CHAPTER-1

INTRODUCTION
# INTRODUCTION

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Man is using metals from ancient times in the form of metal objects for different purposes. The use of any metal is based upon mechanical, physical and chemical properties. These metals and their alloys come in contact with environment, the chemical or electrochemical reaction between a material, usually a metal, and its environment produces a deterioration of the material. This deleterious effect of the metal is commonly known as corrosion. Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in consumption of the material or dissolution into the material of a component of the environment. Corrosion is the interaction between metal with its environment irrespective whether it is beneficial or deleterious usually destructive [Stehle and fontana]. Electrolytic corrosion consists of two partial processes: an anodic (oxidation) and cathodic (reduction) reaction. Corrosion is a natural process and is a result of the inherent tendency of metals to revert to their more stable compounds, usually oxides. Most metals are found in nature in the form of various chemical compounds called ores. In the refining process, energy is added to the ore, to produce the metal. It is this same energy that provides the driving force causing the metal to revert back to the more stable compound. The corrosion word is as old as earth and it was named in different ways as

- Pliny the elder (AD 23–79) wrote about spoiled iron.
- Herodotus (fifth century BC) suggested the use of tin for protection of iron.
- Austin (1788) noticed that neutral water becomes alkaline when it acts on iron.
- Thenard (1819) suggested that corrosion is an electrochemical phenomenon.
- Hall (1829) established that iron does not rust in the absence of oxygen.
• Davy (1824) proposed a method for sacrificial protection of iron by zinc.
• De la Rive (1830) suggested the existence of micro cells on the surface of zinc.
• Whitney (1903) provided a scientific basis for corrosion control based on electrochemical observation. Schonbein in 1836 showed that iron could be made passive. U. R. Evans in 1923 proposed the modern understanding and causes about the corrosion and his classical electrochemical theory.

1.1. Definitions of corrosion
• Corrosion is the surface wastage that occurs when metals are exposed to reactive environments.
• Corrosion is the result of interaction between a metal and environments which results in its gradual destruction.
• Corrosion is an aspect of the decay of materials by chemical or biological agents.
• Corrosion is an extractive metallurgy in reverse. For instance, iron is made from hematite by heating with carbon. Iron corrodes and reverts to rust, thus completing its life cycle. The hematite and rust have the same composition.
• Corrosion is the deterioration of materials as a result of reaction with its environment (Fontana).
• Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with the environment (Uhlig).
In 1960 the term corrosion was restricted only to the metals and alloys and it did not incorporate ceramics, polymers, composites and semiconductors in its regime. The scope of corrosion is consistent with the revolutionary changes in materials development witnessed in recent years.

1.2. Environments and Corrosion
• Air and humidity.
• Fresh, distilled, salt and marine water.
• Natural, urban, marine and industrial atmospheres.
• Steam and gases, like chlorine.
• Ammonia.
• Hydrogen sulphide.
• Sulphur dioxide and oxides of nitrogen.
• Fuel gases.
• Acids.
• Alkalies.
• Soils.

1.3. Consequences of the corrosion

The study showed that approximately 3.1% of the GDP of each country was lost every year by corrosion. The major harmful effects of corrosion are as

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.

2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).

3. Loss of time in availability of profile-making industrial equipment.

4. Reduced value of goods due to deterioration of appearance.

5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).

6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.

7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties,
ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.

8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.

10. Plant shutdowns. Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.

11. Loss of products, leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards. It is well known that at least 25% of water is lost by leakage.


13. Contamination. Corrosion products may contaminate chemicals, pharmaceuticals, dyes, packaged goods, etc. with dire consequences to the consumers.

14. Nuclear hazards. The Chernobyl disaster is a continuing example of transport of radioactive corrosion products in water, fatal to human, animal and biological life.

All corrosion reactions are electrochemical in nature, at anodic sites on the surface of the metal and

The process of corrosion is exactly reverse extractive metallurgy and the oxidation number of the metal changed. In this process the physical, mechanical, or even aesthetic properties of the material get degraded. Corrosion is a diffusion controlled process, it occurs on exposed surfaces of the metals. Most of the metals are unstable in water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals and also corrode when exposed to gaseous materials like acid vapours, formaldehyde gas, ammonia gas, and sulphur containing gases. To prevent the
corrosion various type of materials and phenomenon were used. The materials used to inhibit the corrosion include organic, inorganic compounds and natural products like plant extracts, dyes, oils etc in acidic, basic, salty and neutral mediums. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen. The influence of organic compounds containing nitrogen, such as amines and heterocyclic compounds, on the corrosion of steel in acidic solutions has been investigated by several works.\textsuperscript{1-6}

The corrosion of iron and its alloys is commonly known as rusting. The most widely used metal is iron and its alloy mild steel. Mild steel is a carbon steel typically with a maximum of 0.25% Carbon and 0.4%-0.7% manganese, 0.1%-0.5% Silicon and some traces of other elements. Mild steel is the most common form of steel as its price is relatively low while it provides material properties that are acceptable for many applications. The mild steel is used as: The bars, rods are used primarily in construction. Structural steel products are used in I-beams; channels and angle steel are used in mining, the construction of tunnels, factory structures, transmission towers, bridges, ships and other infrastructure projects. The other uses of the steel are in electrical wires, electrical plates, utensils, containers, automobile industries, household utensils, automobile trims, conveyor belts, elevators, tools, chemical and food processing equipment, building and interior decoration, petrochemicals, nuclear and pharmaceutical equipment.

Hot rolled coils are primarily used for making pipes and have many direct industrial and manufacturing applications, including the construction of tanks, railway cars, bicycle frames, ships, engineering and military equipment and automobile and truck wheels, frames, body parts. Steel plates are used mainly for the manufacture of bridges, steel structures, ships, large diameter pipes, storage tanks, boilers, railway wagons, other railway products and pressure vessels. Cold rolled steel which are used primarily for precision tubes, containers, bicycles, furniture and for use by the automobile industry
to produce car body panels. Cold rolled products are also used for further processing, including for colour coating, galvanising and tinning. The company also produces further processed cold rolled products, including galvanised sheets and tin plates.

1.4. Factors affecting corrosion

Both the metal and environmental conditions affect the corrosion. Factors associated with the metals:

- Effective electrode potential of a metal in a solution
- Overvoltage of hydrogen on the metal
- Chemical and physical homogeneity of the metal surface
- Inherent ability to form an insoluble protective film.

Factors associated with the environment:

- Hydrogen-ion concentration (pH) in the solution
- Influence of oxygen in solution adjacent to the metal
- Specific nature and concentration of other ions in solution
- Rate of flow of the solution in contact with the metal
- Ability of environment to form a protective deposit on the metal
- Temperature
- Cyclic stress (corrosion fatigue)
- Contact between dissimilar metals or other materials as affecting localized corrosion.

1.5. Types of corrosion

1. Direct corrosion:

There are large numbers of chemical reactions in which pure metal may take part where the end products are non-metals. Each of these reactions will produce corrosion if allowed to proceed at the surface of metal. When the metal is in contact with one of these many reactants with which it combine to form a non-metal or to precipitate another metal, corrosion will proceed. If none of the other forms is present then it is the simplest and most fundamental kind of corrosion. The
action is relatively uniform over the whole surface of the metal and proceeds at a fairly uniform rate as the metal is corroded.

The appearance of the surface of metal being corroded in this manner will be relatively smooth but obviously etched. The color of the surface will be same as that of a freshly ground surface of the same metal. The surface appearance is an indication that the corrosion is of direct chemical type unless other signs are present. A common example of this type of corrosion is the action of a good pickling solution on any metal. These solutions besides dissolving or otherwise removing the oxide will leave the metal surface itself etched clean and smooth. The most common condition causing this type of corrosion is an acid solution in contact with metal. Oxidizing agents in the solution may speed up the relation without introducing other forms of corrosion if they are not present in too high relative concentration or activity. If any solid corrosion products or other surface films are formed, they will interfere with the uniform action and if condition tending to produce the measureable electric currents is present they will localize the corrosion. The direct chemical action may still go on at an undiminished rate under these conditions; the local corrosion is likely to be the most serious cause of failure.

2. Corrosion cracking:

The term corrosion cracking is used to include failure of different nature from those known as corrosion fatigue failure, whereas the later results from simultaneous corrosion and fatigue stresses, failure of a corrosion cracking nature derive from simultaneous corrosion and static stresses. These static stresses ordinary exits in the metal from the strain of cold work. Cold worked, high zinc, brass, for instance, will crack more or less spontaneously in an environment that might not be damaging to annealed brass. Cold-worked Monal metal has been known to crack handling Corrosion that produces cracking of this nature is rectangular. The damaging medium must have a high penetrating capacity. Penetrations', leading undoubtedly to some chemical action on the
intergranular material, destroy the tenacity and releases the internal strains, the spontaneous disintegration results. The intergranular attack of duralumin is not strictly corrosion cracking. Stress is not a necessary accompaniment. Improper

3. Cervice Corrosion:
Cervice or contact corrosion is the corrosion produced at the region of contact of metals with metals or metals with non-metals. It may occur at washer, under branchacles, at sand grains, under applied protective films, under pockets formed by threaded joints. Whether or not the stainless steels are free of pit nucleus, they are always susceptible to this kind of corrosion because a nucleus is not necessary. Cervice corrosion may begin through the action of an oxygen concentration cell and continue to form through the action of oxygen, cervice corrosion occur when surfaces of metals are used in contact with each other or with other materials and the surfaces are wetted by the corrosive medium or when a crack or cervice is permitted to exist in a stainless steel part exposed to the corrosive medium. Cleanliness, the proper use of sealant and protective coatings are effective means of controlling these problems.

4. Fretting Corrosion:
The rapid corrosion that occurs at the interface between contacting, highly loaded metal surfaces when subjected to slight vibratory motions is known as fretting corrosion. This trype of corrosion is most common in bearing and bearing supports and often causes a fatigue failure. It can occur in structural members such as truss where highly loaded bolts are used and some relative motion occurs between the bolted contacting surfaces can be well lubricated as in machinery bearing surfaces so as to exclude direct contact with air.

5. Fatigue Corrosion:
Fatigue corrosion is a special case of stress corrosion caused by the combined effect of cyclic stress and corrosion. No metal is immune from some reduction of its environment. Damage from fatigue
corrosion is greater than the sum of the damage from both cyclic stresses and corrosion. Fatigue corrosion failure occur in two stages. During first Damages the metal by pitting and crack formation to such a degree that fracture by cyclic stressing will ultimately occur, even if the corrosion environment is completely removed. The second stage is essentially a fatigue stage in which failure proceeds by propagation by crack and is controlled primarily by stress concentration effects and the physical properties of the metal. Fracture of a metal part due to fatigue corrosion generally occurs at a stress far below the fatigue limit in laboratory air, even though the amount of corrosion is extremely small. For this reason protection of all parts subject to alternating stress is particularly important wherever practical, even in the environment that are only mildly corrosion.

6. Uniform Etch Corrosion:

The surface effect produced by most direct chemical attack is a uniform etching of the metal. On polished surfaces, this type of corrosion is first seen as general dulling of the surface and is allowed to continue, the surface become rough and possibly frosted in appearance. The discoloration or general dulling of metals created by its exposure to elevated temperature is not to be considered as uniform etch corrosion. The use of chemical resistance protective coatings or more resistant materials will control these problems.

7. Stress Corrosion Cracking:

Stress corrosion cracking is caused by the simultaneous effects of tensile stress and corrosion. Stress may be internally or externally applied. Internal stresses produced by no uniform deformation during cold working, but unequal cooling from high temperature and by internal structural rearrangement involving volume changes. Stresses induced when a piece is deformed, those induced by press and shrink fits and those in reverts and bolts are internal stresses. Concealed stress is more important than design stress, especially because stress corrosion is difficult to recognise before it has overcome the design safety factor. The magnitude of the stress varies from point to point
within the metal. Stress in the neighbourhood of the yield strength and generally necessary to promote stress corrosion cracking. But failure has occurred at lower stresses. A few guides in avoiding the problem are
(a). Use metal alloy at no greater than 75% of their yield strength and use exotic materials only where they are actually required.
(b). Avoid assemblies where high tensile loads are concentrated in a small area.
(c). place surfaces under compressive stresses where feasible, by sharpening, sandblasting etc.
(d). Remove stress risers from counter bore, grooves etc.
(e). metal shall be selected from alloys that are highly resistance to stress corrosion cracking.

8. **Pitting Corrosion:**

The most common effect of corrosion on aluminium and magnesium alloys is called pitting. It is a noticeable first as a white or gray powdery deposit, similar to dust, which blotches the surface. When the deposit is clean away, tiny pits or holes can be seen in the surface. Passive metals such as stainless steel resist corrosive media and can performed well over long period of time. However, if corrosion occurs it forms at random in pits. Pitting may be a serious type of corrosion because it tends to penetrate rapidly at nuclei on the metal surface. The breakdown is followed by formation of an electrolyte cell, the anode of which is a minute area of active metal and the cathode of which is a considerable area of passive metal. The large potential difference characteristics of this passive – active cell account for a considerable flow of current with attendant rapid corrosion at small anode. The corrosion resistant passive metal surrounding anode and activating property of corrosion products within the pit account for the tendency of corrosion to penetrate the metal rather than spread along the surface. Pitting is most likely to occur in the presence of chloride ions, combined with such depolarizers as oxygen or oxidizing salts.
Methods that can be used to control pitting include maintaining surfaces clean, applications of the protective coating, and use of inhibitors or cathodic protection for immersion service. Pitting can be prevented or reduced in many instances by the presence of hydroxide chromates or silicate salts. However, these substances tend to accelerate pitting when present in small concentration.

9. Intergranular Corrosion:

Intergranular corrosion is an attack on the grain boundaries of a metal or alloy. A highly magnified cross section of any commercial alloy will show its granular structure. This structure consists of quantities of individual grains and each of these tiny grains has clearly defined boundaries that chemically differ from the metal within the grain center. Frequently, the grain boundaries are anodic to the main body of the grain and when the grain boundaries are in this condition and in contact with an electrolyte, a rapid selective corrosion of the grain boundary occurs. One example of this type of corrosion is unstabilized 300-series stainless steel sensitized by welding or brazing and subsequently subjected to a severe corrosion environment. Another example of intergranular of grain boundary corrosion is that which occurs when aluminium alloys are in contact with steel in presence of an electrolyte. The aluminium alloys grain boundaries are anodic to both the aluminium alloy grain and steel. In later case intergranular corrosion of aluminium alloys occurs. Some austenitic steels are unstable when heated in temperature range of 470 to 915 degree Celsius, after which they become susceptible to corrosion attack at their grain boundaries. The cause of intergranular corrosion has been the subject of much study. Decreased corrosion resistance in austenitic steel is due to depletion of chromium in the area near the grain boundaries, caused by the precipitation of the chromium carbide. This condition can be estimated by the use of stabilized, stainless steel, such as columbium, tantalum or titanium stabilized stainless steels, or by the use of low carbon stainless steel. Molybdenum addition as in type 316 stainless steel decreases the
sensitivity to and the severity of the intergranular attack. Intergranular corrosion can be prevented by adopting one or more of the following methods

- Select an alloy type that is resistant to intergranular corrosion.
- Avoid the heat treatment or service exposure that makes a material susceptible. Normally this occurs with austenitic stainless steel when that is held for some time in the sensitizing temperature range of 47 to 915 degree centigrade.
- Apply protective coating.

10. **Exfoliation corrosion:**

Exfoliation is a form of intergranular corrosion. It manifest itself by lifting up the surface grains of a metal by the force of expanding corrosion products occurring at the grain boundaries just below the surface. It is visible evidence of intergranular corrosion and most even seen on extruded sections where grain thickness is less than in rolled form. Susceptibility of aluminium alloys to exfoliation can be controlled by special metallurgical treatment e.g. T 73 treatment for AA-7075 alloy. Fabrication methods that produce a more equi-axed grain structure are also beneficial.

11. **Galvanic Corrosion:**

Galvanic corrosion is an electrochemical action of two dissimilar metals in the presence of an electrolyte and an electron conductive path. It occurs when dissimilar metals are in contact. It is recognizable by the presence of build up of corrosion at the joint between the dissimilar metals. For example, when aluminium alloys or magnesium alloys are in contact with steel galvanic corrosion can occur.

The galvanic series of metals and alloys are to be used only for general information and must be augmented by experience and knowledge gained of the behaviour of dissimilar metal combinations in field service. When the use of plated steel bolts is necessary on aluminium flanges, the bolts should be separated from the conditions favourable to galvanic corrosion. When dissimilar metals must be used, always
protect both components. A break in the protective coating on the anodic surface will result in severe pitting if the cathodic surface is not protected. This is because of the concentration of current upon the relatively small anodic area exposed when the cathode is uncoated. When practical bolts, rivets and other fasteners should be made of same material as the main structure. When this is not practical, they should be selected from materials higher in the listing so as to distribute the anodic attack over the larger of the two coupled metals. When the anode is large with respect to the cathode, two advantages are realized
a. Because of the anode is being dissolved by the electrolyte, uniform corrosion take place over a relatively large area at a relatively slower rate, thus increasing the service life of the anode.
b. The small cathode areas tend to become polarized, thereby slowing or stopping the reactions. Some of the recommended practices that should be observed to keep galvanic corrosion in minimums are as under
i. Avoid the use of widely dissimilar metals in direct contact.
ii. When dissimilar metals must come into contact they should be separated by using non conducting barrier materials, a paint coating or by plating.
iii. The anode should be as large as feasible in relation to the cathode.
iv. Coat both the anode and cathode with the same material.
v. When possible, install fasteners that have been dipped in epoxy mastic coating.
vi. Avoid use of lock or toothed washer over plated or anodized surfaces.
vii. Use only dry film lubricants that are graphite free.

12. Filiform corrosion:
Filiform corrosion is a unique type of galvanic corrosion occurring under painted surfaces of plated surfaces that do not exhibit good adhesion and under gaskets. It appears as a radial work like corrosion path emanating from the central core of corrosion.
This type of corrosion occurs under painted or plated surfaces when moisture permeates the coating. Lacquers and quick dry paints are most susceptible to the problem; their use should be avoided unless absence of an adverse effect has been proven by field experience. Where the coating is required, it should exhibit low water vapour transmission characteristics and excellent adhesion. Zinc rich coating should also be considered for coating carbon steel because of their cathodic protection quality.

1.6. Methods to study corrosion

Corrosion testing is divided into four types of classification

(i) Laboratory tests, including acceptance or qualifying tests
(ii) Pilot-plant or semi-works tests
(iii) Plant or actual service tests
(iv) Field tests

1. Material and Specimens: Chemical composition, fabrication history, and positive identification of the specimens are all required. In order to avoid confusion and to increase reliability of the tests, many laboratories and companies maintain stocks of the material for corrosion testing only. Size and shape of the specimens vary and selection is often a matter of convenience. Squares, rectangles, disks and cylinders are often used. Small specimens also permit more accurate weighing and measuring of dimensions, particularly for short time tests or where corrosion rate are low. Large specimens are desirable when studying pitting corrosion because of the probability factor involved.

2. Surface preparation: a common and wide used surface finished is produced by publishing with no. 120 abrasive cloth or paper or its approximate equivalent. Prior treatments such as machining, grinding or polishing with a coarse abrasive may be necessary if the specimen surface is very rough or heavily scaled. Clean polishing belts or papers should be used to avoid contamination of the metal surface, particularly when widely dissimilar metals are being polished.
3. Nace test methods: The national association of corrosion engineers promulgated the standard corrosion test methods. TM-01-77 is for metals and alloys for service in sour environments. A threatened tensile specimen is attached within a steel proof ring. The ring is forced to deflect plastically a give amount. The ring tends to return to its original position, but the specimen prevents this and thus bears the load. The specimen is enclosed in a chamber containing a solution of 5% sodium chloride and 0.5% acetic acid. Hydrogen sulphide is continuously bubbled through the solution.

4. Linear polarization: The linear polarization method for measuring corrosion rate is commonly used. The technique is easily performed using simple circuits and can be used to continuously monitor corrosion under a variety of environmental conditions. In this technique, saturated calomel electrode, auxiliary electrode and working electrode are employed. Linear polarization results should always be compared with weight loss or other corrosion rate measurements to ensure the accuracy of the technique.

5. AC Impedance Methods: These methods have frequently been applied to corroding systems in an effort to determine the mechanisms of corrosion process, specifically the nature of rate determining atep or to measure the corrosion resistance, $R_{corr}$, which is inversely related to the corrosion rate.

6. Small Amplitude Cycle Voltammetry: An alternating means of measuring the corrosion or polarization resistance is to use small-amplitude cyclic voltammetry. In this technique a small amplitude (e.g. 10mV) triangular voltage is imposed across the corroding interface using a potentiostat and function generator. The resulting current is then plotted against the voltage using an X-Y recorder to yield a Lissajous figure. The measurement is repeated at different voltage sweep rate and apparent and diagonal resistances are plotted against the voltage sweep rate.

7. In Vivo Corrosion: Orthopaedic devices and other load bearing surgical implants are subjected to the corrosion action of the body fluids.
Mechanical damage due to corrosion is not the major concern since the attack of most alloys is relatively slow. Minute amount of corrosion products released into the body may pose serious biological hazards. For example, nickel compounds are very carcinogenic and there is evidence that gold and other noble metals may reduce local resistance to infection and retard wound healing. These effects are related to both the nature of the metallic compounds produced and their release rate. This, there is a need for accurate measurement of the vivo corrosion rates of various metals and alloys. It is difficult to stimulate the complex conditions existing within living organisms via laboratory vitro experiments. It appears that the only way to ensure accurate data is by in vivo corrosion tests in animals. Since the corrosion rates of useful implant alloys must be very low, weight loss measurements cannot be used. Also, since it is not convenient to remove and replace specimens, periodic weighing and inspection are precluded.

Electrochemical measurements, especially linear polarizations are ideally suited for studies of in vivo corrosion. They are very rapid and sensitive and do not require currents that are biologically damaging. The instantaneous corrosion rate of a specimen can be determined without removing it from the corrosive media.

8. Paints Tests: Paints and other protective coatings are often evaluated in the laboratory and in the field by exposing sheet metal panels, which have been coated. These specimens are placed on racks and exposed to marine, industrial or urban atmospheres and any particular environments of interest. These tests often last for several years and are frequently inspected for evaluation. Appearance of the coating, presence and extent of rusting, under film corrosion and other factors are considered.

1.7. **Role of Inhibitors in Corrosion**

Inhibitors are the chemicals that react with a metallic surface, or the environments this surface is exposed to, giving the surface a certain
level of protection. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion process by either:

a. Increasing the anodic or cathodic polarization behaviour
b. Reducing the movement or diffusion of ions to the metallic surface
c. Increase the electrical resistance of the metallic surface. An inhibitor is a substance, which retard or slows down a chemical reaction.

Thus, a corrosion inhibitor is a substance which, when added to an environment, decreases the rate of attack by the environment on a metal. A corrosion inhibitor may be defined, in general terms as a substance which when added in a small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment.

Rules, equations or theories to guide inhibitor development or use are limited. A synergism or cooperation is often present between different inhibitors and the environment being controlled and mixtures are the usual choice in commercial formulations.

Depending upon the characteristics of inhibitors the different types of inhibitors are as under:

1. Volatile Corrosion inhibitors: Volatile corrosion inhibitors also called vapour phase inhibitors are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values.

In closed vapour spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexacyclopheylene-amine are used. On contact with the metal surface, the vapours of these salts condense and are hydrolysed by any
moisture to liberate protective ions. It is desirable, for efficient volatile corrosion inhibitors, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds, fast action wanting high volatility while enduring protection requires low volatility.

2. Precipitation inhibitors: precipitation inducing inhibitors are film forming compounds that have a general action over the metal surface, blocking both anodic and cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate for example, is used in many domestic water softeners to prevent the occurrence of rust water. In aerated hot water systems, sodium silicates protect steel, copper and brass. However, protection is not always reliable and depends heavily on pH and a saturation index that depends on water composition and temperature. Silicates and phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites; however, they are very useful in situations where non-toxic additives are required.

3. Organic Inhibitors: Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors but, as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors usually designated as film forming, protect the metal by forming a hydrophobic film on the metal surface. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors.
Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines or anionic inhibitors, such as sulphonates will be adsorbed preferentially depending on weather the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors.

4. Cathodic Inhibitors: Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms as (i) cathodic poisons (ii) cathodic precipitates (iii) oxygen scavenger

(i) Cathodic poisons: cathodic poisons are advantageously as corrosion inhibitors by stifling the cathodic reduction processes that must balance the anodic corrosion reaction. However cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be adsorbed by metal during aqueous corrosion or cathodic charging.

(ii) Oxygen scavenger: a chemical that reacts with dissolved oxygen to reduce corrosion, such as sulphite and bisulphite ions that combine with oxygen to form sulphate. This is a redox reaction and requires a nickel or cobalt catalyst. Removal of air from a mud by defoaming and mechanical degassing is an essential first step before a scavenger can lower the dissolved oxygen content.

5. Anodic inhibitors: anodic inhibitors are usually used in near neutral solutions where sparingly soluble corrosion products, such as oxides, hydroxides or salts are formed. They form or facilitate the formation of passivating films that inhibit the metal dissolution reaction. Anodic inhibitors are often called passivating inhibitors. When the concentration of an anodic inhibitor is not sufficient corrosion may be accelerated, rather than inhibited. The critical concentration above which inhibitors are effective depends upon the nature and concentration of the aggressive ions.
6. Mixed Inhibitors: Mixed inhibitors protect metal in three possible ways, physical adsorption, chemical adsorption and film formation. Physical adsorption is a result of electrostatic attraction between the inhibitor and the metal surface. When the metal surface is positively charged, adsorption negatively charged inhibitor is facilitated. Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the surface. Increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface.

Chemical adsorption takes place more slowly than physical adsorption. As temperature increases, adsorption and inhibition also increases. Chemical adsorption is specific and is not completely reversible.

1.8. Corrosion and Economics

While corrosion processes form an interesting basis for scientific studies, which are frequently undertaken as exercises in chemistry and particularly electrochemistry, by far the greatest interest in and concern for corrosion stream from its practical effects and how they may be avoided. Various estimates have been made of the annual economic loss resulting from corrosion. There is no general agreement as to just what should be included in calculating this loss, for example, should the coating on tin cans be included which would not be needed if the contents were not corrosive to steel. It is therefore, fruitless to argue about the figure that should be used. However, there is ample evidence that annual losses attributable to corrosion in North America amount to several billions of dollars and, depending on what is included in the estimate, could well surpass the £ 10 billion figure that has been suggested. An accurate estimate of the loss resulting from corrosion of iron and steel is, of course, out of the question. From certain data, however, which are at hand regarding
the average annual renewal of corrugated metal roofing, wire, pipelines, steel coal cars and similar iron and steel product often subject to severe corrosion, it seems that, because inadequate protection, the annual replacement from this cause, on the average, may reach as much as 2% of the total tonnage in use. It is estimated that about 1,200,000,000 tons of rolled iron and steel products were in use in the world 1931. In recent years the steel produced was 18 times the total tonnage of all non-ferrous metals. On this base it is evident that a large and increasing proportion of the annual production may be required to replace that rendered unserviceable by corrosion. It is true that a large part of the corroded metal is recovered as scrap, but on the other hand, in structures where the metal is not readily accessible the total cost incidental to replacement is often many times the cost of the new material required.

Despite the developments in corrosion resistant alloys over the past few decades, carbon steel still constitutes an estimated 99% of the materials used in the oil industries. It is usually the most cost effective option, being a factor 3-4 times cheaper than stainless steels. Yet its corrosion resistance is poor in aggressive environments and the cost savings can only be realised by adding a corrosion inhibitor to the environment or applying a protective coating to the steel. Inhibitors are used in a wide range of applications, such as oils pipelines, domestic central heating systems, industrial water cooling systems and metal extraction plants.

A particular advantage of corrosion inhibition is that it can be implemented or changed in situ without disrupting a process. The major industries using corrosion inhibitors are the oil and gas exploration and production industry, the petroleum refining industry, the chemical industry, heavy industrial manufacturing industry, water treatment facilities and the product additive industries. The largest consumption of corrosion inhibitors is in the oil industry, particularly in the petroleum refining industry. The total consumption of corrosion inhibitors in the United States has doubled from
approximately £600 million in 1982 to nearly £1.1 billion in 1998. Some of the indirect losses are given as under

1. **Product degradation:**

   The textile and paper industries also are concerned with colour of their finished products. Since the corrosion, products of many metals are highly coloured, care must be, exercised in selection of materials to be used in contact with the finished products. Mills of this type generally are highly automated so accidental product contamination may go, unnoticed until the finished product reaches a customer's plant.

   For example, undesirable rust spots were discovered on paper stock being processed at a paper specialties plant. Careful investigation revealed that a steel electrical conduct past above the paper machine in the paper mill. Corrosion of the steel in the humid paper mill environment permitted iron corrosion products to fall and contaminate the paper.

   Edible products also must be protected from degradation. Vegetable oils tend to become rancid in contact with some materials. Copper base alloys have significantly undesirable effects on edible oils. Accordingly, such products normally handled in nickel, stainless steels, plastics, or aluminium vessels.

2. **Excessive maintenance cost:**

   The cost of maintaining plant and equipment is and operating expense, which directly reduces profit. Therefore, any reduction in maintenance expense would appear desirable from a profit standpoint. In soda ash plants, exposure to sodium chloride, calcium chloride, high humidity, etc., produces an environment spectacularly corrosive to unprotected steel.

3. **Unscheduled shutdowns:**

   The unscheduled shut down of a chemical plant or refinery may involve disruption of activities not only at the plant where failure occurs, but also may interrupt operations of several other plants which depend on the first plant for their supply of raw materials. As a
consequence, it sometimes is considered necessary to provide large storage capacity for certain products as a hedge against disruptions of operations during an unscheduled shut down. The unscheduled shut downs and fear of them represent an immense expanse to industry and there is justification for considerable effort to avoid them.
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