CHAPTER I

INTRODUCTION

Corrosion involves the reaction of a metallic material with its environment and it is a natural phenomenon in the sense that the metal is attempting to revert back to its chemically combined state in which it is invariably found in the earth’s crust. Therefore, corrosion is a process that may be expected to occur and should not be regarded as inevitable.

In this world of high technology, usage of metals has become indispensable in all fields. Along with that increased metal usage the problems associated with the use of metals has also risen as boomerang which intimates the humanity a challenge to overcome the crisis that would occur for the metal resources due to the loss of corrosion. The corrosion of steel as a malignant causing losses and threatens the economy of the nation in excess of 100 billion dollars annually worldwide [1].

Even though the natural resources were being bountiful in the past, they got extinct due to the non awareness of the humankind to save the boon of nature. Hence the available resources could be used only for a critical period if we are not taking enough preventive measures against the corrosion in near future. Thus suitable preventive measures are immediately needed to conserve metals for our future generation.

In fact, a lot of preventive measures such as surface treatments, use of inhibitors, surfactants, anodic protections, cathodic protections, organic coatings, metal oxide coatings etc., are in day to day practice. Among them the use of inhibitors has been widely practiced for a long time against corrosion. But there are
areas where usage of inhibitors has become less significant [2] either due to toxicity when exposed to water bodies of the environment or their adverse health effects.

It is well understood that the nature of protective measures is opted based on the root cause for the corrosion. So, a need of more prevailed protective measure to conserve the metals and their alloys against the various corrosions are required. As the polymer coatings possess many advantages like good conductivity, matrix like formation behaviors, delocalization of electrons or ion conducting ability which makes the polymer layers as effective barriers for both physical and chemical diffusion, they play a great role in protecting metal against corrosion.

For many years, electroactive polymers with their $\pi$-conjugated electronic structures have gained great significance in the field of corrosion as inhibitors, protective as well as decorative coatings and sensors [3-14]. Amidst the advantages there are also certain requisites for a good coating such as improved mechanical strength and good adherence with the metal to be protected which bring rare earth metal oxide coatings to enter the scenario as bilayer along with copolymer coatings.

1.1 CORROSION

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a material or metal due to its reaction with corrosive environment [15, 16]. It is keen to recognize that corrosion involves at least one oxidation reaction (usually the metal undergoes corrosion) and at least one reduction reaction typically involving dioxygen, hydrogen ion and/or water.
**Introduction**

---

**Fig. 1** A schematic illustration for the electrochemical reaction occurring in an electrochemical cell.

- **Anode reaction**: \( 2Fe \rightarrow 2Fe^{2+} + 4e^- \)  
  (1.1)

- **Cathode reaction**: \( O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \)  
  (1.2)

Since nothing can be done to alter the thermodynamics of the corrosion process, corrosion control strategies focus on controlling the dynamics or altering the mechanism of the process. Thus the corrosion has been the subject of scientific study for more than 150 years.

### 1.2 COST OF CORROSION

Cost of corrosion is comprised of both direct loss and indirect loss. In a widely-cited study carried out by the National Association of Corrosion Engineers, NACE, the total direct cost of corrosion in the U.S. was estimated as $276 Billion in 1998, approximately 3.1 % of GDP. However, the closer examination of the NACE data indicates that the corrosion cost is approaching 1 trillion dollars in the U.S. now and will cross the milestone in 2012.
Thus the annual loss and cost debatable for corrosion management are of great importance in modern societies. Not only the economic loss but also has dramatic adverse effect for human beings as well as environment that adds to the cost of corrosion. Hence, there is a great demand for eliminating or reducing corrosion so as to save 20-25 % of that worldwide annual cost of corrosion.

In precise, corrosion being an electrochemical phenomenon can be tackled by the use of electrochemistry and conducting polymers with the proper knowledge and awareness of its consequences [17].

**Consequences of corrosion**

Some important consequences of corrosion are:

- □ Plant shutdowns
- □ Loss of products
- □ Loss of efficiency
- □ Contamination
- □ Nuclear hazards

Moreover the consequences entirely depend on the extent of corrosion and the sensitivity of a particular metal or alloy to the specific environment in which it is exposed.

1.3 **WHY CORROSION STUDY IS INDISPENSABLE?**

Corrosion is a major threat to the environment as it spreads its impact in various forms such as economic inflation, huge disasters, industrial failures, power shut downs etc. The three main reasons for the importance of corrosion study are economy, safety and conservation. So a basic understanding of corrosion as well as
its consequences and their preventive measures plays a pivotal role. To prevent the extinction of metal resources, we need to understand first how these resources are destroyed by corrosion and how they must be preserved by applying corrosion protection technology. Engineering knowledge is incomplete without an understanding of corrosion. Several engineering disasters, such as crashing of civil and military aircraft, naval and passenger ships, explosion of oil pipelines and oil storage tanks, collapse of bridges and decks and failure of drilling platforms and tanker trucks have been witnessed in recent years. So applying the knowledge of corrosion protection can minimize such disasters. For instance, water can become contaminated by corrosion products and unsuitable for consumption. Thus, corrosion professionals must understand the effects of environmental conditions such as soil resistivity, humidity, and exposure to salt water on various types of materials; the type of product to be processed, handled, or transported; required lifetime of the structure or component; proximity to corrosion-causing phenomena such as stray current from rail systems; appropriate mitigation methods; and other considerations such as before determining the specific corrosion problem and specifying an effective solution.

Based on all above discussions, we deal with the classification of corrosion which is important for a corrosion scientist.

### 1.4 TYPES OF CORROSION

Corrosion can be classified based on many criterions.

While considering a system involving temperature, the corrosion can be classified as
Low temperature corrosion

High temperature corrosion.

Corrosion can also be classified as follows:

- **Dry or chemical corrosion**

  Dry corrosion is a form of corrosion that caused by direct chemical action of atmospheric gases such as oxygen, halogen, sulphur dioxide, hydrogen sulphide with metal surfaces (high temperature oxidation) that occur at elevated temperature without a liquid phase.

- **Wet or electrochemical corrosion**

  Wet corrosion is a common form of corrosion, means the direct attack of liquid phase when it is in direct contact with (i) metal or (ii) two dissimilar metals or alloys are either immersed or dipped partially in a solution.

  For example: Condensed humidity or acid or alkali, on metal.

Whereas based on the mechanisms involved, this can be further sorted as

- **(a) Separable anode or cathode type**

  In this type certain areas of the metal can be experimentally identified as predominantly cathodic or anodic where the distance of separation between the areas may be very small and thus there will be a macroscopic flow of charge through the metal.

- **(b) Interfacial anode or cathode type**

  Here one entire interface will be anode and the other will be cathode, thus the charge is transported through a film of reaction product on the metal surface.
(c) Inseparable anode or cathode type

Unlike the other two types the anodes and cathodes cannot be distinguished experimentally but their presence is postulated theoretically.

1.5 FORMS OF CORROSION

The factors influencing corrosion differs for each environmental conditions and thus only a clear understanding of these factors will help to prevent those detrimental failures and loss [18-20].

1.5.1 Uniform Corrosion

Uniform or general corrosion is characterized by the existence of several individual electrochemical processes that occur uniformly over the whole surface of the metal as seen in Fig. 2. Uniform corrosion can be limited or prevented by an appropriate choice of material, including the use of metallic or organic coatings, modification of the medium (pH, temperature, concentrations of dissolved oxygen and electroactive impurities, addition of inhibitors, etc.), and cathodic protection [21]. The consequences of uniform corrosion are a decrease in metal thickness per unit time (or a weight loss per unit area per unit time).

Fig. 2 An example for uniform corrosion.
1.5.2 Pitting Corrosion

Pitting corrosion is particularly insidious and the attack is in the form of highly localized holes that can penetrate inwards rapidly, while the rest of the surface remains intact [22]. Figure 3 shows an illustrative example for a component that got perforated within few days with no appreciable loss in weight on the structure as a whole. Pitting corrosion is most aggressive in solutions containing chloride, bromide or hypochlorite ions. Iodides and fluorides are much less harmful. The presence of sulfides and H$_2$S enhances pitting corrosion, and systematically impairs the resistance criteria for this type of attack.

![Fig. 3 An illustration for pitting corrosion.](image)

The presence of an oxidizing cation (Fe$^{3+}$, Cu$^{2+}$, Hg$^{2+}$, etc.) enables the formation of pits even in the absence of oxygen. However, in the presence of oxygen, all chlorides become dangerous, and this is also true in the presence of hydrogen peroxide. Means of reducing or preventing pitting corrosion is to choose the material most appropriate for the service conditions, avoid stagnant zones and deposits, reduce the aggressiveness of the medium and use cathodic protection.
1.5.3 **Galvanic Corrosion**

Galvanic corrosion or galvanic coupling can be defined simply as being the effect resulting from contact between two different metals or alloys in a conducting corrosive environment [23]. When two different metals or alloys immersed in the same solution are joined together electrically, an electric current will be set up between them, resulting from the short circuit created. The coupling potential must lie between the two potentials for the uncoupled metals and an increase in corrosion is generally observed in the less noble alloy and a decrease or suppression of corrosion in the more noble material. Due to modifications in the electrolyte, inversions may occur in the potential series.

For example,

- Zinc covered with corrosion products can become more "noble" than iron in certain hot waters (problem encountered in domestic hot water tanks).

- Tin can become less "noble" than iron in organic acid solutions (problem encountered in food cans).

Some means of preventing galvanic corrosion could be achieved by choosing the metal combinations in which the constituents are as close as possible in the corresponding galvanic series and by avoiding an unfavorable surface area ratio. Also wherever possible, using a seal, insulator, coating, etc., to avoid direct contact between two different metals, avoid threaded junctions between materials widely separated in the galvanic series. **Figure 4** shows an illustration for the prevailing galvanic corrosion.
1.5.4. Crevice Corrosion

This form of attack is generally associated with the presence of small volumes of stagnant solution in occluded interstices, beneath deposits and seals, or in crevices, e.g. at nuts and rivet heads [24]. Deposits of sand, dust, scale and corrosion products can all create zones where the liquid can only be renewed with great difficulty. Crevice corrosion is encountered particularly in metals and alloys which owe their resistance to the stability of a passive film, since these films are unstable in the presence of high concentrations of Cl⁻ and H⁺ ions.

As can be seen in the schematic illustration in Fig. 5. The basic mechanism underlying the crevice corrosion in passivatable alloys when exposed to aerated chloride-rich media leads to gradual acidification of the solution inside the crevice, leading to the appearance of highly aggressive local conditions that destroy the passivity in interstices, convection in the liquid is strongly impeded and the dissolved oxygen is locally rapidly exhausted.
Introduction

Fig. 5 A schematic representation for crevice corrosion.

The dissolution reaction in the crevice is then promoted and the oxygen reduction reaction becomes localized on the external surface close to the crevice. This "autocatalytic" process accelerates rapidly, even if several days or weeks were necessary to get it under way.

Means of preventing or limiting crevice corrosion

Use welds rather than bolted or riveted joints, design installations to enable complete draining (no corners or stagnant zones), hydrofuge any interstices that cannot be eliminated, and in particular, grease all seals and seal planes, use only solid, non-porous seals, etc.

1.5.5 Erosion Corrosion

Erosion corrosion which is also called as abrasion corrosion is caused by the relative movement between a corrosive fluid and a metal surface (Fig. 6). The mechanical aspect of the movement is important in which the friction and wear phenomena can be involved [25]. This process leads to the formation of grooves, valleys, wavy surfaces, holes, etc., with a characteristic directional appearance comet tails, horseshoe marks, etc. Most metals and alloys can be affected,
Introduction

particularly soft materials (e.g., copper, lead, etc.) or those whose corrosion resistance depends on the existence of a surface film (aluminium, stainless steels).

![Image](image_url)

**Fig. 6 A schematic representation for erosion corrosion**

Means of limiting erosion corrosion can be done by choosing a more resistant material by improving the plant design with adjusting the medium by controlling the oxygen content, lowering the temperature, using inhibitors and by filtering out solid particles.

1.5.6 Fretting Corrosion

Fretting corrosion is a combined damage mechanism involving corrosion at points where two moving metal surfaces make rubbing contact as shown in the **Fig. 7** which demonstrates fretting corrosion that occurs at an axle-cylinder contact point. It occurs essentially when the interface is subjected to vibrations (repeated relative movement of the two contacting surfaces) and for compressive loads [26]. The amplitude of the relative movement is very small, typically of the order of a few microns. When the frictional movement in a corrosive medium is continuous, the resulting process is termed tribocorrosion.
Introduction

Fig. 7 Illustration of fretting corrosion at an axle-cylinder contact point.

Means of preventing fretting corrosion:

- Lubrication with oils or greases to reduce friction and exclude oxygen from the interface.
- Increase in the hardness of one or both materials in contact. Certain material combinations show better friction behavior than other.
- Use of seals to absorb vibrations and exclude oxygen and/or moisture.
- Reduction of the friction loads in certain cases, or on the contrary increase of the friction loads to attenuate vibrations.
- Modification of the amplitude of the relative movement between two contacting surfaces.

1.5.7 Intergranular Corrosion

This type of corrosion is either due to the presence of impurities in the boundaries, or to local enrichment or depletion of one or more alloying elements [27]. For example, small quantities of iron in aluminium or titanium (metals in which iron has a low solubility) segregate to the grain boundaries where they can induce intergranular corrosion. The exfoliation corrosion phenomenon observed in rolled aluminium alloys is usually but not always, intergranular in nature.
Fig. 8 Intergranular corrosion morphology inside a water pipeline.

In this case, the corrosion products occupy a larger volume than the metal "consumed", generating a high pressure on the slivers of uncorroded metal, leading to the formation of blisters. Numerous alloy types can undergo intergranular attack, but the most important practical example is the intergranular corrosion of austenitic stainless steels, related to chromium depletion in the vicinity of the boundaries, due to the intergranular precipitation of chromium carbides (Cr$_{23}$C$_6$), during a "sensitizing" heat treatment or thermal cycle as seen in Fig. 8.

1.5.8 Corrosion Fatigue

Corrosion fatigue is defined as the reduction of fatigue strength due to the presence of corrosive environment [28]. In contrary to the purely mechanical fatigue, the applied stress are no longer static, but cyclic (periodically fluctuating or alternating loads). In the case of steels, the conventional fatigue limit determined from the so-called Wöhler curves (applied stress as a function of cycles to failure $\delta = f(N)$) does not exist for tests performed in a corrosive medium (Fig. 9).
Fig. 9 Applied stress versus cycles to failure.

Whatever the stress level, failure will eventually occur after a finite number of cycles. The cracks are generally transgranular in nature, with little tendency for branching. However, a few small secondary cracks may appear in the vicinity of the main crack. Although there is no direct relationship between the sensitivity to corrosion-fatigue and the mechanical properties of the material, high strength alloys tend to be most highly prone.

Corrosion-fatigue damage can be prevented or reduced by decreasing the tensile stresses, either by the use of stress-relief annealing, by modifying component design, or by applying mechanical surface treatments such as peening, to introduce surface compressive stresses.

1.5.9 **Stress Corrosion Cracking (SCC)**

Stress corrosion cracking is a process involving the initiation of cracks and their propagation, possibly up to complete failure of a component, due to the combined action of tensile mechanical loading and a corrosive medium. Indeed, the
presence of tensile stresses which is dangerous, compressive stresses exerting a protective influence which could cause SCC can be seen in Fig. 10. SCC frequently occurs in media that are little or non-aggressive towards the metal or alloy concerned in the absence of tensile loading (e.g., austenitic stainless steels in high temperature water and steam). The associated weight losses are generally very small and even insignificant compared to the extent of the overall damage incurred.

![Image](image_url)

**Fig. 10 An example for stress corrosion cracking.**

This form of corrosion is of great practical importance and represents a permanent risk in numerous industrial installations, in terms of both the economic consequences and the safety considerations are involved. There is no known category of commercial metals and alloys that is fully immune to SCC. Even materials such as glasses, plastics and rubbers can also be prone to this type of attack in certain conditions. The time necessary for a part to fail by SCC can vary from a few minutes to several years [29].

Means of reducing or preventing stress corrosion cracking are: elimination of residual stresses by stress relieving heat treatments, purification of the medium, choice of the most appropriate material, improvement of the surface condition, avoid
surface machining stresses, perform peeling treatments on welds to induce surface compressive stresses, apply external protection methods.

1.5.10 Hydrogen Embrittlement

The presence of hydrogen atoms in a metal crystal lattice can be extremely detrimental, leading to a catastrophic loss of mechanical strength and ductility. It is generally accepted that the hydrogen is initially adsorbed on the metal surface before penetrating the lattice, where it diffuses in ionic form (i.e., as protons). The hydrogen atoms can have various origins from the surrounding atmosphere containing hydrogen or hydrogenated compounds (H₂S, NH₃, H₂O, etc.) during the electroplating process in which the proton reduction reaction occurs.

For Example:

- Recombination to molecular hydrogen when the metal contains macroscopic discontinuities or microscopic defects. The hydrogen molecules are unable to diffuse away into the lattice and builds up high local pressures, leading to the formation of flakes and blisters, and "ladder-type" cracking.

- Hydrogen atoms, by interacting with lattice dislocations, cause a marked loss in the plastic strain capacity of the metal, which becomes brittle.

Means of preventing blistering and hydrogen embrittlement are:

- Reduce the corrosion rate, modify the electroplating conditions, change the alloy, take appropriate precautions during welding and so on.

- For prevention of blistering: use sound steels containing few inclusions and defects, use coatings "impermeable" to hydrogen (nickel or enamel coated steel tanks, austenitic stainless steel cladding, rubber, polymers, etc.),
employ inhibitors in the case of an aggressive medium operating in a closed circuit, etc.

1.5.11 Microbial Corrosion

Corrosion caused the metabolic activity of various micro-organisms, is called “microbial corrosion” or “Microbiologically Influenced Corrosion (MIC)”. It can apply to both metals and non-metallic materials [30]. This corrosion can take many forms and can be controlled by biocides or by conventional corrosion control methods. There are a number of mechanisms associated with this form of corrosion. Most MIC takes the form of pits that form underneath colonies of living organic matter and mineral and biodeposits. This biofilm creates a protective environment where conditions can become quite corrosive and corrosion is accelerated.

![Image](image.jpg)

**Fig. 11 A schematic illustration for microbial corrosion.**

Thus a thorough knowledge of different corrosions along with their causing agents alone cannot provide a success to an industrialist who seeks for cent percent economy. Hence a view on types of metal and reasoning for selecting a specific type as per the need were carried out in the following discussions.
1.6 STAINLESS STEEL

“Stainless Steel” as is it is coined, the term implies a resistance to straining, rusting, pitting, moisture and pollution. The German word “rostfrei” was, in fact, used by the inventor for this material because the alloy was considered to be “absolutely rustproof in damp air” [31].

The American Iron and Steel Institute (AISI) lists more than 40 approved wrought stainless steel according to chemical composition and other properties. The American Society for Testing and Materials (ASTM) calls for the same specifications with additional requirements of mechanical properties and dimensional tolerance. The Alloy Casting Institute (ACI) specifies composition for cast stainless steels within the categories of corrosion and heat resisting alloys. The various types of stainless steel which are mainly employed can be given as follows;

1.6.1 Ferritic

Chromium-iron alloys with 17-27 % chromium and low carbon content, with magnetic properties. Cooking utensils made of this type contain the higher chromium levels. Type 430 is the most commonly used ferritic and is called as ferritic due to its analogous ferrite phase having body centered cubic atomic structures. Ferritic stainless steel is similar to those of carbon steel in their mechanical properties, are magnetic and less ductile.

1.6.2 Martensitic

Chromium - iron alloys with 10.5 – 17 % chromium and their carbon content can be controlled carefully by quenching (quickly cooled in water or oil) and tempering (heated then cooled). These alloys are ferromagnetic in nature and they
are hardenable because of the phase transformation from that of body centered cubic to body-centered tetragonal phase and these are commonly used in making knives. Martensitic grades are strong and hard, but are brittle and difficult to form as well as weld. Type 420 (S42000) is a typical example for this type of stainless steel.

1.6.3 Austenitic

This is the largest category of stainless steel, accounting for about 70 % of the overall production. The austenitic class offers the most resistance to corrosion in the stainless group, owing to its substantial nickel content and higher levels of chromium. Chromium-nickel-iron alloys with 16-26 % chromium, 6-22 % nickel (Ni), and low carbon content, with non-magnetic properties (if annealed - working it at low temperatures, then heated and cooled). Hardenable by cold-working (worked at low temperatures) as well as tempering (heated then cooled). Ductility (ability to change shape without fracture) is exceptional for the austenitic stainless steels.

Excellent weldability and superior performance in very low-temperature services are additional features of this class. Hence with these excellences, the development of austenitic stainless steel was one of the most significant metallurgical accomplishments of the twentieth century. Reducing the nickel content in austenitic stainless steel significantly reduces its price. Nickel’s ability to stabilize and form austenite is however, an integral part in the processing of austenitic stainless steel, and if the nickel content is to be reduced appreciably.

Two additional classes worth mentioning include duplex (with austenitic and ferritic structures), and precipitation Hardening stainless steel are used in certain extreme conditions.
1.7  LOW NICKEL STAINLESS STEEL

Low nickel stainless steel belongs to AISI of type 200 stainless steel comprises austenitic chromium-nickel-manganese stainless steel that were developed in the 1950’s. There has been a wide variety of application for stainless steel as constructive metallic supports of catalytically active systems in exhaust gas converters. It also plays a significant role as constructive materials for pipe works in power plants, cooling water systems, oil and gas production industries due to its good workability, corrosion resistance and low cost [32].

Nickel costs $20000 /tonne (2011) and is expected to increase which make the stainless steel series of high nickel content as costly. Hence the composition of stainless steel with low nickel content of 4 % with an increased chromium level up to 17 % determines a competitive role in much application like industries, pipelines storage tanks etc. Therefore the alloying of steel plays an important task in improving the mechanical strength and in reducing the cost of stainless steel material using other austenitic forming elements, such as carbon, nitrogen, manganese and copper need partial or complete replacement of nickel [33, 34].

1.8  CORROSION PREVENTION MEASURES

Corrosion and its control is an important, but often neglected element that could cause catastrophic accidents in oil and gas industry. Corrosion engineering seeks to minimize corrosion costs for a particular owner or operator. Because of the distorting influence of taxation on costs, it does not necessarily minimize total corrosion costs for society as a whole. Selection of a material for use in a corrosion situation must be based on sound economics. Both the cost of the material and the
ongoing cost of preventive measures must be included. In the view of an corrosion
expert, the preventive measures are wide such as usage of inhibitors, using a design
that will avoid corrosion, changing potentials and applying coatings etc., based on
the prevailing conditions to prevent corrosion on metals has been underway using
different techniques along with the consideration of economical and constructive
supports in many industrial applications. In precise, even though the class of
stainless steel is uncorrodable, exposure under corrosive conditions may initiate less
rapid corrosion. The prolonged corrosive attack would lead to detrimental effects in
all applications, thus corrosion control using appropriate method plays a key role
and are discussed subsequently.

1.8.1 Proper Designing of the Material

The designing of the material should be in such a way that, even if corrosion
occurs, it must be uniform not intense and should never be a localized corrosion
[35,36].

1.8.2 Corrosion Inhibitors

A substance which effectively decreases the corrosion of a metal while
added in small quantities to the aqueous corrosive environment is coined as
inhibitors. Based on the inhibition mechanism the corrosion inhibitors can be given
as follows;

• Anodic Inhibitors
• Cathodic Inhibitors
• Mixed Inhibitors
• Volatile corrosion Inhibitors
1.8.3 Cathodic Protection

- Sacrificial anode type

In this protection method, the metallic structure to be protected will be connected to more anodic (active) metal which would act as a sacrificial anode and thus the cathodic part (metal need to be protected) will be safe against corrosion.

Metals such as aluminum or zinc are fitted to the ship side or in the tank at strategic positions which form the anode of the corrosion cell making the steel of the ship plating the cathode. The sacrificial anodes are gradually corroded away and have a life of about 2-4 years when they have to be replaced, usually at dry dock.

- Impressed current type

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, a sufficient d.c. current is applied to an insoluble anode, buried in the corroding medium and connected to the metallic structures to be protected.

1.8.4 Protective Coatings

Protective coatings function by virtue of the interposition of continuous physical barriers between the coated-surface and its environment. Conducting polymers and ceria/copolymer bilayer coatings imparts both mechanical and physical properties such as wear resistance, hardness. Thus the protective organic coatings encourage the use of low cost steel alloys instead of corrosion resistant high cost alloys for construction supports which reduces the cost [37]. The economic argument in relation to corrosion control is really concerned with the conflict between capital costs and maintenance costs. Protective coatings could thus offer a
better solution for the argument based on the nature of corrosive environment. The deciding factor may even be the ready availability of the resources needed for corrosion prevention using cost effective agents. These coating in general must have the basic properties such as,

- Good resistance to corrosion
- It must be good adherent with the substrate used
- Must provide a uniform surface coverage
- Sufficient thickness
- A low diffusion rate to corrosive ions

**Excellence of coating towards corrosion control**

Thus among the varied protection techniques, the coatings on the substrate against corrosion protection has literally proved its advantages for more than three decades. The coatings provide significant cost savings to waste packages, design and mitigate aggressive corrosion conditions of the environment. Coatings tend to act as barriers against corrosion between the metal and the corrosive environment by being adherent to substrate, provides an enhanced life and minimize the maintenance costs for the substrate considerably.

According to the nature of corrosion resistance offered they can be further classified as follows;

- Conversion coatings
- Anodic coatings
- Cathodic coatings
- Barrier coatings
Moreover among all, barrier coatings prevail as significant can be given in detail as

- **Metallic coating**

  Protection of metal from corrosion by the use of metal coatings may be achieved by cathodic coating (chromium on steel) and anodic coating (zinc on steel). The coating of metals using metal oxides such as Al₂O₃, Chromates etc., are hazardous to the environment as well as health and thus their usage in coatings or surface treatments on metallic substrates are restricted in many countries to avoid the carcinogenic diseases.

- **Non-metallic coatings**

  Two types of nonmetallic coating are used for corrosion protection. They are inorganic coatings

  - **Organic coating**

    In many industries epoxy, chlorinated rubber and polyvinyl chloride coatings are widely used which serves as a barrier to water, oxygen and prevent the occurrence of a cathodic reaction beneath the coating

    Examples: varnishes, paints, enamels and lacquers.

  - **Inorganic coating (varnishes, paints, enamels and lacquers**

    These coatings are performed using ceramics and glass. These coatings are impervious until they are not mechanically damaged.

    Examples: vitreous enamels, portland cement, oxide film coating.
From the above discussion the barrier coatings are seemed to have greater significance in the anticorrosion performance for a metal, which insisted us to work on the copolymer (Organic) coatings and their electrochemical performances.

1.9 POLYMER

The word polymer is derived from the classical Greek words *poly* meaning “many” and *meres* meaning “parts”. A polymer is a long chain molecule that is composed of a large number of *repeating units* of identical structure. Polymers can be classified as conducting and nonconducting as per their conductivity nature [38].

1.9.1 Types of Polymers

Polymers can be classified widely as homopolymers and copolymers based on the repetition of monomer units. The electrodeposition of conducting polymers on electrode surfaces has been a very active research area in electrochemistry for almost two decades. The great deal of interest for the copolymer in this coating technology is due to the large number of potential applications of the conducting polymer.

Based on the conductivity polymers can be classified broadly as conducting polymers and non conducting polymers.

1.9.2 Conducting Polymers

Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity [39]. The electrical properties can be fine-tuned using the methods of organic synthesis and by
advanced dispersion techniques [40]. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, super capacitors, biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs [41]. The new nanostructured forms of conducting polymers particularly provide fresh air to this field with their higher surface area and better dispersability.

1.9.3 Mechanism for the Conductivity of Polymers

Conducting polymers have backbones of continuous sp$^2$ hybridized carbon centers. One valence electron on each center resides in a $p_z$ orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons [38]. Thus, the conjugated $p$-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band.

To be an ideal protective cover against atmospheric or electrochemical corrosion a polymer must present a structure without free ions, water or oxygen. Also the mobility of the ions must be equal to zero, as well as the oxygen and water diffusion coefficients.
The modification of conducting polymer films can be achieved by application of some top coatings, cementation of metal, or with adduct in monomer unit which is generally an aromatic ring.

1.10 ELECTROCHEMICAL SYNTHESIS OF POLYMERS

Electrochemical synthesis involves electrolysis of a solution containing both monomer and electrolyte. A monomer molecule will receive an electron at the cathode to become a radical anion, and a monomer molecule will give up an electron at the anode to form a radical cation. The radical ions then initiate free radical (and/or ionic) polymerization. This type of initiation is especially useful for coating metal surfaces with polymer films. The advantages of electrochemical methods are short measurement time and mechanistic information that they provide which help not only in the design of corrosion protection strategies but also in the design of new anticorrosive agent.

1.10.1 Free Radical Polymerization

Free radical polymerization is a method of polymerization by which a polymer forms by the successive addition of free radical building blocks. Free radicals can be formed via a number of different mechanisms usually involving separate initiator molecules. Following its generation, the initiating free radical adds (nonradical) monomer units, thereby growing the polymer chain.
1.11 TYPES OF SYNTHESIS

**Step growth polymerization**

Step growth polymerization is usually used for monomers with functional groups such as OH, COOH etc. It is usually a succession of non-catalyzed, chemical condensation reactions associated with the elimination of low-molar-mass side products e.g., water.

**Addition polymerization**

Addition polymerization involves the polymerization of olefinic monomers. This type occurs via a chain reaction. The monomers are converted into polymers by opening of the double bond with a free radical or ionic initiator. The products will have the same chemical composition.

**Insertion polymerization**

This type of polymerization occurs via an insertion of a monomer at the end of the growing chain.
1.12 HOMOPOLYMER

Conducting homopolymer such as polyindole, polypyrrole and polythiophene have been found to reduce sufficiently the corrosion of iron, steel and other oxidizable metallic materials [42,43]. These polymers can be electrochemically deposited on the oxidizable metal and used for anticorrosion performance to the metal against the corrosive environment. But there are limitations with the applications of conductive homopolymer films as anticorrosive coating on oxidizable metals such as the possible presence of open porosity throughout the coating that make the homopolymers least protective towards metallic corrosion and also less adhesive amidst their low conductivity. These criterion arise a need for a copolymer coating as it could substantiate the necessity of a protective coating.

1.12.1 Role of Copolymers in Corrosion Protection

For many years electroactive polymers have gained prime importance in the field of anti-corrosion coatings and sensors. Garnier et al., [44] was the first to report polyindole electrochemically synthesized and used subsequently for a variety of purposes. Polymers are able to exhibit physical barrier behavior. They are also capable to provide anodic protection to steel. But the main advantage of conducting copolymers is that they acts as good barrier due to the redox behavior improving the protection than that could be afforded by other materials. The anticorrosive performance of copolymer coating was investigated and they seemed to exhibit a significant physical barrier property against the formation of corrosive products for longer periods Copolymers coatings are more advantageous with increased conductivity, good thermal stability and a higher degree of backbone conjugation.
owing to their intriguing electronic as well as redox properties and thus can form substitutes for homopolymer coatings [41].

1.13 NEED FOR BILAYER COATING

In real the copolymer coatings will have better corrosion performance but deprived of mechanical properties such as hardness, adhesive strength and wear resistance. This demands a presence of adherent conductive coating in our study which on coated with copolymer forms a bilayer comprised of an improved mechanical properties along with enhanced corrosion protective behavior. The major problems associated with conducting polymer films as anticorrosion materials are the possible presence of open porosity throughout the coatings, which will lead to the water up taking of process occurring along these pores. In fact, the hydrophilic groups of monomers given rise to increase of water amount held by coating continuously. As a result, the coatings become saturated with electrolyte solution and leads to disadvantages.

Yet there are constraints with the use of copolymer coatings, much attention has been paid for improvement of these types of coatings for various purposes, due to economy and striking properties offered by conducting polymers such as ease probability, conductivity and retain of redox behavior in itself. Thus the bilayer coating worked out has proved a closely packed morphology, suitable for acting as both physical and chemical diffusion barriers.

1.13.1 Trend of bilayers

During the past decade, many researchers have devoted much effort towards bilayer or multilayer coating towards anticorrosive performance. This was done with
an aim of attaining the desirable properties and also to nullify the drawbacks of the individual coatings. Moreover these bilayers as well as the multilayered coatings are highly anticipated with no porosity, improved adhesion towards the substrate, an impervious nature with increased mechanical strength and good protection performance against corrosion.

1.14 CERIA AS AN ANTICORROSIVE AGENT

Cerium has a considerable interest as a promising agent against corrosion which is nevertheless studied as an environmentally friendly alternative as it acts as mixed type inhibitor reducing both cathodic and slightly anodic activities. The rare earth metal oxide (ceria) coatings possess a good mechanical strength and have no deterioration for considerable duration even in adverse environmental conditions which makes it a better anticorrosive agent.

Thus in our work, the copolymer coating have better corrosion performance but deprived of mechanical properties such as hardness, adhesive strength and wear resistance. This demands a presence of adherent conductive ceria coating in our study which on coated with copolymer forms a bilayer comprised of an improved mechanical properties along with enhanced corrosion protective behavior. Thus the ceria/copolymer bilayer coating provides an equivalent anticorrosive performance and improved mechanical strength than the individual copolymer coating. To obtain a good combination of mechanical properties and corrosion resistance, a perfect optimization of bilayer coatings using copolymer and rare earth element has been carried out in order to achieve a better barrier performance against LN SS corrosion as per the requisites.