

PASSIVITY

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Introduction to Passivity:

Phenomenon passivity is closely related to protection of metals from corrosion. Term passivity is first utilised by 'Schonbein' in 1836 to describe the strange behaviour of iron in concentrate HNO_3 . Now it is commonly accepted this phenomenon to all the metals

A piece of iron when dipped in dilute HCl evolves H_2 gas, replace Ag from AgNO_3 and Cu from CuSO_4 solution. But if same piece of iron is first dipped in conc. HNO_3 or chromic acid for some time and then reacted with above reagents, it remain unattacked. Thus iron by treatment of conc. HNO_3 is rendered inert or passive and the phenomenon is known as '*Passivity*'.

"The inertness exhibited by metal under conditions in which chemical activity is to be expected is called *chemical passivity* and the substances which cause this phenomenon are called *passivators*".

Common passivators are conc. HNO_3 , chromic acid, heating in air.

Alternative Definition of Passivity:

"Phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series". Passivity is the result of the formation of highly protective but very thin and quite invisible film on the surface of metal or of an alloy, which make it noble. Such film is considered to be insoluble, nonporous and of "*Self healing nature*" that when broken will repair itself.

Examples of passive metals and alloys are: Ti , Al , Cr , stainless steel containing Cr . This material exhibit corrosion resistance in oxidizing environments, but in reducing environment they become active. Experiment shows passivity of certain metal falls in order: $\text{Ti} \rightarrow \text{Al} \rightarrow \text{Cr} \rightarrow \text{Be} \rightarrow \text{Mo} \rightarrow \text{Mg} \rightarrow \text{Ni} \rightarrow \text{Co} \rightarrow \text{Fe} \rightarrow \text{Mn} \rightarrow \text{Zn} \rightarrow \text{Cd} \rightarrow \text{Sn} \rightarrow \text{Pb} \rightarrow \text{Cu}$

It may be noted that passivation is not constant state. In presence of oxygen the oxide film will be automatically repaired when ever any damage occurs.

Theories of Passivity: Many theories have been advanced but none of them can give complete explanation. However, all theories fall in four groups:

1. Gaseous Film Theory:

According to this theory, a thin film of gas is said to adhere to the said surface of metal and rendering it passive. The gaseous film may be of oxygen or of nitric oxide or of any gas.

Drawbacks:

- Theory fails to explain the passivity of lead in presence of sulphuric acid.
- It also fails to explain why passive iron is rendered active by scratching the surface?

2. Physical Theories:

- a) Catalytic Theory: According to this theory pure iron is normally passive, but may be made active by the presence catalyst like hydrogen. This theory is not able to explain passivity fully.

- b) Valance Theory: According this theory active iron is in the bivalent state. While passive is in the trivalent state. Theory failed to explain all type of passivity's.
- c) Allotropic Theory: According to this theory, active metal is converted to passive metal due to stable allotropic modification.

3. Oxide Layer Theory:

Hypothesis of Faraday:

- The metal surface was oxidised.
- The surface oxide film would be so thin as to be invisible.
- The oxide layers could not be dissolved by acids. As a result of metal being completely shielded by the layer of oxide, it could no longer dissolve anodically. In other world metal becomes passive due to the formation of an oxide film on its surface.

Objections: This theory held its ground for many years until Hittorf(1898) shown that:

- The properties of oxide responsible for passivity must be different from those of any known oxide of the metal.
- In certain cases films other than oxides like: phosphates, silicates, nitrites are also the causes of passivity.

Thus slight modification of oxide theory required which may be summarised as: "Any protective film formed on the surface during the chemical action is sufficient to cause passivity" and the modified theory termed as '*Protective Layer Theory*'.

Evidences in favour of this theory:

- In case the thin protective layer is removed mechanically or chemically, the metal is rendered active again.
- When passive iron is heated with conc. HNO_3 up to 75°C , it become active due to ferric oxide on the surface of passive iron begins to dissolve in conc. HNO_3 at 75°C .
- It has been shown that polarised light is not reflected to the same extent by active and passive form of given metal.
- Iron is rendered passive also by other oxidizing agents like fused nitrate, chromic acid confirming that the passivity is due to formation oxide film on the surface of metal.
- A large number of metals like Al, Cr, Bi, Co and Ni become passive with conc. HNO_3 due to the formation of their oxide film on their surfaces.

Thickness of the film:

It is proved that the rate of film growth is inversely proportional to the thickness of film.

$$\frac{dy}{dt} \propto y^{-1} \quad \text{or} \quad \frac{dy}{dt} = k y^{-1} = \frac{k}{y} \quad \text{_____ (1)}$$

Where, y = thickness of film, t = time and k = constant.

On integrating equation-(1) gives,

$y^2 = 2kt + \text{constant}$(equation of parabola)

Thus the rate of film growth must obey the parabolic law.

4. Theory of Electronic Configuration:

Postulates by H. H. Uhlig:

- Passive metals belong to transition group of the periodic table. Examples of this are: Cr, Ni, Co, Fe, Mo and W.
- The transition metals have an incompletely filled *d*-orbital and tend to fill up with electrons.
- The passive condition corresponds to that with incomplete *d*-orbitals and active condition to that when *d*-orbitals are filled up.

Is Passivity a Universal Phenomenon?

Recent development indicate that phenomenon passivity is not limited to metals like iron, chromium etc. but almost too all metals.

Applications of Passivity:

- Cast iron retorts are used for manufacture of nitric acid by heating KNO_3 with conc. H_2SO_4 . The oxide film formed on the surface of the retort due to passivity protects iron from corrosion.
- Aluminium is generally used in air craft industry. The oxide is deposited on aluminium to resist corrosion. The Al-article is made as an anode and dipped in a cell containing 3% chromic acid solution. When electricity is passed an excellent protective film is deposited which resists corrosion up to a remarkable extent.
- Stainless steel is covered by an oxide film to prevent its corrosion which is used in the manufacture of automobile parts.
- Metals which are susceptible to corrosion are made passive by alloying with passive metal such as Cr, Ni, Mo.

Electro-chemical Passivity:

It is recognised same as chemical-passivity, the difference is that it is brought about by anodic oxidation.

Definition: “In electrolysis the anodes sometimes become passive if a high current density is passed is termed as electro-chemical passivity”.

Important points:

- Electro-chemical passivity is shown by all metals under suitable conditions but depends also on electrolytic solution.
- It may be caused by a small current passing for a long time or heavy current for a short time.
- The electrical energy is wasted because it is utilized for causing passivity as well as in performing chemical reactions.

This type of passivity is important evil (υδσπ) in electro-chemical industries because large portion of electric-energy is wasted when anode becomes passive. On the other side important use of it is for deposition of an oxide film on aluminium anode.

Mechanical Passivity:

In certain cases, the metal becomes passive due to the formation of visible, insoluble and comparatively thick oxide film is called mechanical passivity, For example: PbO_2 on a lead surface in dilute H_2SO_4 .

Main Points:

- The film deposited on the anode leads to increase the resistance of a cell.
- Mechanical passivity has been observed with Fe, Co, Ni and other metal in alkali hydroxide solution along with Tl, Sb and Bi in aqueous H_2SO_4 .

Mechanism: The possible mechanism of film formation is:

- It can be readily formed when solubility product of certain poorly soluble substances like $PbSO_4$ is exceeded.
- It may be produced by electrophoresis of colloidal particles present in the bulk of the solution.

Uses: Mechanical passivity is utilising for the manufacture of a low power electrolytic rectifier from aluminium.

CORROSION**Introduction:**

As soon as metals are extracted from their ores, the reverse process begins, i.e., nature tries to convert them back in to the form in which they occur. Mostly oxides are formed during this process and depending upon the presence of impurities sulphides, carbonates, sulphates etc. may also be formed.

“The process by which the metals have tendency to go back to their combined state is called corrosion”. OR “In other words, corrosion is exactly the reverse of extraction of metals”.

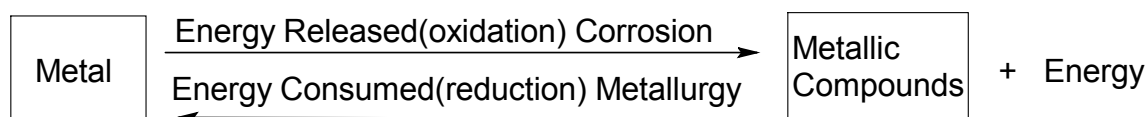


Fig. 1.1- Corrosion and reduction processes

Modern Definition:

“The deterioration of a substance because of its reaction with its environment”. Under this definition, the term corrosion may be applied to gradual transformation of the metals into compound state, to weathering of timbers and concrete, to the leading of glass, to the cracking of plastics etc.

However, metals are still considered to be the major materials subject to corrosion.

Economic Aspects of Corrosion: The economic aspects of corrosion are of two fold.

- The cost of replacement of materials and equipments lost through corrosion. The current estimation is nine billion dollars per year for replacement of pipes, building products, auto parts, water heater and other items subject to corrosion.
- The limitation of progress in certain areas because of corrosion problem. Most corrosion costs are due to the corrosion in electrolyte or wet corrosion.

Types of Corrosion:

Corrosion of metal occurs by attack of surrounding environments/ medium on the surface of metal. It is possible in ways. Viz., **I.** Direct chemical corrosion or dry corrosion **II.** Electro-chemical corrosion or wet or Immersed.

I. Dry or Chemical Corrosion: This type of corrosion is due to chemical action of atmospheric gases such as O_2 , X_2 , H_2S , SO_2 , N_2 . The extent of corrosion depends on:

- Chemical affinity between the corrosive environments and solid metals.
- Ability of reaction products to form a protective film.

There are three main types of chemical corrosion.

1. Oxidation Corrosion

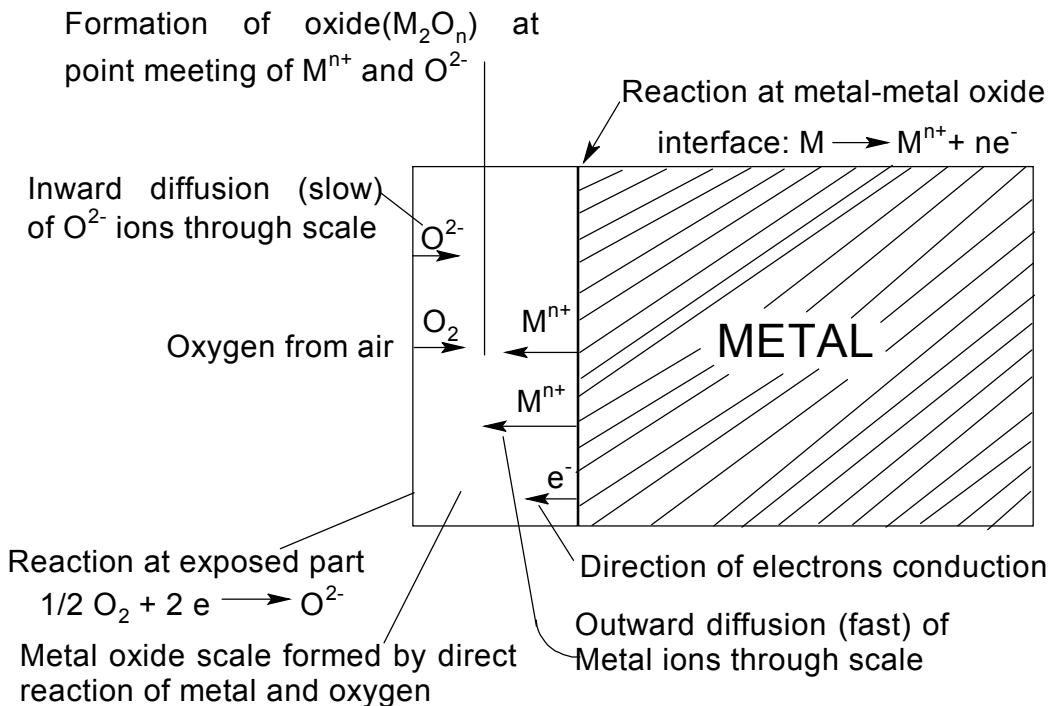
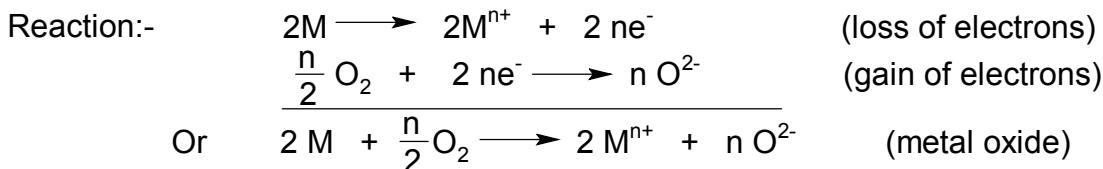


Fig. 1.2 Oxidation mechanism of metals

It is brought by direct action of oxygen on metals. Alkali and alkaline earths are rapidly oxidized at low temperature. At high temperature excepting Ag, Au and Pt almost all metals are oxidized.



Mechanism: Oxidation occurs first at the surface of metal to form oxide scale forms a barrier that tends to restrict further oxidation. For oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse through the scale to the underlying metal. Since metal ion is smaller than O^{2-} its diffusion occurs faster.

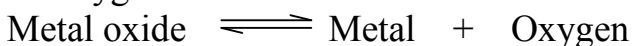
The **nature of the oxide film** formed plays an important part in corrosion process and decides the further corrosion.



If the film is:

➤ *Stable:* A stable layer is fine grain in its structure and behaves as protective coating in nature, thereby shielding the metal surface. The film on Al, Sn, Pb, Cu etc. are stable. Consequently, further corrosion is prevented.

➤ *Unstable:* In this case the oxide layer formed decomposes back in to the metal and oxygen.



Consequently oxidation corrosion is not possible in such case. Thus Ag, Au, Pt do not undergo corrosion.

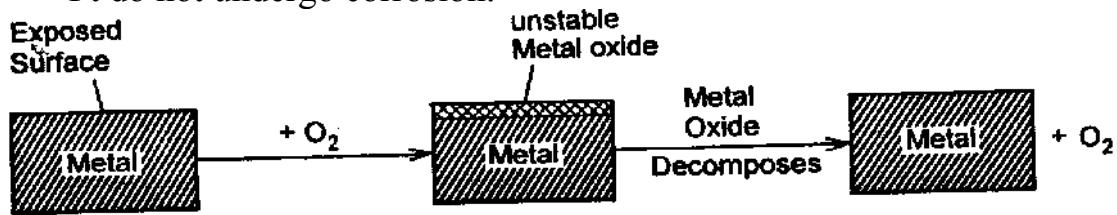


Fig. 1.3- Unstable oxide layer

- **Volatile:** The oxide layer volatilizes as soon as formed, thereby leaving the underlying metal surface exposed for further attack leading to excessive corrosion eg. MoO_3 is volatile.

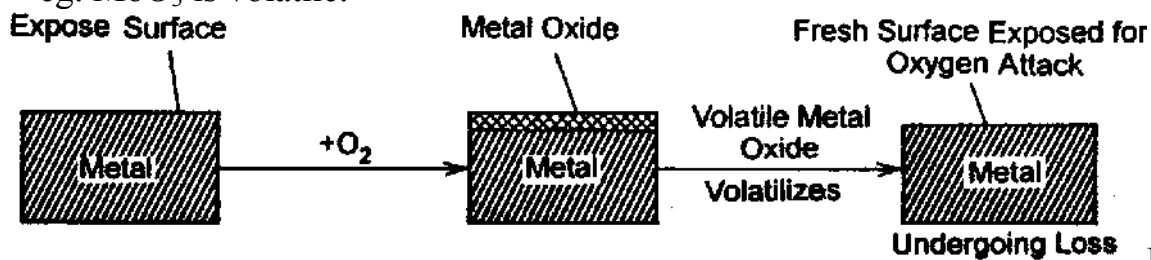


Fig. 1.4

- **Porous:** Oxide film cracks. In such case the atmospheric oxygen have access to the underlying surface of metal through cracks of the layer, thereby the corrosion continues to unobstructed till the entire metal is completely converted into its oxide.

Pilling-Bedworth Rule: “An oxide is protective or non-porous if the volume of oxide greater than volume of metal from which it is formed, but if the volume of the oxide is less than the volume of metal, the layer is porous (non protective).”

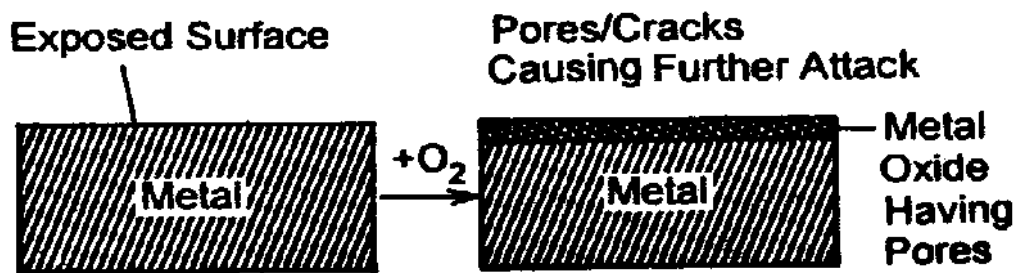


Fig. 1.5- Porous oxide layer

Alkali and alkaline earth metal form oxides of volume less than metal (non protective) and is insufficient to cover completely the entire metal-surface. On the hand metal like aluminium form oxide whose volume is greater than volume of metal-Al. Consequently, an extremely tightly-adhering non-porous layer is formed.

2. Corrosion by Other Gases:

The corrosion by gases like SO_2 , CO_2 , H_2S , Cl_2 , F_2 depends on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of film on the surface.

- If the film formed is protective (non protective), the film protects the metal from the further attack.
- If the film formed is non protective (porous), the whole metal is gradually destroyed. For example dry Cl_2 attack on tin (Sn) forming volatile SnCl_4 which

volatilizes immediately from Sn-surface leaving fresh metal surface for further attack.

➤ **Corrosion by hydrogen:**

a) The attack of hydrogen is known as **hydrogen embrittlement**. This is due to formation of atomic hydrogen by chemical action occurring at a metal surface. $\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}$. The atomic hydrogen diffuses readily into the metal and collect there in metal voids, where it recombines to form molecular hydrogen. $\text{H} + \text{H} \rightarrow \text{H}_2$

As diffusion proceeds the pressure of hydrogen inside the metal voids continues to increase. This causes lowering of the strength and ductility of the metal i.e. metal becomes weak.

b) At high temperature atomic hydrogen is formed by the thermal dissociation.



This hydrogen is chemically active and readily combines with C, S, O, or N usually present in metals. For example atomic hydrogen combines with carbon in steel at high temperature forming methane, which causes cracking in the metal. As a result of metal becomes brittle and weak. This phenomenon is known as “**decarburization**”.

3. Liquid-Metal Corrosion:

It is due to chemical action of flowing liquid metal at high temperature on solid metal or alloy and has been found to occur in devices used for nuclear power. The corrosion reaction involves either:

- Dissolution of a solid metal by a liquid metal or
- Internal penetration of the liquid metal into the solid metal.

Corrosion by Gaseous Environments: In this type of corrosion the metal is surrounded by gases present in the surrounding environment.

Effect on metal: Metal is consumed and the metal properties are changed.

The factors determining the rate of corrosion reaction are different for different conditions:

[A] For Metal Sheltered From Rain:

(a) Moisture: The amount of moisture present in the atmosphere is recognised in the “*principle of critical humidity*”, which applies to most of the metals. The % age humidity below which the corrosion is negligible and above which it is appreciable is called the “*critical humidity value*”. For iron, 50-60% is called critical humidity value of iron.

For iron there is one more value of critical humidity viz., 80-90%. At this value the surface of metal covered with red rust.

(b) Suspended impurities in air: It has great effect. In case of iron the formation of red rust can be prevented if it is allowed to come in contact with air which is free from any suspended impurities. The suspended particle in air may be classified under three broad headings:

- *Intrinsically active particles:* These are active particle which can bring about the corrosion by themselves For example NaCl and $(\text{NH}_4)_2\text{SO}_4$ in town air.

- *Intrinsically neutral particles*: These are themselves chemically inactive but have a good capacity for adsorbing gases from the atmosphere. For example amorphous carbon present in the atmosphere can adsorb many gases and can enhance the rate of corrosion.
- *Neutral particles*: These are neither chemically active nor capable of adsorbing active gases of the atmosphere. Thus such particles have no influence on the rate of corrosion reaction like crystalline silica.

(c) Effect of active gases: The rate of corrosion seriously influenced by presence of active gases in atmosphere like, SO₂, CO₂, H₂S. Trace amount of SO₂ present in atmosphere yield CuSO₄ film on the surface of Cu.

(d) Nature of primary film of corrosion: If the film is continuous and adheres to the surface it stops the further corrosion and film is said to be the protective type. For example, aluminium and heavy metal form continuous and protective oxide film on its surface. But if the film is not continuous or it may leave the surface, then corrosion is occurring rapidly. For example alkali and alkaline earth metals form porous layers and do not offer any resistance to further corrosion. **[B]**

Metal Exposed to Outdoor Atmosphere:

This type of corrosion takes place in the same manner as in indoor atmosphere. The only additional factor which comes into play is rain. Previously it was thought that, the effect of the rain on corrosion was generally adverse but now it is known that rain is not necessarily a disadvantage because it may help to develop a product having protective quantities as in case of Cu. Thus it helps to retard the corrosion. However, rain may have effects on corrosion as under:

- It may remove a corrosion product as in the case of nickel.
- Rain may help to develop a product having protective quantities in case of copper.
- The rate of corrosion may be increased by removal of the coating.

Theories of Corrosion by Gaseous Environments:

Postulates:

- i. The gas is dissolved in the metal as molecules, atoms or ions to form solution. This is followed by diffusion of the gas in metal.
- ii. A solid or liquid product is formed on the surface. Reaction continues by the diffusion of the gas or metal atoms or ions through the surface film. The film may be of oxide, carbonate or sulphide.
- iii. If film is non porous affords protection to the metal from further attack, metal said to be in passive state.
- iv. When film is porous it causes serious corrosion.

Corrosion Products:

Three important types of products formed on the surface of the metal.

- Products may be unstable.



In such case no corrosion occurs as in case of noble metal-Pt.

- The products may be volatilized at high temperature, e.g., Mo, W.
- Products may be stable. Most of the metals fall into this category.

Further this subdivided into three types.

- i. The product film which cannot completely covers the metallic surface. This causes serious corrosion.
- ii. The product film may be non porous and built up to certain thickness. In this case corrosion decreases with time.
- iii. In some cases, non porous film may be brittle and may cracks after some time, deeper corrosion may occur.



II. Immersed or Wet or Electrochemical Corrosion:

The corrosion occurs due to the existence of separate ‘anodic’ and ‘cathodic’ areas between which current flows through the conducting solution. At anodic area oxidation takes place. Hence corrosion always occurs at anodic areas.

At anode: $\text{M} \rightarrow \text{M}^{n+} + n \text{e}^-$

The metallic ions and some other ions formed at cathodic part diffuse towards each other through conducting medium and form a corrosion product.

There are four types of immersed corrosion:

1. Chemical Corrosion:

It is due to electro-chemical reaction between metal and its surrounding liquid.

Factors affecting the rate of corrosion:

- a) *Concentration of salts*: Increase in concentration of salt increases the rate of corrosion. However, beyond certain concentration the rate of the corrosion is decreased. It is thought to be due to a lower solubility of oxygen in more concentrated solution.
- b) *Depth of immersion*: The rate of corrosion is directly proportional to the depth of immersion.
- c) *Concentration of dissolved oxygen*: Increases in the concentration of dissolved oxygen increases the rate of corrosion.
- d) *Temperature*: Corrosion increases with increase in the temperature.
- e) *Nature and concentration of cation of the medium*: In most of cases, corrosion in a liquid medium is due to substitution of hydrogen by the metal in the corroding medium (acid corrosion). When metallic salts are present in the corroding medium is substituted by the corroding metal. The concentration of cation (metal ion) influences the rate of corrosion. For example, concentrated alkali carbonate does not corrode iron but dilute one corrode it to some extent.
- f) *Nature and concentration of anions of the medium*: All anion have no influence but trace of halide affect the corrosion as these help in dissolving protective film.
- g) *Nature of corrosion products*: Products fall into three categories:
 - i. Those which are soluble, corrosion are continuing.
 - ii. Those which are fixed to metal and insoluble. The metal will be protected from futher corrosion.
 - iii. Those which do not fix to metal and discontinuous, the corrosion will be serious.
- h) *Electrical conductivity of corroding medium*: As electrical conductivity increases the rate of corrosion increases.
- i) *Position of metal in E.M.F.-series*: The more basic the metal the more readily it will corrode.

- j) *pH*: The lower the pH the greater the corrosion.
 k) *Presence of colloids*: J. Newton Friend reported that the presence of colloids inhibits the corrosion.
 l) *Presence of bacteria*: In some cases it has influence

2. Underwater Corrosion:

This includes corrosion in water pipes of all types, heating system, steam boilers. Water is in sufficient amount whereas the air is limited.

3. Underground Corrosion:

Corrosion of pipes, underground structures, corrosion of iron in concrete comes under this category. It is sometimes complicated due to presence of various salts in the soil. Corrosiveness of a soil depends upon its acidity, electrical conductivity, its moisture and salt content, presence of bacteria.

4. Concentration Cell Corrosion:

It is due to electrochemical attack on the metal surface exposed to electrolyte of varying concentration. This may be the result of local differences in metal ion concentration, caused by slow diffusion of metal ions produced by corrosion.

Differential aeration corrosion is most common type of concentration cell corrosion and it occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential at differently aerated areas. Experiments have shown that: “*Poor oxygenated parts are anodic*”. If a piece of Zn-metal is partially immersed in dilute solution of NaCl and the solution are not agitated properly then the part above and closely adjacent to the water-line become cathodic, on the other hand parts immersed to greater depth show smaller concentration of oxygen and become anodic. So, a difference of potential is created, which cause a flow of current and zinc will dissolve at the anodic areas.

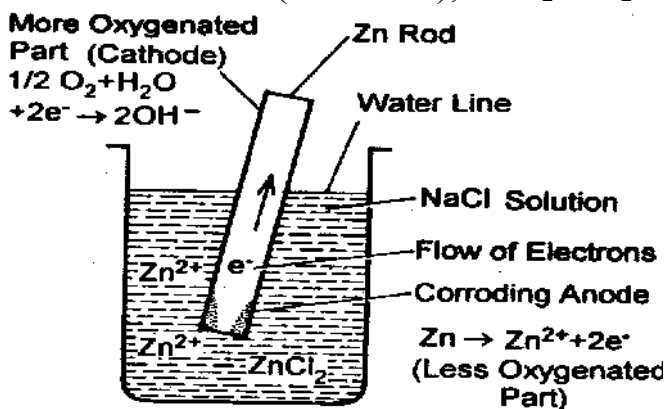
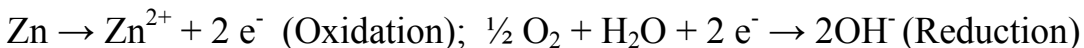


Fig. 1.6- Mechanism of differential aeration attack

In a similar way, iron corrodes under drops of water. Area cover by water having less access of oxygen become anodic in respect to the areas freely exposed to air.

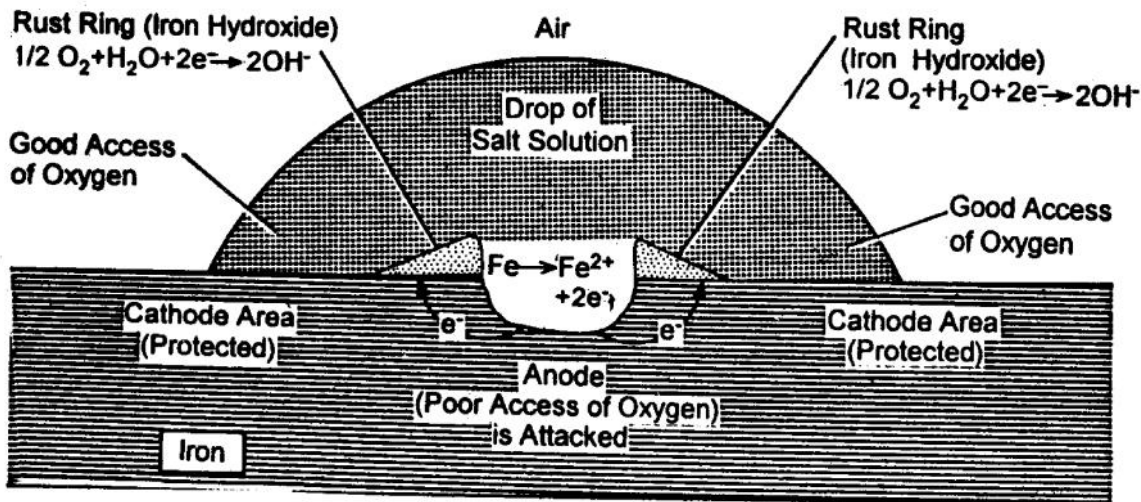


Fig. 1.7- Corrosion of iron under drop of water

Theories of Immersed Corrosion:

Various theories have been proposed but accepted theory is the modern electrochemical theory. Most of theories are concerned with iron metal as it is most common metal to undergo immersed corrosion.

(a) Carbonate formation theory or Acid theory:

According to this theory a little amount of an acid is necessary for corrosion to take place. Even carbon dioxide dissolved in water is enough. Initial corrosion started by joint action of CO_2 , H_2O and O_2 .

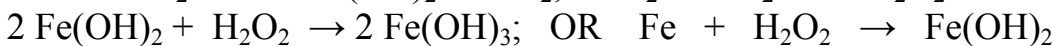


Thus H_2CO_3 regenerated which may further attack to the metal and thus corrosion proceeds.

Limitations: Theory is not supported by practical observations. Theory does not explain corrosion taking place in absence of CO_2 .

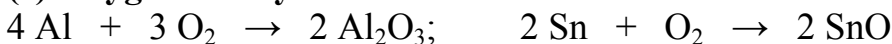
(b) Peroxide theory:

According to this theory, iron reacts with water to liberate hydrogen which is converted to hydrogen peroxide by dissolved oxygen.



Limitations: Theory is not supported by practical observations. Theory fails completely because pure hydrogen peroxide has no effect on Fe-metal. It is also reported that the reagents which destroy H_2O_2 do not prevent corrosion.

(c) Oxygen theory:



These oxides have the same colour as that of the metals. But when copper attacked by oxygen to form black copper oxide. This type of reaction cannot proceed in the absence of moisture.

Limitations: Theory is not supported by practical observations and cannot explains corrosion in all cases.

(d) Electro-chemical Theory:

This theory explains corrosion fully. According to theory the chemically non uniform surfaces of metals behave like small electric cell in presence of water containing dissolved oxygen and carbon dioxide.

Main Points:

- i. The covered end of the metal acts as the anode where iron form Fe^{2+} ion by oxidation:

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (\text{loss of electron})$$
- ii. A less electro-positive metal like copper present as an impurity conducts away the electrons and develops the cathode where hydroxyl ions are formed.

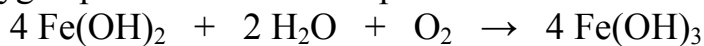
$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$$

H_2 so liberated may get accumulated at the cathode and causes polarization which might bring a stop to corrosion, but atmospheric oxygen acts as depolariser.

$$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$$
- iii. Now there exist galvanic flow of oppositely charged ions on the surface of the metal and they combine to form a compound.

$$\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$$

$\text{Fe}(\text{OH})_2$ is then converted basic carbonate by carbon dioxide and oxygen present in the atmosphere.



It follows that, "Any corrosion process can be related to an electro-chemical process in which cathode and anode formed on the surface of metal and electrolyte, such as water or salts solution must be present to permit ionic flow to form the corrosion products".

It is expected that the elements on the top of electro-motive force series more easily gets corroded. Although, aluminium is placed near top of the series, yet it resists atmospheric corrosion effectively due to formation of oxide film (protective) on its surface which prevents further corrosion.

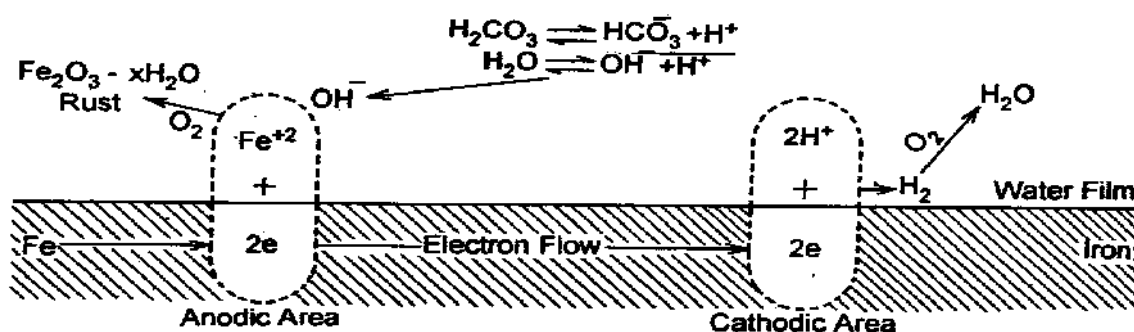


Fig. 1.8

(e) Differential Aeration Theory:

This theory had been established by 'Evans'. A cell is set up between iron dipping in oxygen free water and oxygen containing water and current flows, non aerated part of iron acting as anode and aerated one as cathode.

Prevention of Corrosion:

As we know that corrosion reactions are all surface reactions, it follows that protection of the surface of the metal should be primary object to prevent its corrosion. The methods adopted for prevention of corrosion of metal can be classified into four categories.

I. Methods Based on Proper Designing:

The design of material should be such that “Corrosion even if it occurs, is uniform and does not result in intense and localized corrosion”.

Important Designing Principles are:

- “Avoid the contact of dissimilar metals in the presence of corroding solution”. Otherwise corrosion is localized on more active metal.
- When two dissimilar metals are to be in contact, the anodic material should have large area as possible, whereas the cathodic metal should have as much smaller area as possible.
- If two dissimilar metals in contact have to be used, they should be as close as possible to each other in the electro-chemical series.
- Whenever the direct joining of dissimilar metal is unavoidable, an insulating fitting may be applied between them to avoid metal-metal electric contact.

II. Methods Based on the Treatment of Metals: This includes following methods.

- a) *Alloying of the metal:* By alloying, corrosion can be decreased in two different ways.
 - Homogeneity of metal is increased which results in a decrease in corrosion.
 - In some cases oxide film form on the surface of the metal. For example silicon-iron alloy called Durrion which is very resistant to acids due to formation of silicon dioxide film on its surface.
- b) *Removal of strains:* The strain in the metal can be eliminated by heating treatment and annealing as these strains are focal points for corrosion.
- c) *Polishing the surface:* Corrosion decreases due to:
 - Removal of oxygen concentration cell.
 - Decreasing the surface area because a smooth surface has a small area exposed to corrosive medium than non polishing surface.
- d) *Producing insoluble oxide coating:* Metal like Cr, Al, Ni are capable of forming insoluble and tenacious oxide film on their surfaces giving protection to further deeper corrosion. These films can be produced artificially:
 - Bawer and Barf Process: A protective film of Fe_3O_4 is produced on the surface of iron by heating in steam at 900°C .
 - Rffungaton Process: Protective film can be produced by placing the metal in the molten mixture of $\text{KNO}_3 + \text{MnO}_2$.
- e) *Electroplating:* When a noble metal like Au, Ag, W, Pt is electroplated on the base metal, it protects the base metal by virtue of its noble character. Generally tin and nickel plating are employed. As far as the coating is continuous, it affords protection.
- f) *Covering with metals by other than electro-deposition:* Recently several methods have been developed. Some of these are describe below.
 - **Hot dipping:** The metal is coated by film of metals having low melting points such as: Zn, Sn, Pb. This process is carried out by dipping cleaned metal in the

hot solution of metal. It is reported that during hot dipping an alloy is formed where two metals meet.

Example: *Galvanising of iron (covering iron surface by zinc):* One ounce of Zn is enough to coat square feet of surface.

Protective action: The thin coating of Zn in galvanised iron does not permit iron to have a direct contact with air and moisture and hence no corrosion takes place. Even when the protective Zn-coating is broken, iron is steel protected because zinc occupies a position above iron in electro-chemical series. Hence zinc loses electrons and then it passes into a solution as Zn^{2+} ion at the anodic area. Hydrogen discharged from the surface of iron at the cathodic area. At area where the surface coating is not damaged, Zn is not corroding itself due to adhering of the layer ZnO on it.

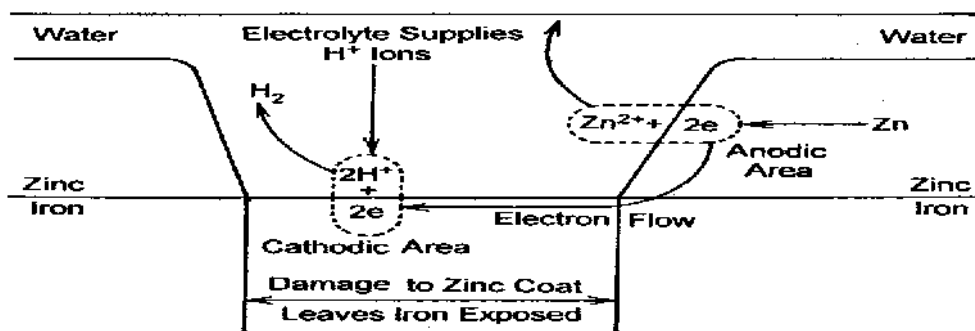


Fig. 1.9

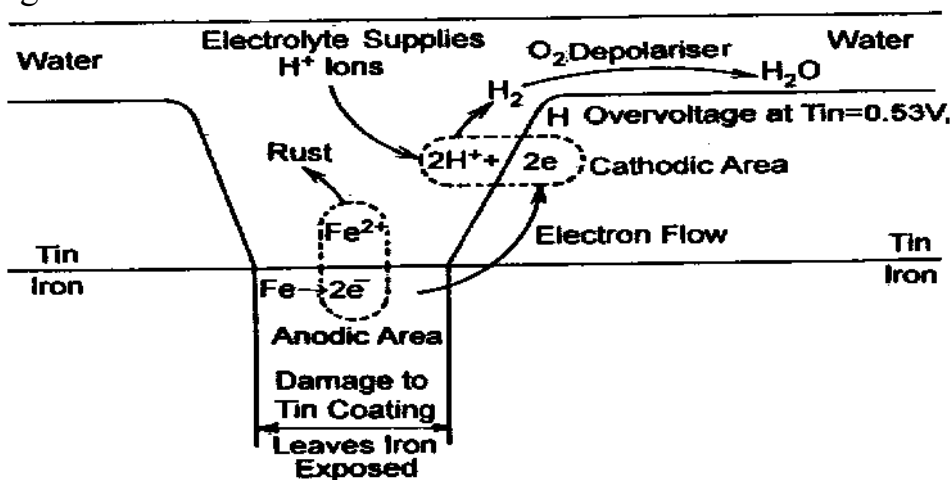


Fig. 1.10

Similarly one can explain the protective action of tin. Sn-coating however is not as durable as Zn-coating.

- **Metal Spraying:** A coating by metal spray is utilized for huge structures like bridges and used when hot dipping is not possible.
- **Cementation:** In this method, metal to be deposited forms alloys with the surface on which deposition is taking place. The article to be treated are packed in powder coating metal in drum which can be rotated and which is heated at a temperature somewhat below the m. p. of more fusible metal. Although this process is costly, it furnished uniform films and used in coating screen, bolts, nuts and other similar articles.

- g) *Covering with paints*: Protective layer can be formed on the metal surface by paints oils, tars, Bakelite silica and glass. However, paints and glass are generally used. Red paint is ideal for iron surface. Primary coating contains $ZnCrO_4$ and red lead is followed by secondary coating containing Fe_2O_3 gives mechanical protection.
- h) *Making the metal cathodic by external e.m.f.*: The e.m.f. of corrosion is very small. When an external e.m.f. of greater magnitude and in opposite direction is applied to metals, anodic metal become cathodic and will not corrode. A potential of 6 to 10 volts is sufficient to prevent the corrosion.

III. Methods Based on the Treatment of Medium:

- a) *Change of state of medium*: If the state of medium like H^+ ion concentration, conductivity or concentration of dissolved O_2 of medium is changed, the rate of corrosion is decreased to a great extent. Small amount of Na_2CO_3 or KOH are added to change the H^+ ion concentration. $K_2Cr_2O_7$ is added to the medium to produce protective oxide film on metal.
- b) *Corrosion Inhibitors*: The substances which bring about chemical alteration of the metal surface so as to make the same corrosion proof are called corrosion inhibitors. Effective corrosion inhibitor organic compound is quinoline. $K_2Cr_2O_7$ is used as corrosion inhibitor to the cooling water in radiators of the cars. According to recent theory due to G. H. Cartlidge, the action of corrosion inhibitor is to inactive metal surface chemically and protect from rusting. Very dilute solution of $KTcO_4$ may be used as corrosion inhibitor. But we cannot use because its quantity available in the world is not sufficient for this purpose. There are two types of corrosion inhibitors:
- *Anodic inhibitors*: Chromates, phosphates, tungstates have high oxygen content forming a sparingly soluble compound with a newly formed metal ion. This compound forms protective film.
 - *Cathodic inhibitors*: They are of two types. In acidic solution, the main reaction is evolution of hydrogen. $2 H^+ + 2 e^- \rightarrow H_2$ Consequently, corrosion may be reduced by:
 - i. Slowing down the diffusion of H^+ and it is considerably decreased by organic inhibitors like amines, mercaptans, heterocyclic nitrogen compounds, urea etc are adsorbed at the metal surface.
 - ii. Increasing the over potential of hydrogen evolution. As_2O_3 or Sb_2O_3 are used for this purpose because they deposit adherent film of metal-As or Sb at the cathodic area.

IV. Methods Based on External Influence: Method should be adapted to the following processes to check corrosion due to external influence.

- a) Painting the metal with light proof paint to keep off light from the surface of the metal.
- b) Detection and removal of stray current.
- c) Prevention of bacterial growth. Suitable antiseptics and bactericides are generally added to the medium to check the corrosion.

From the above methods it is evident that corrosion of the metal can be prevented in an effective manner by the methods based on '*Treatment of Metal*'.