is a natural phenomenon experienced in our day to day life. Corrosion can be stated in different forms where according to international standard definition is "impairment due to physicochemical interaction between the metal and its environment". Alternatively International Union of Pure and Applied Chemistry (IUPAC) states corrosion as "irreversible interfacial reaction of material with environment resulting in consumption of dissolution of material". Practically corrosion is unavoidable[1,2] that can occur in several forms. Initially it could occur on the overall surface of the metal resulting in loss of weight of material. Familiar localised corrosion is another form where isolated areas are prone to corrosion. Deterioration due to corrosion also takes place at the grain boundaries due to the difference in resistance. As the detrimental effects of corrosion are enormous, the research behind corrosion has begun over a long period. Failure assets noticed in highways, buildings, bridges, industrial components, waterways, ports, automobiles, telecommunication, mining, electronics, home appliances and gas transmission pipelines leading to economical issues, in turn reflects on the public sectors. The study initiated by the NACE International, the Corrosion Society has documented the corrosion costs accounted by various countries. As per the Indian scenario, direct costs of corrosion in the year 1984-85 was estimated to Rs. 4076 crores whereas a five-fold increase of more than 25000 crores per year was reported in recent days which implies the serious issues pertaining to corrosion out of which one third of the annual loss is avoidable. In general, metals are usually present in the stable oxidised form as ores from which they are extracted. These extracted metals have a tendency to react with atmosphere to form metal oxides (**Fig. 1**). It is important to notice that whether corrosion process is confined to metals. Discussions state that corrosion can occur on natural and manmade materials including both metals and non-metals such as plastics, ceramics and concrete. Why do metals corrode? is an unanswerable question for a long period where the answer could be correlated from thermodynamics.

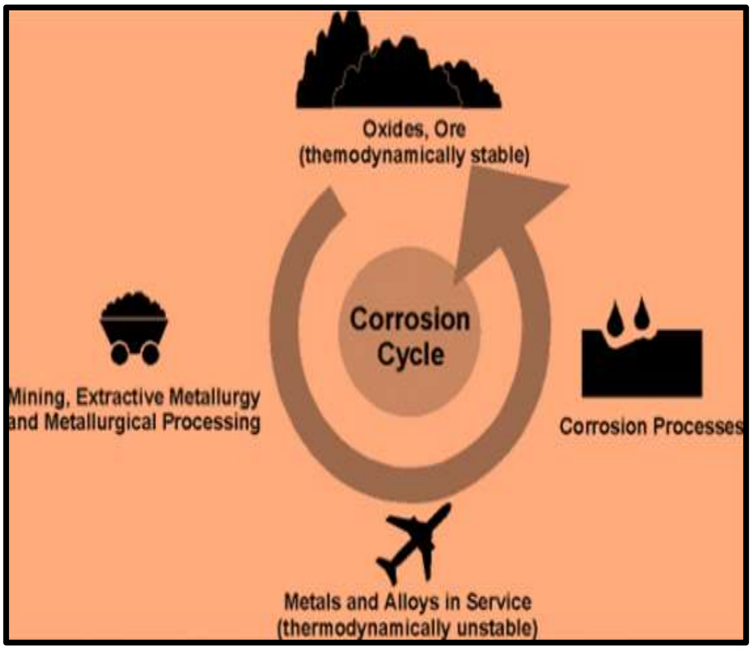
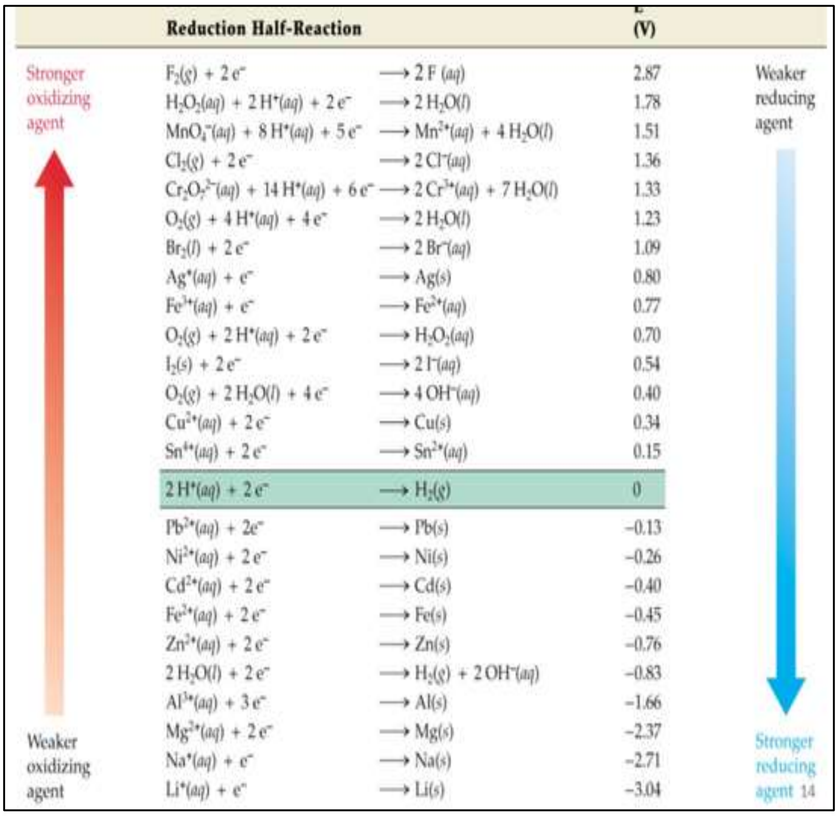


**Fig. 1 Schematic illustration of corrosion process**

Thermodynamics is the science of flow of energy which specifically deals with the occurrence of corrosion process within the given environment. It is a known fact that most of the engineering metals known for its worth occurs in nature in the form of ores which requires lot of energy to extract those metals from their ores. To site few examples, hematite ($Fe_2O_3$) an ore of iron, bauxite ($Al_2O_3.H_2O$) an ore of aluminium, smaltite ore, a combination of sulphur and arsenic, complex ore of nickel (kupfer-nickel), ruby ore ($Cu_2O$), copper glance ($Cu_2S$), or pyrite ($CuFeS_2$) used to extract the copper. However it should be noticed that the metals obtained as such in nature as free metals termed as noble metals differ in its potential when compared with the metals undergoing extraction. Flow of energy in corrosion process occurs in the form of electrical energy. In order to elucidate the energy difference between two metals, a new term potential was introduced where potential difference between metal of higher potential (anode) to the metal of lower potential (cathode) can be determined which facilitates the flow of electrons. Potential of each metal when compared to other is a unique number which is able to differ. Thus a standard scale is essential to compare and establish the potential difference of various metals as universal reference. For this purpose, a standard electrode is considered, known as reference electrode against which the potential of the metal measured seems to be reproducible as shown in **Fig. 2**.



| Reduction Half-Reaction | | (V) |
|---|---|---|
| $F_2(g) + 2e^-$ | $\longrightarrow 2F^-(aq)$ | 2.87 |
| $H_2O_2(aq) + 2H^+(aq) + 2e^-$ | $\longrightarrow 2H_2O(l)$ | 1.78 |
| $MnO_4^-(aq) + 8H^+(aq) + 5e^-$ | $\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$ | 1.51 |
| $Cl_2(g) + 2e^-$ | $\longrightarrow 2Cl^-(aq)$ | 1.36 |
| $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$ | $\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ | 1.33 |
| $O_2(g) + 4H^+(aq) + 4e^-$ | $\longrightarrow 2H_2O(l)$ | 1.23 |
| $Br_2(l) + 2e^-$ | $\longrightarrow 2Br^-(aq)$ | 1.09 |
| $Ag^+(aq) + e^-$ | $\longrightarrow Ag(s)$ | 0.80 |
| $Fe^{3+}(aq) + e^-$ | $\longrightarrow Fe^{2+}(aq)$ | 0.77 |
| $O_2(g) + 2H^+(aq) + 2e^-$ | $\longrightarrow H_2O_2(aq)$ | 0.70 |
| $I_2(s) + 2e^-$ | $\longrightarrow 2I^-(aq)$ | 0.54 |
| $O_2(g) + 2H_2O(l) + 4e^-$ | $\longrightarrow 4OH^-(aq)$ | 0.40 |
| $Cu^{2+}(aq) + 2e^-$ | $\longrightarrow Cu(s)$ | 0.34 |
| $Sn^{4+}(aq) + 2e^-$ | $\longrightarrow Sn^{2+}(aq)$ | 0.15 |
| $2H^+(aq) + 2e^-$ | $\longrightarrow H_2(g)$ | 0 |
| $Pb^{2+}(aq) + 2e^-$ | $\longrightarrow Pb(s)$ | −0.13 |
| $Ni^{2+}(aq) + 2e^-$ | $\longrightarrow Ni(s)$ | −0.26 |
| $Cd^{2+}(aq) + 2e^-$ | $\longrightarrow Cd(s)$ | −0.40 |
| $Fe^{2+}(aq) + 2e^-$ | $\longrightarrow Fe(s)$ | −0.45 |
| $Zn^{2+}(aq) + 2e^-$ | $\longrightarrow Zn(s)$ | −0.76 |
| $2H_2O(l) + 2e^-$ | $\longrightarrow H_2(g) + 2OH^-(aq)$ | −0.83 |
| $Al^{3+}(aq) + 3e^-$ | $\longrightarrow Al(s)$ | −1.66 |
| $Mg^{2+}(aq) + 2e^-$ | $\longrightarrow Mg(s)$ | −2.37 |
| $Na^+(aq) + e^-$ | $\longrightarrow Na(s)$ | −2.71 |
| $Li^+(aq) + e^-$ | $\longrightarrow Li(s)$ | −3.04 |

Fig. 2 Electrochemical series

## 1.2 Need for corrosion prevention

In recent days, huge economical loss resulting due to the corrosive environment has made mandatory to focus on the needs of corrosion prevention or importance of corrosion due to the following reasons that could forecast the steps to minimise its effects.

- As materials are the precious resources of our country, to avoid metal crisis it is essential to know its importance.
- Implementing the usage of metals in all fields of technology
- Usage of rare and expensive metals under special protection mode.
- Usage of new highly strengthened alloys which is more prone to corrosive environment.
- Increased effects of air and water pollution due to corrosive environment.
- Air crafts, ships, automobiles and other transportation modes cannot be implemented without proper knowledge about corrosion.
- Engineering disasters like explosion of pipe lines, collapsing of bridges, leakage and explosion of oil storage tanks, crashing of civil and military aircraft witnessed in recent years emphasises the importance of corrosion.
- Implantation of metals within the human body capable of undergoing corrosion has now deserved unique attention
- Failure of safety standards in a catastrophic manner.

## 1.3 Consequences of corrosion

The consequences of corrosion is an unavoidable task that could vary depending on the safety, reliability, operating equipment or structure under examination. Even though the metal loss is quite small, the resulting consequences seems to be more as listed below[3],

- Reduced metal thickness resulting in loss of mechanical strength.
- Structural failure or breakdown (e.g. bridges, aircraft, cars) leading to hazardous effects to the environment.
- Shutdown of nuclear power plants, causing severe problem to industries and consumers.
- Deterioration of appearance, reduces the valuability of goods.
- Fluid contamination in pipelines due to heavy metal release results in huge loss.
- Technically important properties like friction, ease of fluid flow, electrical conductivity, surface reflectivity and heat transfer across the surface of metal could get lost.
- Time consumption in repairing the equipments.
- Blocking of the pipelines by corrosion products leading to mechanical damage of pumps, valves etc.,
- Complexity and expenses in replacing equipment are high that can withstand certain level of corrosion.
- Chernobyl disaster (1986), where the discharge of radioactive corrosion products in water led to severe damage to mankind is an example for severe effect of corrosion.

## 1.4 Theories of corrosion

The following are the proposed theories of corrosion.

### (i) Local cell theory

According to this theory, occurrence of corrosion is reasoned due to the creation of more number of local or micro electrochemical cells due to heterogeneities at the metal surface. This heterogeneity is attributed to impurities, different phases, metal defects or non-uniform stress distribution etc., Corrosion is generally an electrochemical process where a potential difference could be generated between two different metals or different areas of single metal when connected electrically to a standard electrode. This difference in potential could be either positive or negative that allows the current to pass through the metal resulting in cathodic and anodic reactions. Each metal surface is accompanied with cathodic and anodic sites which are usually developed due to,

- internal stress at work station
- metal surface with compositional differences
- irregularity at the metal surface

### (ii) Wagner and Trauds' theory

It is a theory concerned with the corrosion of pure metals proposed by Wagner and Traud. This theory states that impurities and other surface heterogeneities are not required for a corrosion reaction to proceed. However for a corrosion process, some cathodic reaction must proceed simultaneously on the metal surface. Though corrosion reaction is complicated, it can be easily comprehended as an electrochemical reaction adopting the following three ways,

- metal loss occurs at the anodic area where the loss of metal from Fe to $Fe^{2+}$ takes place.
- two electrons released flow to the cathodic area.
- completion of the electric circuit is done by the consumption of electrons flowing to the cathode by the oxygen of aqueous medium to form –OH at the metal surface.

As per the above mentioned theories, three basic parameters are essential which could initiate corrosion reaction. Protecting any one of the step could obviously result in hindering the corrosion process. Observation reveals that the cathodic reaction which with a large surface area can be compared to anodic area can allow corrosive agents like oxygen, water and electrons facilitating the flow of electrons resulting in increased corrosion rate[4].

## 1.5 Principles of corrosion

The following are the main types of principles which include,

- Thermodynamic principles
- Electrochemical principles
- Physical and chemical principles
- Metallurgical principles

Among the four principles, thermodynamic and electrochemical principles play a vital role in predicting the corrosive tendency of metals.

### (i) Thermodynamic principles

The spontaneity of a chemical reaction can be elucidated from the thermodynamic principles. Theoretical possibility of a chemical reaction can be assessed from thermodynamic principles. It is applicable for free energy, electrical double layer and pourbaix diagrams[5,6]. It is capable of explaining the corrosion reactions based on the stability of chemical species whereas corrosion rate cannot be predicted. According to this principle, when two metals are connected to each other, metal lying in lower position of galvanic series behaves as anode and begins to corrode. On the other hand, metal in the higher position of galvanic series tends to support cathodic reaction. For ex. in case of zinc connected with copper, zinc behaves as anode and copper behaves as cathode.

### (ii) Electrochemical principles

Corrosion behaviour of metals are extensively dealt with the aid of electrochemical principles. Corrosion reaction can be indicated in the form of partial reactions where metal oxidation takes place at anode and metal reduction at cathode. Corrosion partial reactions occur at metal-solution interface at equal rates. Electrochemical nature of corrosion could be dealt by considering an example where iron dipped in hydrochloric acid results in vigorous reaction as represented below accompanying the dissolution of iron and evolution of hydrogen,

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{[Anodic reaction]}$$

$$2H^+ + 2e^- \longrightarrow H_2 \quad \text{[Cathodic reaction]}$$

$$Fe + 2H^+ \longrightarrow Fe^{2+} + H_2 \quad \text{[overall reaction]}$$

## 1.6 Classification of corrosion

The major classification of corrosion includes chemical or dry corrosion and electrochemical or wet corrosion as described below,

### (i) Chemical or dry corrosion

When the atmospheric gases like oxygen, hydrogen sulphide, nitrogen, halogens or anhydrous liquid sulphur dioxide directly react with the metal surface, chemical or dry corrosion results. The extent of chemical corrosion depends on either the chemical affinity between metal and corrosive environment or the ability of formation of film on the metal surface.

Main types of dry corrosion includes the following,

- Oxidation corrosion- when the metal is bought into direct contact with oxygen in the absence of moisture at low or high temperature.
- Corrosion by hydrogen – otherwise termed as hydrogen embrittlement. It takes place at ordinary temperature where hydrogen gas attacks the metal surface.

- Liquid-metal corrosion – It arises at higher temperature where the liquid metal penetrates into the solid metal or alloys.

### (ii) Electrochemical or wet corrosion

Electrochemical corrosion takes place when two different metals are connected in presence of an electrolyte or when a metal is in contact with conducting liquid. Different types of electrochemical reactions can be predicted based on the corrosive environment which is either acidic or neutral.

Acid medium: Anode : $M \longrightarrow M^{n+} + ne^-$

Cathode : $2H^+ + 2e^- \longrightarrow H_2$

Neutral medium: Anode : $M \longrightarrow M^{n+} + ne^-$

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Electrochemical corrosion is further classified into the following types

- Interfacial anode/cathode – One complete interface is considered as cathode whereas the other as anode. This type is accompanied with the transfer of charges across the film formed on the metal surface.
- Separable anode/cathode – In this type, selected areas of metal is identified experimentally as predominant anodic or cathodic site whose separation distance is too small in the orders of millimetres or fractions accompanying macroscopic flow of charge in the metal.
- Inseparable Anode/Cathode Type – Experimental differentiation of cathodic and anodic sites are not possible in this method.

## 1.7 Types of corrosion

Major types of corrosion includes uniform and localized corrosion.

### (a) Uniform corrosion

This type of corrosion takes place evenly on the metal surface with the formation of cathodic and anodic sites whose position changes with time. As the metal is uniformly disturbed, one can observe even decrease in thickness of the metal which is well recognisable, monitored easily and protected in a suitable manner.

### (b) Localised corrosion

Localised corrosion is a non-uniform corrosion where the cathodic and anodic sites are fixed and the corrosion proceeds in a desired portion of the metal. The position of cathode and anodic sites remains unchanged. This type of corrosion takes various forms as represented below (**Fig. 3**) which is difficult to identify and to monitor its progress resulting in huge loss.

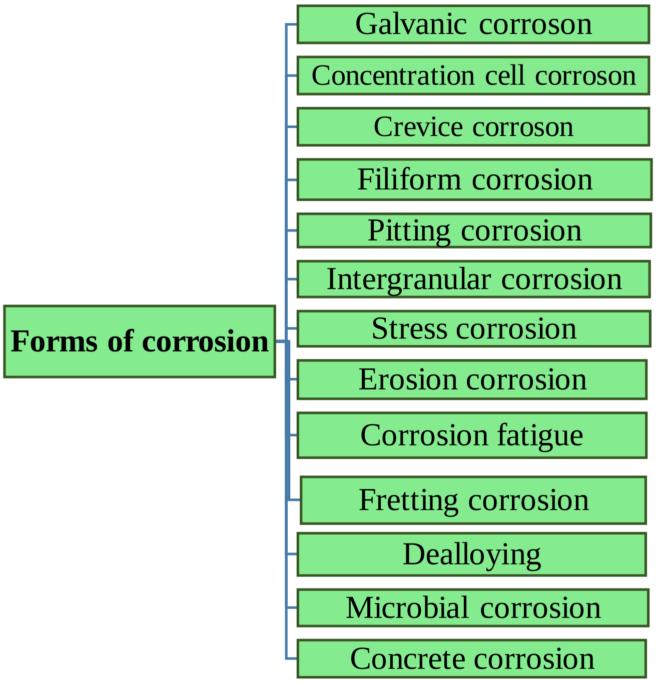


**Fig. 3 Forms of corrosion**

### 1.7.1 Forms of corrosion

#### (i) Galvanic corrosion

When two different metals are in contact with each other in presence of an electrolyte galvanic corrosion takes place as shown in **Fig. 4**. Out of the different metals, more negative metal behaves as anode whereas positive metal behaves as cathode. The difference in potential generated creates the current to flow through the circuit. However galvanic corrosion is directly related to the ratio of cathode metal to anode metal[7]. The rate of galvanic corrosion is more at the junction of two metals whereas increased distance between two metals could minimise the rate of galvanic corrosion. Preventive measures of minimising the galvanic corrosion includes selecting similar materials, cathodic coating, minimising the ratio of cathode – anode area, insulation of different metals to avoid galvanic coupling and adopting sacrificial anodes protecting the galvanic junction[8].

Fig. 4 Galvanic corrosion

### (ii) Concentration cell corrosion

When two or more parts of the metal is in contact with the electrolyte, concentration cell corrosion results which is associated with joints, scales, debris, gaskets, loose films etc., as displayed in **Fig. 5.** Its rate of corrosion depends on the concentration of oxygen where metal exposed to lower oxygenated area behaves as anode and more oxygenated area behaves as cathode. This could be prevented by sealing faying surfaces to exclude moisture or could be proceeded with proper protective coatings.

Fig. 5 Concentration cell corrosion

### (iii) Crevice corrosion

Crevice or contact corrosion is confined to the space or crevices occurring between the contact of metals or metal and a non-metal[9]. The shape of crevice being deep or narrow leads to severe corrosion. It is mainly facilitated by the potential difference between the materials existing in the inner and outer areas of crevice which could be merely a design fault. Crevice corrosion can occur under any environment, particularly aluminium and stainless steel are more prone to this type under chloride medium (sea water). This is similar to pitting corrosion which arises due to the increase in pH, depletion of oxygen level and increased chloride level. It is noticed that, even non-metallic materials such as plastic, wood, glass, rubber, concrete, wax, asbestos and living organisms are responsible in creating crevice corrosion. In general, crevice corrosion takes prolonged time to initiate oxidation of metal but gets accelerated later on as shown below (**Fig. 6**).

**Fig. 6 Crevice corrosion**

### (iv) Filiform corrosion

Filiform corrosion occurs at the surface without destroying the components of the metal. It is a form of crevice corrosion that occurs on plated or painted surface due to the permeation of moisture into the coatings as shown in **Fig. 7.** Degradation of the coating takes place when the corrosion product extends from the origin of corrosion pit. Minimising filiform corrosion is possible by careful preparation of surface prior to coating or using suitable coating strategy that are resistant to corrosion with minimised appearance of holes.

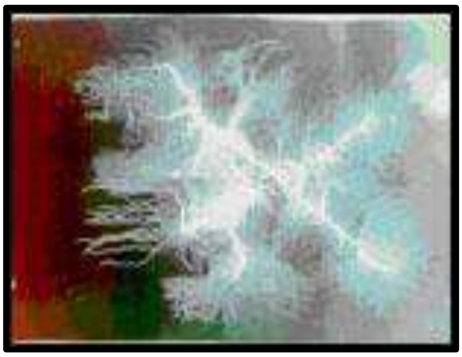


**Fig. 7 Filiform corrosion**

### (v) Pitting corrosion

It is a form of localised corrosion creating microscopic defects on the metal surface. It is noteworthy that a small pit can cause a breakdown of total engineering system[10,11]. As it is difficult to predict and prevent, it seems to be more dangerous than uniform corrosion. Large surface area behaves as cathode whereas small pits act as anode initiating pitting corrosion as displayed in **Fig. 8**.

Pitting corrosion usually occurs under stagnant condition which is measured in terms of pitting factor, a ratio between deepest metal penetration to average metal penetration. Pits formed could appear smaller at the surface but possess large cross sectional area deep into the metal. The morphology of the pit such as size, shape, depth of penetration could be found by the metallographic analysis of cross sectioned sample. As per the American Society for Testing and Materials (ASTM)[12], extent of pitting corrosion could be summarised as shown in **Fig. 8**. However this corrosion can be minimised by proper cleaning of surface, protective coatings or addition of inhibitors. Considering certain factors such as corrosive medium and its acidity, concentration of chloride and oxidiser, temperature, metal composition and impurity level could also contribute towards minimising pitting corrosion.

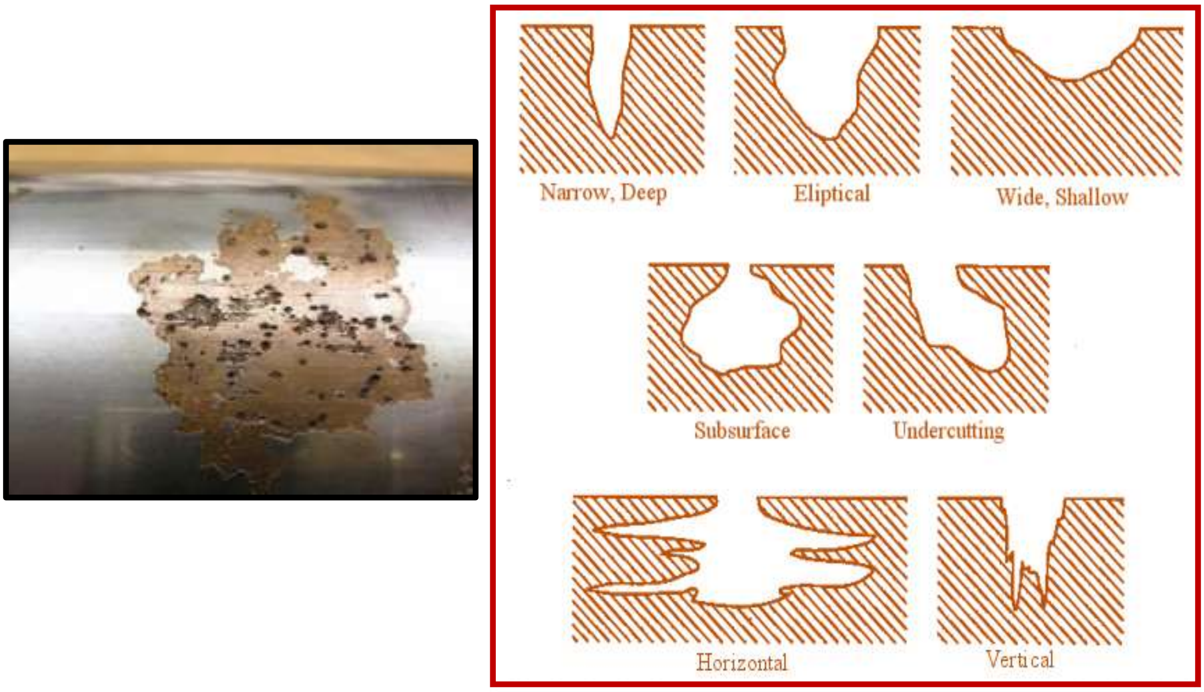


**Fig. 8 Pitting corrosion**

### (vi) Intergranular corrosion (IGC)

Intergranular corrosion is more reactive in grain boundaries rather than grain matrix which takes place rapidly with a deep penetration into the metal resulting in catastrophic failures[13]. Most of the metals are prone to intergranular corrosion (**Fig. 9**) out of which iron-nickel-chromium alloy is to be considered seriously because of its commercial importance. IGC is supposed to cause due to,

- presence of impurities at grain boundaries
- enriched elemental composition of alloy
- depletion of any of the element in grain boundary

However intergranular corrosion can be prevented by selecting suitable alloy or adopting suitable heat treatment.

**Fig. 9 Intergranular corrosion**

**(vii) Stress corrosion cracking (SCC)**

It is a brittle failure under low tensile stress exposed to environment. For stress corrosion to take place, presence of tensile stress in corrosive medium is essential. This sort of corrosion takes place due to the joint action of tensile stress exerted on the corrosive environment that could result as shown in **Fig. 10**.

**Fig. 10 Stress corrosion**

The stress could obviously arise from the load applied, residual stress, manufacturing methodology or a combination of all. One of the major problem to be noticed in stress corrosion is that it is extremely difficult to detect the initial stages of stress corrosion until it results with major issues. Main factors that could cause stress corrosion is portrayed in **Fig. 11**. Significant effect of stress corrosion could be noticed from material chemistry and microstructures whereas tensile stress arises from welding, machining, grinding and heat treatment works. Certain metallurgical factors like chemical composition, grain orientation, compositional distribution, dislocated structures and environmental factors like temperature can also induce stress corrosion[14]. Possibility of reducing stress corrosion includes either coatings or selection of suitable alloy or proper heat treatment or machining in stress free condition.

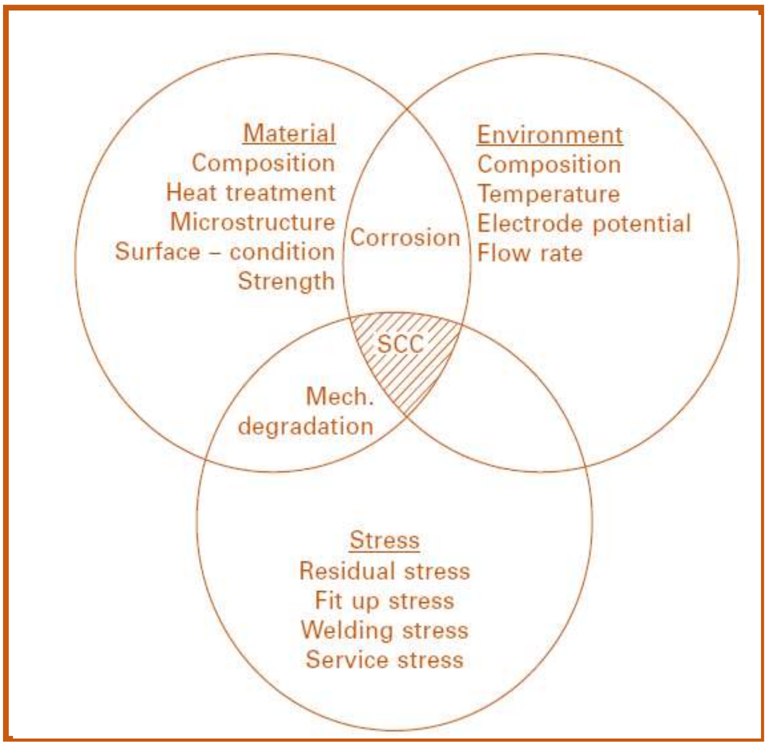


Fig. 11 Requirements of stress corrosion

### (viii) Erosion corrosion

Erosion corrosion otherwise termed as impingement corrosion takes place in an enhanced rate due to the relative motion of corrosive environment (liquid or gas) with the metal (**Fig. 12**). Agitators, copper pipes and centrifuges are certain sites of erosion corrosion. Metal surface undergoing erosion corrosion will be free from corrosion products (pits, grooves, rounded holes and valleys) retaining a fairly clean brighter surface.

Fig. 12 Erosion corrosion

Weight loss of the metals resulting is obviously greater than pure electrochemical corrosion and mechanical erosion[15]. Though extensive studies has been done in order to differentiate erosion and corrosion process, still it is a complex strategy to explain clearly but it is a combined synergistic effect[16]. Modifying the system design, removing particulate matter, using materials that can resist erosion can all minimise erosion corrosion process. Using corrosion resistant alloys or harder alloys like flame spray can minimise erosion corrosion.

### (ix) Corrosion fatigue

Corrosion fatigue results due to the combination of cyclic stress and corrosion alternatively, which is a special case of stress corrosion (**Fig. 13**). As its name implies, reduction in fatigue strength of metal results in the presence of aggressive corrosive environment. Fatigue condition arises at fatigue limit which is higher critical value than cyclic stress[17]. None of the metal can be deviated from the cyclic stress under corrosive environment. This can be controlled by using protection strategy or lowering the cyclic stress.

**Fig. 13 Corrosion fatigue**

### (x) Fretting corrosion

Fretting corrosion occurs at the interfaces of highly loaded metal surface with slight vibration or two surfaces in contact under humid or dry conditions (**Fig. 14**). Friction oxidation, chafting, false brinelling and wear oxidation are the alternate terms used to indicate this phenomena. The movement lies in the range of 1-100μm[18]. It is one of the root cause in creating excessive damage and loss in aeronautics, wind mills, automobiles and biomedical sectors. The profile of fretting corrosion includes contact pressure, crevice pressure, displacement and velocity of the two contacting surface[19]. According to Ren, porosity, chemical compositions, rigidity, surface contact and its nature also plays a vital role. Resulting fretting corrosion was distinguished into three regions[20] like stick, mixed stick-slip and gross slip. Stick mode is experienced with no fatigue crack formation, small oxidising effect in case of mixed-stick slip whereas severe damage was witnessed in case of gross slip. Lubricating the contacting surface is one of the prescribed method to minimise fretting corrosion.

**Fig. 14 Fretting corrosion**

**(xi) Dealloying**

It is a rare form exhibited in gray cast iron, copper alloys and some more alloys. It mainly arises when the active component of metal is lost in alloy while retaining corrosion resistant material in porous sponge nature on the metal surface (**Fig. 15**). It can be controlled by using resistant alloys or inhibited specimens.

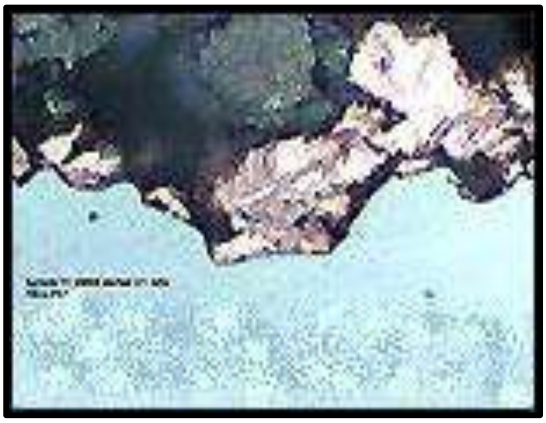


**Fig. 15 Dealloying**

**(xii) Microbial corrosion**

Microbial corrosion otherwise called as microbiologically influenced corrosion is induced by the microbes that can take many forms and controlled by biocides or certain control methods (**Fig. 16**).

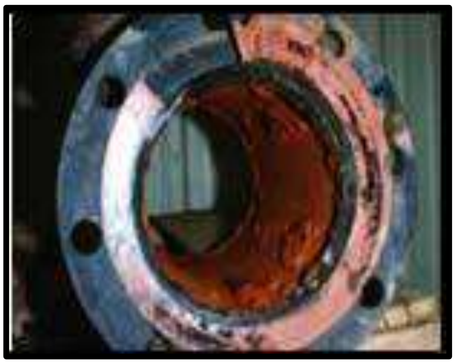


Fig. 16 Microbial corrosion

### (xiii) Concrete corrosion

Concrete is a versatile material used in construction process which is reinforced with steel bars. These steel retain the structural duration for a long time until it begins to corrode which happens predominantly when exposed to chloride induced medium as shown in **Fig. 17**. Corrosion of steel leads to cracking through which moisture and salt leaches into the metal surface resulting in pronounced metal loss.

Fig. 17 Concrete corrosion

## 1.8 Mechanism of corrosion

It is generally known that most of the important metals are extracted from their ores utilising large amount of energy. The extracted compounds are supposed to be in metastable state capable of getting reverse to its original state. Though various mechanisms have been suggested, corrosion is generally an electrochemical reaction associated with two simultaneous reactions ie., oxidation which occurs at anode and reduction occurring at cathode. In order to facilitate this electrochemical corrosion process the following three requirements are essential.

- Potential difference existing between the adjacent sites of a metal surface
- Presence of electrolyte is required to provide the solution conductivity, behaving as a source to be reduced at cathode.
- Presence of electrical path providing the flow of electrons.

Once the electrochemical reaction sets in, iron moves into the solution as ferrous ions constituting anodic reaction. The electrons released as a result of anodic reaction, could build negative charge on the metal surface. Continuous metal dissolution is applicable when the electrons released can move to the cathodic sites of the metal surface resulting in cathodic reactions, where the electrons react with certain reducible components of electrolyte and gets removed from the metal. However according to Faradays laws, the rate of cathodic and anodic reactions must be equal facilitating the flow of electrons called corrosion current. Thus one can understand the detailed insight of corrosion process by considering the most important electrochemical reactions occurring in the corrosion of iron as illustrated below,

Anodic reaction : $Fe \longrightarrow Fe^{2+} + 2e^{-}$ —— (I)

Cathodic reaction : $2H^{+} + 2e^{-} \longrightarrow H_2$ —— (II)

$H_2O + 1/2O_2 + 2e^{-} \longrightarrow 2OH^{-}$ —— (III)

Anodic reaction (I) commonly results in the conversion of iron to its oxidised state whereas reaction (II) occurs in acidic medium with the evolution of hydrogen. Oxygen reduction shown in reaction (III) commonly takes place at a pH 6.5-8.5 leading to the formation of corrosion product (iron (II) hydroxide) as a combination of anodic and cathodic products as shown in equation (IV),

$$Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_2 \quad \text{—— (IV)}$$

Due to the partial oxidation in air, iron (II) hydroxide which is expected to be in white colour appears greenish colour.

$$2Fe(OH)_2 + H_2O + 1/_2O_2 \longrightarrow 2Fe(OH)_3 \quad \text{—— (V)}$$

Combined oxidation and hydration leads to reaction (V) with the formation of iron (III) oxide in the formation of rust which is a complex mixture whose constituents are difficult to identify depending on the rate of hydration and oxidation. However the extent of corrosion process can be determined based on the reduction reaction taking place at cathode which in turn depends on the corrosive environment. Excess of electrons generated reduces the hydrogen ions resulting in the formation of molecular hydrogen in the absence of air and oxygen. Presence of air can lead to oxygen reduction or hydrogen evolution. However it is a difficult task to predict the corrosion rate based on hydrogen evolution as limited mechanism has been predicted for oxygen reduction. As a whole, corrosion is generally detachment of metal atoms from metal at anode followed by the movement of electrons to the cathode where neutralisation of charged hydrogen ions take place. Besides, lot of researchers, Bockris and his co-workers has greatly contributed to the study of dissolution and deposition of iron.

### 1.9 Factors affecting the rate of corrosion

Major factors influencing the rate of corrosion includes primary and secondary factors. Primary factors depend on nature of metal, whereas secondary factors depend on environmental conditions.

#### (a) Nature of metal

#### (i) Oxidation potential

Electro motive series (EMF) provides basic criteria for metals to be corroded or not. Based on this series, it can be generally concluded that the metals of positive potential (cathode) have a tendency to resist corrosion whereas metals with negative potential (anode) are highly prone to corrosion[21]. The difference in the electrode potential can be predicted using the below expression,

$$E_{potential} = E_{cathodic} - E_{anodic}$$

$E_{cathodic}$ and $E_{anodic}$ are the potential of cathode and anode. $E_{potential}$ refers to the potential difference between metals. Greater potential difference between the two metals will result in a facile corrosion process.

#### (ii) Cathode and anode area

The relative area of cathode and anode areas decides the extent of corrosion. Cathodic area greater than anodic area will result in higher corrosion rate as the demand for electrons at cathodic area increases which could be facilitated by the anodic reaction resulting in metal dissolution.

#### (iii) Appearance of metal surface

Highly polished, clean and smooth surface of the metal free from pores has the ability of resisting corrosion. Rough aggregated surface of metals with imperfections, dislocations and point defects are more liable for corrosion compared to smoother surfaces.

#### (iv) Purity of the metal

Pure metals in homogeneous condition never undergoes corrosion. Minute trace of impurity present introduces a heterogeneous condition which is an essential parameter for a corrosion reaction to proceed with. Introducing the impurities sets an electrochemical cell where the corrosion takes place around the impure zone due to certain local action. Decreasing the impurity increases the corrosion resistance of the metal.

### (v) Nature of oxide film

The nature of oxide layer formed on the metal surface could be either stable or unstable or volatile depending on the volume of the metal consumed which leads to pilling Bedworth rule as stated below,

- when the volume of oxide layer formed is more than the volume of metal consumed, then the resulting layer will be non-porous and protective.
  Ex. oxides of Al, Cr and Ni
- when the volume of oxide layer formed is less than the volume of metal consumed, then the resulting layer will be porous and non-protective.
  Ex. oxides of Mg, Ca and Ba

### (vi) Soluble nature of corrosion products

The corrosion products formed on the metal surface could be either soluble or insoluble or volatile. However soluble or volatile layer formed gets detached from the metal surface leaving the fresh surface of the metal exposed to aggressive medium resulting in an enhanced corrosion rate. The insoluble layer formed acts as a protective barrier thereby protecting the metal surface from corrosion.

## (b) Nature of the corrosive medium (environment)

### (i) Influence of temperature

Temperature is an important parameter that can affect the corrosion process in many ways. In general, increase in temperature increases the corrosion rate as the corrosion process is activation controlled ie., governed by metal oxidation. According to thermodynamic considerations, one can expect speed fast chemical reaction on increasing the temperature[22]. The limited soluble nature of corrosive product could be increased by increasing the temperature resulting with drastic corrosive reaction. For ex. iron undergoes corrosion linearly on increasing the temperature from 40 to 160$^{o}$C in a closed system, whereas in an open system linear increase up to 80$^{o}$C is noticed after which it begins to decrease.

### (ii) Effect of dissolved oxygen

As oxygen participates in cathodic reduction process in neutral and alkaline medium, the presence of dissolved oxygen plays a vital role in predicting the complications of corrosion process. Absence of dissolved oxygen, diminishes the corrosion rate to zero in alkaline and neutral medium. Presence of dissolved oxygen, increases the participation of oxygen in cathodic process. Once ferrous ion formed gets converted to ferric ion, it is further oxidised to hydrous ferrous ferrite ($Fe_3O_4 . nH_2O$). Though increased oxygen level accelerates the corrosion rate, at a particular threshold level corrosion rate drops due to the formation of passive dense protective layer[23]. As per the report stated by Cohen[24] presence of oxygen could initiate corrosion 65 times faster than the absence of oxygen resulting in the breakdown of the film.

### (iii) Effect of ions

Some ions have the capability of inducing corrosion whereas certain ions have opposite effect. For ex. chloride ions if present in the corrosive medium destroys the protective layer formed on the metal surface thereby increasing the corrosion. But the same medium with presence of silicates will favour the formation of silica gel that could behave as a protective barrier in preventing corrosion. Even the nature of electrolytes decides the corrosion phenomena to an extent[25].

### (iv) Rate of fluid velocity

Fluid flow which in turn depends on many factors such as fluid constituents and fluid physical properties becomes a complex term in determining the corrosion process. However the rate of fluid flow sometimes become beneficial in preventing the localised corrosion like pitting and crevice where high mass transfer of oxygen maintains passive state. On the other hand, absence of flow will slow down the transfer of oxygen that cannot retain the passive surface. Fluid flow can initiate a process called impingement, ie., erosion of loosely bound protective layer from the metallic surface[26]. Studies made by Butler and Stroud[27] showed that increasing the flow rate increased the corrosion process to an extent which tend to decrease after further increase in flow rate due to the formation of a protective film.

### (v) Effect of pH

It is generally observed that the corrosion rate is highly pronounced in acidic pH rather than basic or neutral medium. Different metals respond at different pH levels. For ex. aluminium metal suffers high corrosion rate at high pH. But in the case of zinc, iron or magnesium, hydrogen evolution is a thermodynamically favoured reaction. However the corrosive nature of any metal under acidic medium is highly pH dependent. Decrease in pH value facilitates the hydrogen evolution in turn increasing the corrosion rate or disturbing the protective layer formed on the metal surface exhibiting either activity or passivity or immunity. However in case of iron, the rate of corrosion is slow in oxygen free medium until pH tends to be less than 5. At lower pH approximately around 4 in the presence of oxygen, corrosion gets stimulated by oxidising $Fe^{2+}$ to $Fe^{3+}$ and subsequent reverse reaction at cathode. Lesser acidic solutions facilitate the formation of rust by oxidising $Fe(OH)_2$ which is formed by the combination of excess $OH^-$ ions and $Fe^{2+}$.

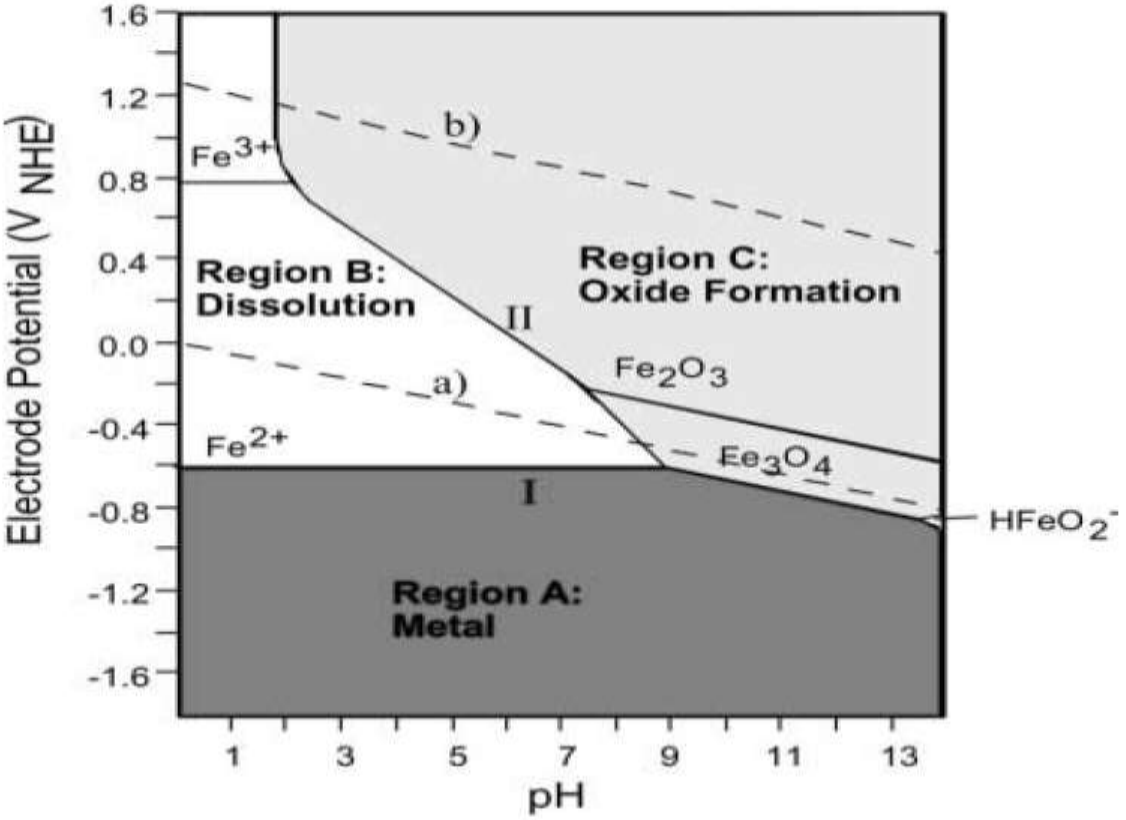


**Fig. 18 Porbauix diagram**

To make a detailed study, Pourbaix diagrams can be considered which is an application of thermodynamics to the corrosion process. Observation of these plot helps to understand the response of metal under relevant potential and pH[28,29]. The plot shown in **Fig. 18** corresponds to iron metal in water. Three regions are exhibited in the plot where in region A, iron is inert and stable. Region B shows the active dissolution of iron followed by the formation of oxide layer in region C. As a concluding remark, increase in pH decreases the corrosion rate.

### 1.10 Methods to control corrosion

The pronounced effect of corrosion in everyday life has made everyone to contribute certain strategies to minimise corrosion to an extent. It involves the application of suitable and economical method to reduce the corrosive effect to an acceptable level. Modern methods of corrosion control was first executed by Dr. Willis Rodney Whitney in the early 20th century adopting electrochemical nature. However the following methods shown in **Fig. 19**, can be experienced to decrease the metal dissolution (corrosion).

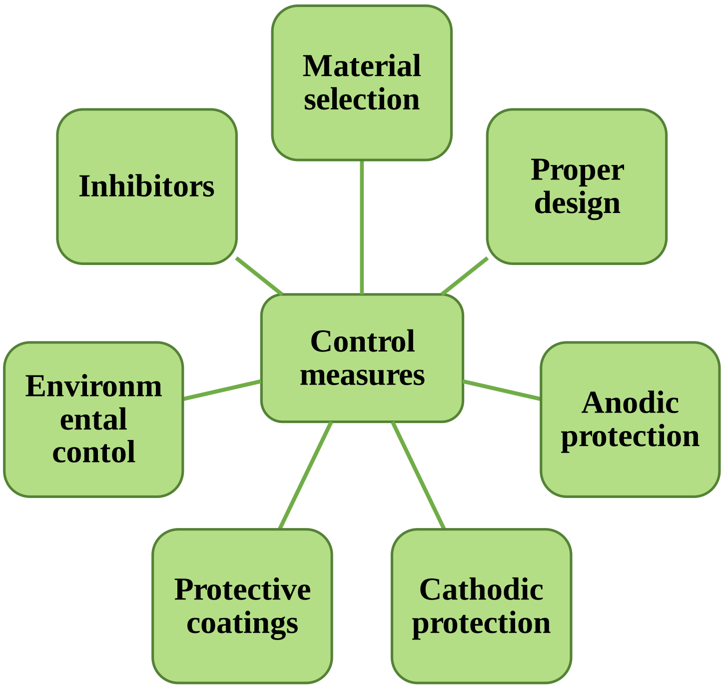


**Fig. 19 Corrosion control methods**

### (i) Material selection

Selection of a material with high corrosion resistance could be done based on its cost, ease of production and mechanical strength. Significant reduction of corrosion can be witnessed by using pure metals whereas impure metals introduce a heterogeneous condition that could enhance corrosion process. Inadequate properties and expensive nature of pure metals limits its usage but unavoidable in specific cases. However selection of corrosion resistant material is a complicated process which is a compromise between technical competence and economical constraints. Three main steps could be considered in adopting the metal that includes fulfilment of requirements, economic condition, selection and evaluating strategies.

### (ii) Proper design

Designing plays a vital role in corrosion resistance. Proper designing could avoid major losses if done before construction or operation of the equipment. Based on the cost, availability and existing resources, difference in design can arise which cannot be maintained as an absolute factor. Most of the chemical industries come across 58% loss due to improper plant designing. Compared to inappropriate material selection, improper designing predominates that could bring huge loss. A designer should acquire adequate knowledge about corrosion phenomena which could help in selecting proper design, in turn retarding corrosion[30].

### (iii) Anodic protection

This method is used highly under electric field where a protective coating can be generated on the base material in order to protect the metal immersed in aggressive medium. Though it is an electrochemical method of corrosion control, it depends on passivity where supply of controlled current favours impervious oxide coverage (passivity) thereby decreasing metal dissolution. Anodic protection of metal can be done by controlling the potential of working electrode with respect to reference electrode and shifting to more anodic direction. The anodic protection achieved at a potential range is termed as protection range corresponding to passive region. Anodic polarisation behaviour can be noticed due to the formation of protective layer which is insoluble in chemical environment and electrically resistive. Formation of this layer makes the metal passive. Chemical systems which are normally corrosive, undergoes anodic protection favouring the formation of passive film on the metal surface.

### (iv) Cathodic protection

Cathodic protection can be adopted to protect underground and marine structures. Cathodic protection can be done by using more reactive metal (sacrificial anode) or by supplying external power that could change the charge of the metal surface. Main theory involved in cathodic protection is forcing the electrode potential of the metal to come under immune zone where corrosion reactions are impossible. It is considered as one of the foremost important method as it makes the metal unreactive. Excess metal involved in controlling the potential and electrical power consumption makes it expensive. The following are the methods of cathodic protection,

### (a) Impressed current method

This method is applied to protect the underground structures and the ship hulls immersed in sea water as shown in **Fig. 20**. In order to protect the metallic structure, electrical current is applied where the negative terminal is connected to the metal to be protected followed by the positive terminal to the auxiliary anode. Charging of structure takes place until immunity region is reached. Observation of the figure shows the underground pipeline connected to the negative terminal makes its potential more negative thereby functioning as cathode. It is one of the effective and specialised method if proper design and operation is made.

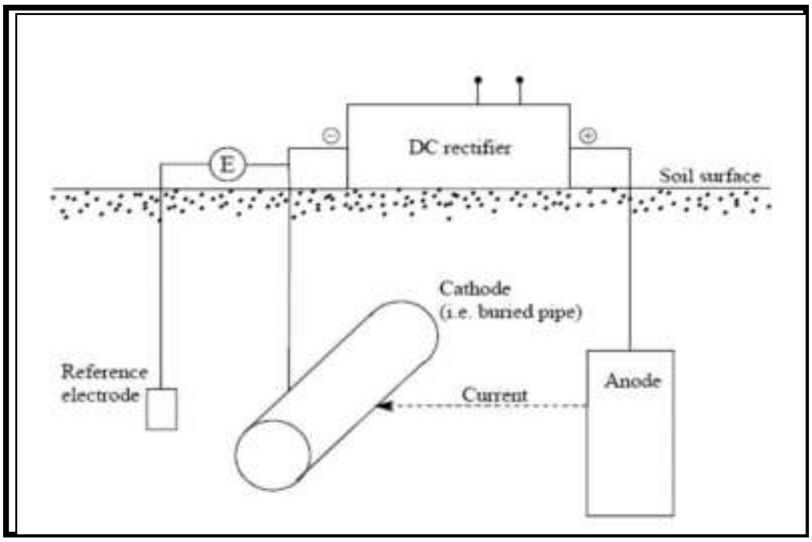


**Fig. 20 Impressed current method**

### (b) Sacrificial anode method

It is based on the principle that the metal structure to be protected when connected with more active metal (more anodic metal), the primary corrosion will be focussed on the more active metal thereby retarding the corrosion of the original metal structure (**Fig. 21**). As per the galvanic series, more active metal being anode suffers more corrosion than cathode being less active metal. Thus this method is termed as sacrificial anodic method as more corrosion occurs on the anodic part ie., sacrificial anode in this case.

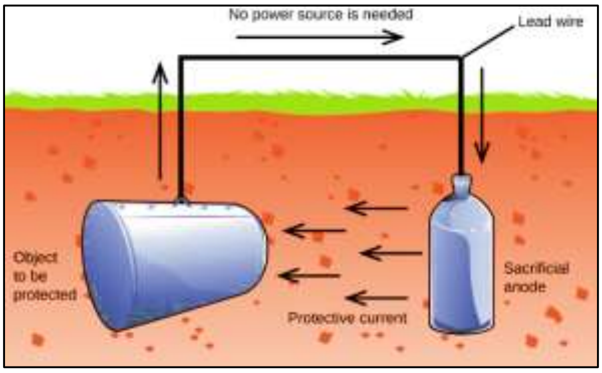


**Fig. 21 Sacrificial anode method**

To mention some of the sacrificial anodes, aluminium, zinc or magnesium can be considered which on complete corrosion will be replaced successively according to the operation. Protection of underground pipelines and cables, marine structures, tanks and boilers could be achieved by this method. It has some of the advantages such as low cost, no power requirement and less maintenance along with its installation in remote area. Due to mutual interference, it cannot be applied for bulk objects and its frequent replacement of anode limits its application[31].

### (v) Protective coatings

Most of the engineering applications demand corrosion resistant materials which is practically impossible due to its high cost, unavailability and ease of fabrication. Quenching these problems seems to be difficult. Though metals such as steel is easily available with low cost fulfilling the necessary criteria, its tendency to get corroded, makes to think of an alternate that could protect the steel surface. One such method that could be adopted is application of protective coatings. These coatings once applied behaves as a protective barrier thereby hindering the contact between metal and aggressive environment. It has got wide recognition as it is capable of providing long term protection ranging from atmospheric protection to immersion condition. As it is capable of providing little strength, structural integrity could be maintained.

### (vi) Environmental factors

This method is a complicated process applicable to closed systems like cooling water treatment, boiler water treatment and waste water treatment. This method could be done with the aid of adding an external agent that could either reduce pH, destroy organic matter, act as inhibitors, reduce dissolved oxygen level or remove scale forming substances. Removing some aggressive reagents like oxygen, microorganisms, solid particulates responsible in creating crevices, specific ions could also implement this method of corrosion control.

### (vii) Inhibitors

Corrosion inhibitors are the substances that are capable of reducing the corrosion at lower concentrations without affecting the environmental components. Inhibitors could be of solid (coatings, concrete or coal slurry), liquid (organic solvents, water, aqueous solution) or gas (vapour) which is selected on the basis of dispersability and solubility. It has got wide range of application in petroleum refineries, chemical manufacturing, water treatment and product additive industries where it acts as a perfect defence against corrosion. Extensive research has been carried out for corrosion inhibitors[32-34] which finds comfortable in closed system with adequate supply of inhibitors. Application of inhibitors should be carefully noticed as one inhibitor can protect specific metal from corrosion, whereas the similar inhibitor could not render protection for the other metal. However the inhibitors used should fulfil the following conditions[35].

- Good protection at lower concentration
- Protect the exposed materials from aggressive medium
- To remain effective at higher temperature and velocity

- Rate of corrosion should not change drastically
- Deposition of reaction products on the metal surface should not occur.
- Suppression of both localised and uniform corrosion should take place.
- It should be efficient for a long duration and
- Reduced toxicity

Most of the inhibitors should be capable of forming a protective film thereby protecting the metal surface from the attack of aggressive medium. In general, organic compounds possessing polar groups with heteroatoms like N, S, O and P atoms has more tendency of adsorbing on the metal surface due to its free electrons. Compounds credited with multiple bonds favour effective adsorption[36,37]. Mechanism of adsorption could be either physical (weak Coulomb force of attraction between inhibitors and metallic atoms) or chemical (strong chemical bonds between inhibitors and metallic atoms). The added inhibitors could act in a way that could retard either cathodic reaction or anodic reaction or both. It is a complicated strategy to design the mechanism of inhibitive action on the metal surface which could depend on the environmental conditions such as concentration, temperature, pH, concentration of anions and other species, molecular structure, functional moieties and nature of metal. But in general, inhibitors could depend on any of the following factors based on which the mechanism of inhibitive action could be decided.

- Adsorption and surface charge on metal
- Structure and functional group of inhibitor
- Inhibitor – water molecule interaction
- Interaction of metal-adsorbed species
- Secondary action – inhibition rendered by the products of corrosion reaction due to primary reaction.
- Blocking reactive sites and forming a surface barrier.
- Modification of electrical double layer
- Involvement in electrode reactions

Such inhibitors based on its electrochemical process can be broadly classified as follows,

- Anodic inhibitors
- Cathodic inhibitors
- Mixed inhibitors

**(a) Anodic inhibitors**

Anodic inhibitors commonly termed as passivation inhibitors works by retarding the anodic reactions in turn reducing the corrosion rate. These inhibitors could be applied in approximate neutral pH levels which is accompanied with sparingly soluble corrosive products like oxides, hydroxides or salts[38]. Passivating inhibitors include oxidising anions (chromates, nitrates, nitrites) and non-oxidising ions (phosphate, tungstate, molybdate) which shifts the corrosion potential to the anodic direction by passivating the metal. The added anodic inhibitor adsorbs on the metallic surface forming protective barrier on the anodic sites which minimises the exposure of metal to aggressive medium and reduces the corrosion rate by increasing the anodic potential. It is important to maintain the concentration of inhibitors above optimised level[39] whose absence could increase the corrosion rate. If the concentration of the inhibitor is too high, anodic current density becomes less than the cathodic current density at primary passivation potential thereby shifting the potential to nobler direction[40]. Insufficient amount of inhibitor provides improper surface coverage leaving the corrosion sites that could result in the formation of localised corrosion, pitting (reduced anodic area to cathode) or generalised corrosion (break down of passivity). The below **Fig. 22**, illustrates the action of anodic inhibitor where it reacts with the resulting ions ($M^{n+}$) released at anode resulting in the formation of insoluble hydroxides that gets deposited on the metal surface.

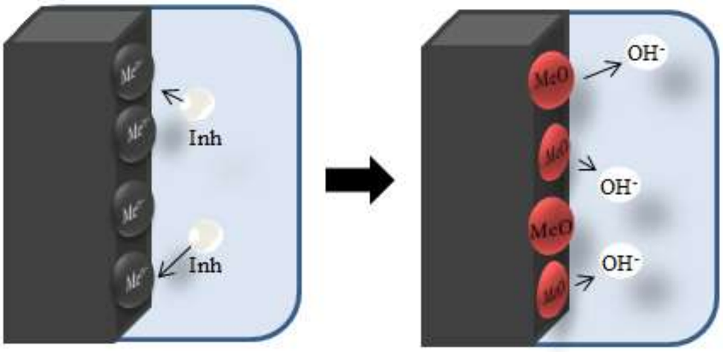


**Fig. 22 Mechanism of anodic inhibition**

**(b) Cathodic inhibitors**

Cathodic inhibitors comprises of cathodic poisons and cathodic precipitators. Different cathodic poisons hinders the reduction of corrosion rate by different mechanisms. To be specific, certain poisons like selenides and sulphides get adsorbed on the metal surface whereas arsenic and antimony has the capability of forming a metallic layer which is reduced at cathode. Cathodic poisons like silicates, borates and phosphates limits the transport of oxygen to the metal by forming a protective film. Cathodic precipitators enable the formation of barrier (insoluble compounds) on the cathodic sites by increasing the alkalinity. As the cathodic area decreases, the cathodic corrosion gets retarded. Polyphosphates, zinc, calcium and magnesium salts can be accounted for corrosion precipitators. The changes observed in cathodic Tafel slope as well as down ward shift ensures that the added inhibitor acts by altering the mechanism and blocking the active sites.

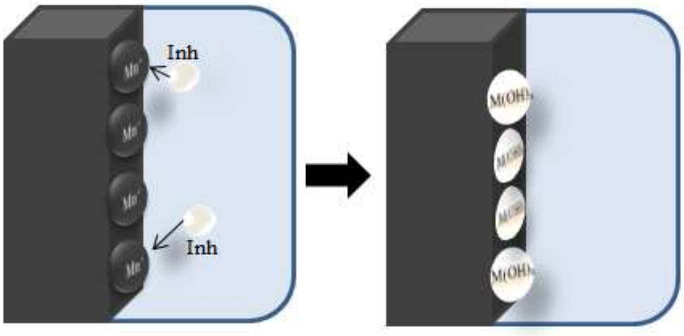


**Fig. 23 Mechanism of cathodic inhibition**

Cathodic inhibitors when added to the aggressive medium enables the formation of insoluble precipitate as a barrier on the metal surface even under complete immersion being predominant than anodic inhibitors. **Fig. 23**, shows the schematic illustration of cathodic inhibiton. Cathodic inhibitors also enables decreased corrosion rate by removing oxygen (reducible species) which can be done by using oxygen scavengers, by vaccum de-aeration and by boiling to decrease the dissolved oxygen levels.

### (c) Mixed inhibitors

Mixed inhibitors are the important class of organic inhibitors comprising of almost 80% that do not fall under cathodic or anodic type. It acts by adsorbing on the metal-solution interface resulting in a stable bond thereby decreasing the metal dissolution. Thus mixed inhibitors are otherwise termed as adsorption inhibitors which could be evidenced from **Fig. 24**. Mixed inhibitors act through the surface adsorption phenomena which mainly depends on the type of electrolyte, surface charge, concentration, contact time[41] chemical structure, cross linking ability, thereby forming a hydrophobic film surrounding the metal. In general, presence of polar functional groups with heteroatoms like S, O, N or P and pi-electron density decides the extent of effectiveness rendered by the inhibitor. The polar sites behave as reactive centres for the adsorption process[42] which results in the blocking of sites responsible for corrosion. Though organic inhibitors are effective and efficient, its biological toxicity and environmental hazards paves the way to find alternate material. Heterocyclic compounds can be accounted for mixed type of inhibitors. Adsorption inhibitors capable of forming the barrier includes volatile inhibitors, surfactants and oil and water based inhibitors.

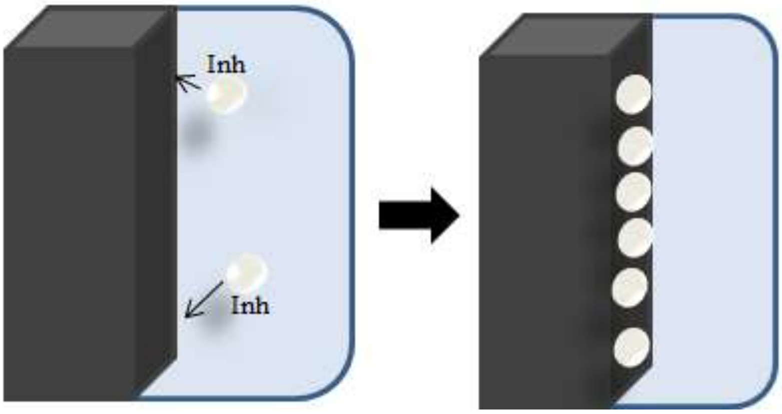


**Fig. 24 Mechanism of adsorption inhibitors**

### (d) Volatile inhibitors

Volatile inhibitors otherwise called as vapour phase inhibitors (VPIs) are used under closed environment where it gets volatised towards the corrosion sites. Volatile nature of corrosion product formed on the metal surface enables the fresh surface of the metal to get corroded. The vapours of the added volatile inhibitors settles on the metal surface as microscopic crystals which dissolves the moisture thereby displacing the water molecules and forming a monomolecular thin transparent film. For ex. oxidation of molybdenum accompanies the formation of molybdenum oxide which is volatile. Addition of basic compounds (morpholine, hydrazine) to the boilers get transported through steam in order to retard the corrosion occurring in condenser tubes by modifying the pH to less acidic level. On the other hand, cyclohexylamine, hexamethylene and dicyclohexylamine behaves as suitable volatile inhibitors for shipping containers.

### (e) Surfactants

Surfactants are the organic compounds mainly comprising of amphiphilic molecules. Combination of hydrophilic and lipophilic molecules are termed as amphiphilic molecules. These molecules are constructed in a way where polar hydrophilic group (head) is attached with non-polar hydrophobic group (tail). Surfactants soluble in both polar and non-polar solvents are additionally credited with good inhibition, low toxicity, easy formulation and low cost[43]. Once the surface concentration of the surfactants become high, its inhibitive action sets in due to the interaction between surfactant hydrocarbon chains by means of weak van der

Waals force of attraction resulting in the formation of an organised structure called hemimcelle, capable of blocking the reactive sites and reducing the corrosion rate[44].

### (f) Oil and water based inhibitors

Oil and water based inhibitors are another class of adsorption inhibitors which acts by hindering the interaction between the metal-water interface through the formation of coatings. Though the film formed is heavy, depending on its specificity it could be soft, coloured, oily, semi hard or transparent with high water repelling property. Water based inhibitors resist oxidation and corrosion process by modifying the metal surface character. Since thin transparent films formed by the water inhibitors could not restrict the interaction of water-metal interface completely, they are less effective than the oil based inhibitors.

### (g) Synergistic inhibitors

Synergistic inhibitors are the blended form of one or more inhibitors ie., either cathodic or anodic or both that can ensure enhanced inhibiton efficiency than that of efficiency rendered by single inhibitor. Few ex. include chromate-phosphates, polyphosphate-silicate, zinc-tannins or zinc-phosphates etc.,.

### (h) Green inhibitors

In order to find an alternate to the existing inhibitors, eco-friendly inhibitors called as green inhibitors are focussed nowadays which are primarily concerned with safety and human health considerations.  Bio-degradability, low cost and eco-friendliness of the plant extracts enriched with phytochemical constituents such as amino acids, alkaloids, tannins, pigments, saponins and flavonoids makes it a promising material in rendering good inhibitive action[45]. Though the green inhibitors are judged as cheap and eco-friendly compounds, it could not fleet longer in certain circumstances due to its laborious time consumption and solvent based extraction and purification methodologies that can lead to environmental issues.

## 1.11 Adsorption process

Adsorption occurs at the surface of the solids forming a thin layer of liquid, gases or dissolved substances depending on their mode of contact. The mutual interaction occurring at the metal-electrolyte boundary leads to the adsorption of ions or neutral molecules on the surface of the bare metal when immersed in solution. The interaction between adsorbate-adsorbate, adsorbate-adsorbent or adsorbate –solvent could be of electrostatic or chemical mode of interaction. Based on the nature of force involved in the interaction, two types of adsorption could be classified as follows[46],

- Physical adsorption – This mode of adsorption is due to the weak vanderwaal's force of interaction between surface charge and ions or dipoles of the inhibitors where the surface charge of the metal depends on free corrosion potential ie., zero charge potential (PZC). Zero charge potential is the potential of the metal against a reference electrode. The dissolved substances of the electrolyte will be adsorbed by the electrode at zero charge potential indicating the net charge of electrode as zero. Thus based on positive or negative potential with respect to zero charge potential makes the electrode to behave either as cathode or anode.
- Chemical adsorption – This type of adsorption leads to the formation of single layer of molecules, atoms or ions on the metal surface by strong covalent bonds which is irreversible. This results due to the electron transfer between metal and the inhibitor molecule added. Chemisorption occurs at slow rate with high activation energy which depends on temperature. Chemisorption being specific to certain metals, depend on the presence of lone pair electrons, multiple bonds, aromaticity and pi-electron clouds.

The following are the important factors which determines the adsorption of inhibitors on the metal surface[47],

- Surface charge – Adsorption may be influenced by the electrostatic force existing between the charge of the metal and ionic charges or dipoles of the inhibitors at the metal-electrolyte interface.
- Structure and functional group of inhibitor – Inhibitors possessing lone pair electrons, multiple bonds, pi-electrons, organic ring system and loosely bound electrons undergo electron transfer to form co-ordinate bond with stronger adsorption. Similarly functional groups containing the elements of group V and group VI of periodic table also facilitates strong adsorption. Thus the inhibition mode depends on the decreased electronegativity lying in the order of $O < N < S < P$.
- Interaction of adsorbed species – The adsorbed species on the metal surface may undergo various interactions either synergism or antagonism which could impart inhibition with suitable mechanistic information.
- Adsorbed inhibitors reactivity – The action rendered by the added inhibitors is called as primary action whereas secondary action results due to the action of reaction products of primary inhibition. The product formed by the secondary action is also inhibitive.

## 1.12 Adsorption isotherm

The adsorption of the added additives (inhibitors) can adopt various mechanism like physisorption, chemisorption, back bonding, electrostatic attraction or complex formation which could block the sites of the metal surface geometrically thereby reducing the area of the metal susceptible for reaction. Inhibiton of corrosion may be due to the electrocatalytic effect of the added compounds or its product which alters the activation energy barriers of anode and cathodic reactions[48,49]. Adsorption is generally defined as the amount of adsorbate adsorbed on the adsorbent at constant temperature as a function of pressure (gases) or concentration (liquids). The first isotherm published by Freundlich was purely empirical which was followed by semi empirical isotherm designed by Irving Langmuir which was based on the following assumptions.

- adsorbent surface being uniform
- no interaction between the adsorbed molecules
- similar mechanism for all adsorption
- monolayer formation

However the above mentioned postulates are seldom true. Surface is always accompanied with certain imperfections, adsorbed molecules need not be inert ever, mechanism never remains the same and monolayer formation is not possible in all cases. Though these problems were acknowledged by BET analysis, Langmuir adsorption isotherm is considered as a fore most choice of adsorption isotherm. Thus in addition to Langmuir model, certain models are discussed.

### (a) Langmuir isotherm

Langmuir adsorption isotherm is generally represented as shown below, where C, $\Theta$ and K represents inhibitor concentration, surface coverage and equilibrium constant.

$$\frac{C}{\theta} = \frac{1}{K} + C$$

A straight line obtained from the plot of C/$\Theta$ vs C gives the slope value close to unity emphasising that each inhibitor molecule occupies one active site on the surface of the electrode. On the other hand, large value of equilibrium constant K reveals stronger adsorption of the inhibitor on the metal surface.

### (b) Temkin isotherm

Temkin isotherm stated as shown includes concentration (C), surface coverage ($\Theta$), adsorption equilibrium constant (K) and attractive parameter (a).

$$\theta = -\frac{2.303\log K}{2a} - \frac{2.303\log C}{2a}$$

Linear relationship arises from a plot of $\theta$ vs log C resulting with a slope and intercept equal to -2.303/2a and -2.303logK/2a from which the attraction parameter ‘a’ derived shows attraction if positive and repulsion if negative within the adsorbed layer[50].

### (c) Flory Huggins isotherm

It represents a straight line on plotting $\log(\theta/C)$ vs $\log(1-\theta)$ with a slope ‘x’ and intercept log K. Value of ‘x’ being positive represents the adsorbed species as bulky ones that could replace the water molecules from the metal surface. It is generally represented as,

$$\log(\theta/C) = \log K + x\log(1-\theta)$$

where C, $\theta$, K and x represents concentration, surface coverage, equilibrium constant and size parameter.

### (d) Frumkin isotherm

Frumkin adsorption isotherm includes the similar terms as mentioned in the above isotherms except ‘α’ which represents interaction among the adsorbed layer. It is expressed as follows,

$$\log(C * \frac{\theta}{1-\theta}) = 2.303\log K + 2\alpha\alpha$$

Plot of $\log(C*\theta/1-\theta)$ vs $\theta$ gives a straight line with a slope ($2\alpha$) and intercept (2.303logK) from which α value deduced being positive insist the attraction of inhibitor on the metal surface.

## 1.13 Techniques used to evaluate corrosion

Metal dissolution in the aggressive medium and its protection mode in presence of added additives (inhibitors) could be evaluated based on the following techniques.

- Non-electrochemical techniques
- Electrochemical techniques
- Non-destructive techniques

### 1.13.1 Non-electrochemical techniques

#### (a) Mass loss method

Mass loss method is one of the most widely used corrosion monitoring technique which simplifies the measurement of corrosion rate allowing to compare the resistance of corrosion of one metal with the other under standard conditions[51,52]. The samples considered for evaluation could be of any metal as per the requirement with standard geometry commonly referred as coupons or test specimens. The preferred coupons were ensured with mirror finish using fresh silicon carbide sheets each time to avoid the contamination of impurities on the metal surface. It was followed by degreasing with suitable solvent, dried and stored in a desiccator for further use to avoid the atmospheric contact. It is noteworthy that the comparison of metal specimens can be made only when treatment of metal surface done is identical. With the aid of plastic wires, glass hooks, holders or test racks one can suspend the coupons within the test medium for the stipulated time. To avoid certain errors, standard procedures can be adopted from ASTM or NACE standard. Based on the immersion tests, a close examination of the changes occurring in the sample immersed could be examined by calculating the difference in mass loss between the weight of the sample before and after immersion. From this difference in mass loss, the extent of corrosion that a metal has undergone ie., corrosion rate can be predicted with the help of below expression,

$$\text{Corrosion rate}\,(\text{gcm}^{-2}\text{hr}^{-1}) = \frac{534 \text{ x W (gms)}}{\text{D x A (cm}^{2}\text{) x T (hrs)}} \text{ x } 100$$

534 is a constant, W is the weight loss in grams, D is density in g/cm$^3$, A is area exposed in cm$^2$ and T is time in hrs.

### 1.13.2 Electrochemical measurements

The corrosion process undergoing an electrochemical mechanism can be assessed by various electrochemical methods which aims in determining the corrosion rates, potential of corrosive reactions, elucidating critical potential and mechanism of corrosion[53]. Such electrochemical measurements include open circuit potential (OCP), linear polarisation resistance (LPR), electrochemical impedance (EIS) and potentiodynamic polarisation technique (PDP). The above measurements were done using a three electrode network with the aid of suitable potentiostat with computer assisted software.

#### (a) Open circuit potential measurements (OCP)

Open circuit potential measurement records the potential of an electrode irrespective of the external current as a function of time occurring on the electrode surface. Since both cathodic and anodic reactions occur simultaneously on the metal surface, both the reaction rates are equal which represents the sample in equilibrium potential also known as corrosion potential or open circuit potential. OCP can be used as a parameter in deciding the resistance of metal to corrosion where more positive OCP value indicates lesser prone to electrochemical corrosion and vice-versa.

### (b) Linear polarisation resistance (LPR)

Linear polarisation resistance is an important technique to determine corrosion rate instantaneously[54]. In this method, a small potential in the range of ± 20mV is applied between the electrodes and the current is measured. Since the applied potential does not influence natural corrosion, LPR is considered as non-destructive method. The potential applied makes the metal to corrode at a faster rate that can produce current due to the passage of metal ions into the solution. The objective of LPR measurement is to determine polarisation resistance ($R_p$) which is a sign of resistance towards oxidation of metal. Thus lower value of $R_p$ indicates higher rate of corrosion and vice-versa. Using the below Stern-Geary equation, polarisation resistance ($R_p$) can be determined.

$$R_p = \frac{b_a * b_c}{2.3 * (I_{corr}) * (b_a + b_c)}$$

where $R_p$, $I_{corr}$, $b_a$ and $b_c$ represents polarization resistance, corrosion current, anodic and cathodic Tafel slopes. Based on the resulting LPR graph, the inhibiton efficiency can be calculated using the below expression.

$$\text{Inhibition effeciency } (\%) = \frac{LPR_i - LPR_{blank}}{LPR_i}$$

where $LPR_i$ and $LPR_{blank}$ corresponds to the linear polarisation resistance values of inhibited and uninhibited medium.

### (c) Electrochemical impedance spectroscopy (EIS)

Detailed insight into the mechanism of corrosion can be determined from electrochemical measurements for inhibitive and coating system. Impedance is measured as the proportionality factor between voltage and current. The response of an electrode can be assessed from the electrochemical impedance spectroscopy by varying the frequency range. It is a non-destructive technique applied to evaluate the corrosion kinetics applying the frequency in the range of 0.1 Hz – 1000 Hz with an amplitude of 20 mV. The results obtained can be interpreted from the equivalent circuit model at electrode-electrolyte interface. The essential parameters used in fitting the equivalent circuit includes solution resistance ($R_s$), double layer capacitance ($C_{dl}$) and polarisation resistance ($R_p$)[55]. High signal to noise ratio results with a small amplitude whereas large amplitude results in non-linearity.

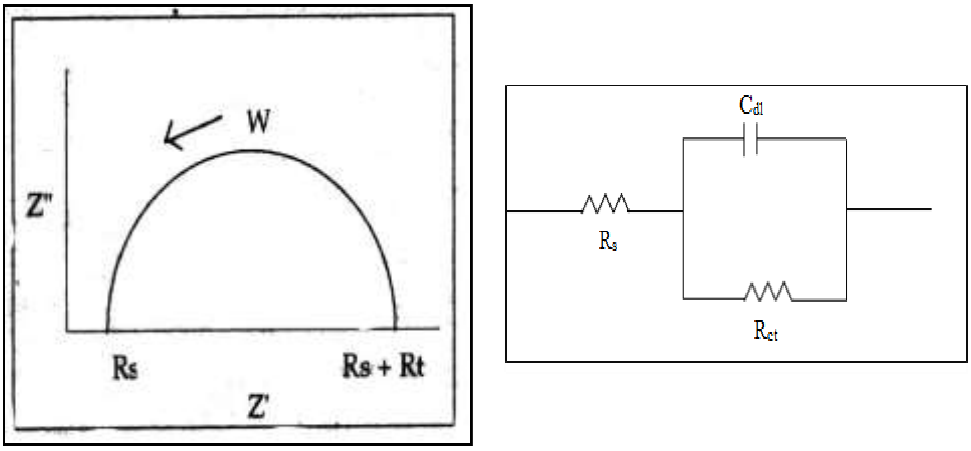


**Fig. 25 Representation of Nyquist lot and equivalent circuit**

Impedance measurements are often represented in the form of Nyquist plot (**Fig. 25**) which is a parallel combination of charge transfer capacitance ($R_{ct}$) and double layer capacitance ($C_{dl}$) in series with solution resistance ($R_{sol}$). It is a plot of Z'' (imaginary part) and Z' (real part). Nyquist plot is a semicircular plot of Z'' vs Z' whose difference between impedance of low frequency and high frequency gives $R_{ct}$ as used in AC corrosion. Increased double layer capacitance could be attributed due to the increased electrical double layer or decreased local dielectric constant that is derived from the below equation,

$$C_{dl} = \frac{\varepsilon\varepsilon_o s}{d}$$

where $\varepsilon_0$, $\varepsilon$, d and S represents permittivity of free space, local dielectric constant, protective layer thickness and surface area of electrode[56].

In order to fit the data more accurately, constant phase element (CPE) is used as double layer capacitance which is obtained by the below expression,

$$Z_{CPE} = R_s + \frac{R_{ct}}{1 + R_{ct} Y(jw)_n}$$

where Y represents CPE constant, j is square root of -1, n indicates roughness or heterogeneity of the metal surface. The CPE constant n = 0 for resistance, -1 for inductance, +1 for capacitance and 0.5 for Warburg impedance.

Relaxation time ($\tau$), is the time taken for charge distribution to return to the equilibrium point after electrical disturbance. The relaxation time ($\tau$) is represented as per the below expression,

$$\tau = 1/2\pi f_{max} = C_{dl}R_{ct}$$

In general, charge transfer resistance ($R_{ct}$) resulting from the impedance measurements indicates the sign of corrosion ie., larger $R_{ct}$ value results with lesser corrosion and vice-versa which influences the adsorption of inhibitor on the metal surface. Metal immersed in an electrolyte generates a double layer between the electrolyte and the metal termed as electrical capacitor. However the added inhibitors with lower dielectric constant either replaces already adsorbed ions or water molecules with higher dielectric constant owing to the adsorption of the added additives on the surface of metal thereby reducing its electrical capacity. Based on $R_{ct}$ values, the inhibiton efficiency is elucidated from the following expression,

$$\text{Inhibition efficiency } (\%) = \frac{R_{ct(inh)} - R_{ct(Blank)}}{R_{ct(inh)}} \times 100$$

where charge transfer resistance in the presence and absence of inhibitors are represented as $R_{ct(inh)}$ and $R_{ct(Blank)}$.

### (d) Potentiodynamic polarisation technique (PDP)

PDP is an important and effective tool in testing the corrosion process whose results are displayed in the form of polarisation curve. Potential sweep, cyclic voltammetry or linear sweep voltammetry are the other terms used to represent potentiodynamic polarisation technique. Polarisation can be otherwise defined as the shift of the electrode potential from their equilibrium causing a decreased current density. This method mainly focusses on measuring the current generated by varying the potential within the selected range which identifies the potential region where electrode activity could take place. In this method, corrosion reaction occurring on the surface of the metal can be controlled making it independent to behave either as cathode or anode. In general polarisation curves can be obtained by scanning the current and recording the potential or vice versa. The controlled changes observed from the steady state behaviour, by the application of potential or current determines the corrosion[57].

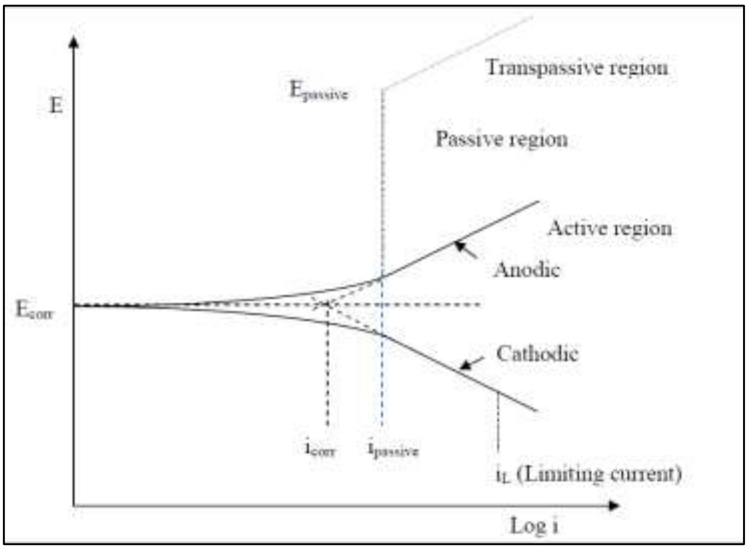


**Fig. 26 Polarisation curve**

From the polarisation curve shown in **Fig. 26**, one can predict corrosion current ($I_{corr}$), corrosion potential ($E_{corr}$), anodic and cathodic Tafel slopes ($b_a$ and $b_c$). Detailed illustration of the **Fig. 27** shows various details where the formation of a protective passive barrier at metal - solution interface is represented as dotted lines. Increase in potential at the anodic direction displayed a passive limiting current ($i_{passive}$). Sharp increase in current density results with the pitting corrosion thereby creating break down of passivity where trans passivity sets in.

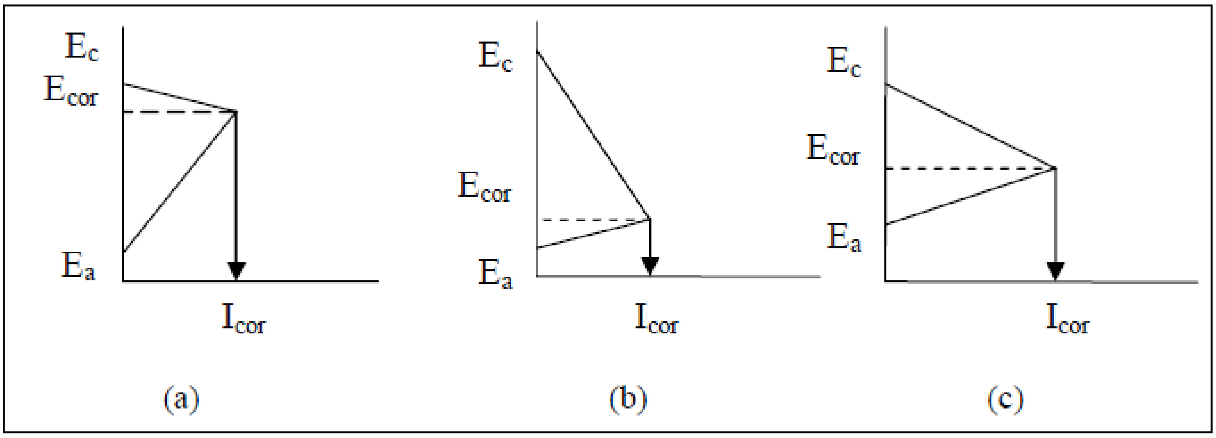


**Fig. 27 Polarisation curves under a) anodic control b) cathodic control c) mixed control**

Corrosion process is initiated due to the flow of current from anodic to cathodic region which is determined by the open circuit potential difference. One of the important factor that controls the polarisation is the concentration of the aggressive species which can get either accumulated at the anode or depleted at cathode determining the progress of corrosion reaction. If the anode undergoes polarisation, the corrosion rate is controlled by anodic polarisation followed by the determination of corrosion current by the anode (**Fig. 27(a)**). **Fig. 27(b)** shows the cathodic polarisation where the corrosion current is under cathodic control. Both the electrodes undergoing polarisation will reveal mixed control as depicted in **Fig. 27(c)**. Depending on the extent of polarisation and parameters obtained, the inhibition efficiency of polarisation technique is calculated using the formula as shown below.

$$\text{Inhibition efficiency } (\%) = \frac{I_{\text{corr(blank)}} - I_{\text{corr(inh)}}}{I_{\text{corr(blank)}}} \times 100$$

where $I_{\text{corr(blank)}}$ and $I_{\text{corr(inh)}}$ represents the corrosion current densities in the absence and presence of inhibitors.

**(e) Hydrogen detection method**

Atomic hydrogen resulting from cathodic corrosion reaction diffuses without combining to form hydrogen molecules. In certain cases, these atomic hydrogen diffuse faster into the materials resulting in the thickness of material as an indicative for corrosion. As the materials are prone to hydrogen blistering and embrittlement, detection of hydrogen should be carried out either by probe or hydrogen monitoring technique electrochemically. In the probe type set up, hydrogen is allowed to diffuse through thin walls of the probe tubes and inserted into the system where the increased pressure as an indication of hydrogen diffusion is measured with pressure gauge or transducer. In the electrochemical set up, hydrogen diffusing through the wall is electrochemically measured by fixing the probe on the surface of the wall. This consists of a palladium foil as working electrode tied with auxillary and reference electrode in sulphuric acid electrolyte medium. With an aid of potentiostat, the anodic potential of the palladium foil is fixed where hydrogen diffusing from the foil is allowed to oxidise with an indication of hydrogen penetration rate.

### 1.13.3 Non-destructive techniques (NDT)

American society for non-destructive testing defines non-destructive testing as " determination of the objects physical condition without affecting its ability". This technique generally applies a probing energy form to analyse the material properties or any material imperfections. Based on the requirements, NDT engineer can preferably choose the right method. The NDT method could be possibly classified as represented below.

- Visual and optical NDT
- Ultrasonic NDT
- Eddy current

- Thermographic NDT
- Magnetic stray flux method
- Potential drop method
- Radiographic method
- Acoustic emission detection method

In order to apply specific method to a specific problem, NDT is able to predict all the parameters including instrumentation, acceptance criteria, calibration levels which is additionally credited with handbooks of key references offered by the ASNT. Thus the below illustration explains the above classification in detail.

### (a) Visual and optical NDT

The most common NDT method over a long duration is visual and optical testing which accompanies a trained inspector coupled with tools like flashlight and magnifying glass. Visual testing stands as a first choice in quality and maintenance stream. Besides looking into the merits of visual testing, one should concentrate on its limitations which makes the task really challenging. In such tough conditions, a device called borescope equipped with miniaturized camera can be fixed at the end of the cable and the images can be viewed in the video screen by inserting a camera into the regions where visual inspection is restricted. Nowadays enhanced visual and optical NDTs play an important role in detecting the deformations on the metal surface generated due to pitting corrosion. Instruments based on digital speckle correlation[58], moire, electronic speckle pattern interference and holography has been implemented nowadays. Direct optical metrology method is used under laboratory conditions to measure pillowing caused by corrosion process.

### (b) Ultrasonic NDT

Ultrasonic NDT method includes unrestricted test objects including metals and even solids. It is an extremely important method which is based on detecting and generating mechanical vibrations or waves within the object to be tested. As the name implies, ultrasonic refers to the sound waves in the frequency range of 1 to 10 MHz which is above human hearing capacity. As the velocity of ultrasonic waves depend on the materials modulus and density, it is suitably used in material characterisation. Since it gets strongly reflected at the boundaries accompanied with change in material property, it is highly useful in thickness measurement and crack detection. Phased array ultrasonics made into portable instruments has gained good attention where the ultrasonic elements within a single transducer allows precise results when introduced into the object under test.

### (c) Eddy current NDT

Eddy current NDT otherwise called as electromagnetic testing (ET) is one of the important method used to analyse the objects throughout their life span. Eddy current NDT works in a principle that, when an alternating current is applied to the conducting coil placed close to the test specimen, the test specimen in turn opposes the alternating current by generating Eddy current which is sensed by similar coil or magnetic field sensors. ET techniques being portable and inexpensive, are helpful in detecting the cracks occurring on the metal specimen. This method is considered as the most common method for aircrafts. Advances made in Eddy current technology such as multichannel portable instruments for fast inspection, magnetic sensors for computer hard drives emphasises its significance.

### (d) Thermographic NDT

Thermal response of the test objects are measured using thermal sensing cameras as sensing objects. It is otherwise termed as infrared imaging method mainly based on the distribution of heat across the surface of test object. Temperature distribution is mapped in a non – contact manner. Thermography includes monitor, IR scanner and a control unit. By careful examination, the corrosion affected areas can be elicited based on thermal distribution. Imaging of disbonds and delaminations in composites can be successfully predicted using flash thermography techniques. Some of the recent significance like usage of high quality cameras with low cost, usage of mechanical energy to stimulate localised heating opens a new field of application.

### (e) Magnetic stray flux method

This method is specifically used to find the defects occurring nearby or under the surface of ferromagnetic materials which due to different magnetic permeability compared with non-magnetic inclusions produces flux on magnetisation. The changes occurring in the cross section of the magnetic lines makes the magnetic line of force to come out of the material including stray flux. The cracks lying below the surface is accompanied with small stray flux whereas the crack in parallel has no tray flux. This method is assisted by magnetising the material primarily and then detection of stray flux is followed. In addition, magnetic probes are also used as detectors for stray flux.

### (f) Potential drop method

Potential drop method is used to measure the depth of the crack. Electric current passed through a work piece is associated with a constant potential drop that is measured between two probes remaining at a constant distance if no crack is observed between the probes. But, if cracks are present between the probes, large voltage drop is observed when compared with crack free case due to the flow of current to a longer distance depending on the depth of the crack.

### (g) Radiographic method

Radiography is one of the important NDT method which gained vast attention after Roentgen's discovery of X-rays in 1895[59]. Even in the earlier days, it was an important technique which was acknowledged by its usage in detecting discontinuation in castings, forgings or welding materials. Most of the issues were readily detected by this technique. Even cracks were able to be detected by this radiographic method where orientation and residual stress should be considered. Despite of its safety and expense, radiography is considered as a wide spread technique by implementing it as digital radiography. In order to detect the hidden defects within the material, radiographic methods are used with the application of X-rays or gamma rays. This method is used to identify the cracks, defects of the components during service, blockages by deposits and abrasive resistance. X-rays and gamma rays can penetrate through the solid material due to its shorter wavelength which is selected based on the nature of problem. On the passage of radiation, it is noticed that only lesser radiation is adsorbed on areas with defects and walls of small thickness. The amount of radiation adsorbed depending on the site will be received by the photographic plate placed behind the irradiated object. A new type of radiographic image based on neutrons can be designed with neutron radiography. This method works on the principle of interacting the neutrons with the nucleus of the atoms rather with the orbital electrons as followed in conventional model. It is capable of imaging lower atomic number distributed with higher atomic number matrix.

### (h) Acoustic emission detection method

It is a high frequency stress wave form which is generated by the rapid release of strain occurring within the material during deformation, crack growth, transformation of phase and scale cracking. Acoustic emission method detects minute acoustic emission signal rendered by the material under stress. When the obtained signals are properly analysed, data concerned with location of defects and its initiation can be predicted. Acoustic emission are of continuous and burst type. Burst type are of short span pulse in the range of 10 μs to a few ms in length associated with strain twining and the development of micro and macro cracking. It has more amplitude compared with continuous type which is similar with Gaussian random noise with varying amplitude depending on acoustic emission activity. Determination of onset localised corrosion, active flaws, surveillance of pressure vessels detection of fatigue fracture, stress corrosion cracking and hydrogen embrittlement are based on the acoustic emission test. The accuracy rendered by the acoustic emission testing is more when compared with the other non-destructive testing methods.

Contributions made by organic compounds containing heteroatoms like O, N, S and P with aromaticity in protecting the metal specimens are always expected to be high. But its tedious synthetic strategy and high cost slowly let to fleet towards eco-friendly green corrosion inhibitors. Though the green inhibitors resulted with a maximum inhibition efficiency, its laborious time consumption and usage of solvents in extraction and purification of the plant extracts has paved the way for the selection of appropriate research problem. Based on the above issues, the present work has been targeted towards polymers, specifically linear aliphatic and aromatic polyesters. A thorough review of literature revealed that limited work has been carried out using polymers in protecting the metal specimens. In order to portray the applications of polyesters in diverse areas, the synthesised polyesters were experimentally evaluated for the prime objectives listed below,

- Evaluation of anti-corrosive potential of synthesised polyesters for mild steel in 0.5 M $H_2SO_4$ test medium.
- Study of enhanced inhibition efficiency in presence of nano metal oxides extracted using *Persia Americana* (avocado) seeds.
- Influence of polyesters in metal protection under various acidic medium.
- Response of selected inhibitors for rebar corrosion in simulate concrete pore solution.
- Protection of titanium alloys in simulated body fluid in presence of selected inhibitors.
- Application of polyester as electrolyte in energy storage devices.

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