

Corrosion is a natural process that converts a refined metal into a more chemically-stable form such as oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually a metal) by chemical and/or electrochemical reaction with their environment.

Corrosion of metal is defined as the spontaneous destruction of metals in the course of their chemical, electrochemical or biochemical interactions with the environment. Thus, it is exactly the reverse of extraction of metals from ores.

Example: - Rusting of iron

A layer of reddish scale and powder of oxide (Fe_3O_4) is formed on the surface of iron metal.

A green film of basic carbonate [$CuCO_3 + Cu(OH)_2$] is formed on the surface of copper, when it is exposed to moist-air containing carbon dioxide.

Consequences (Effects) of Corrosion: -

- 1) Due to formation of corrosion product over the machinery, the efficiency of the machine gets failure leads to plant shut down.
- 2) The product contamination or loss of product due to corrosion.
3. Corrosion releases the toxic products.
4. Health (e.g., from pollution due to a corrosion product or due to the escaping chemical from corroded equipment.)

Cause of Corrosion

In nature, metals occur in two different forms.

1. Native state
2. Combined state

Native state - Native states means free or uncombined state. In general ~~the~~ these metals are non-reactive in nature. They are noble metals which have very good corrosion resistance. ~~Examples~~
Example: Au, Ag, Pt etc.

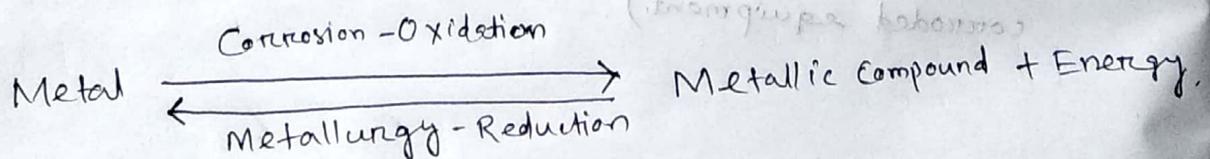
Combined state - Except noble metals, all other metals are highly reactive in nature which undergoes reaction with their environment to form stable compounds called ores and minerals. This is the combined state of metals. ~~Example~~
Example: Fe_2O_3 , ZnO , PdS , $CaCO_3$, etc.

Metallic Corrosion: -

The metals are extracted from their metallic compounds (ores). During the extraction, ores are reduced to their metallic states by applying energy in the form of various processes. In the pure metallic state, the metals are unstable as they are considered in excited state (higher energy state).

Therefore as soon as the metals are extracted from their ores, the reverse process begins and; form metallic compounds, which are thermodynamically stable (lower energy state). Hence, when metals are used in various forms, they are exposed to environment, the exposed metal surface begin to decay (conversion to more stable compound).

This is the basic reason for metallic corrosion.



Although corroded metal is thermodynamically more stable than pure metal but due to corrosion, useful properties of a metal like malleability,

ductility, hardness, luster and electrical conductivity are lost.

Theories of Corrosion:-

Based on the environment, corrosion is classified into (i) Dry or Chemical Corrosion and (ii) Wet or Electrochemical Corrosion.

Dry or Chemical Corrosion:-

The dry or chemical corrosion is defined as the direct chemical attack of metal surfaces by the atmospheric gases present in the environment such as, oxygen, halogen (F, Cl, Br, I), hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid.

Example: (i) silver materials undergo chemical corrosion by atmospheric H_2S gas.
(ii) Iron metal undergo chemical corrosion by HCl gas.

Types of Dry or Chemical Corrosion:-

1. Corrosion by oxygen or Oxidation corrosion
2. Corrosion by Hydrogen
3. Liquid Metal Corrosion

Corrosion by Oxygen or Oxidation Corrosion:-

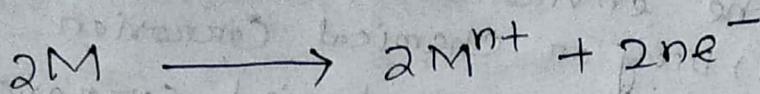
Oxidation corrosion is brought about by the direct attack of oxygen at low or high temperature on metal surfaces in the absence of moisture.

Alkali metals (Li, Na, K etc) and alkaline earth metals (Mg, Ca, Sn etc.) are rapidly oxidised at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidised.

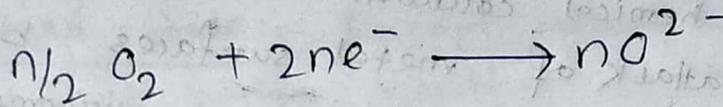
The reactions of oxidation corrosion are as follows:

Mechanism:

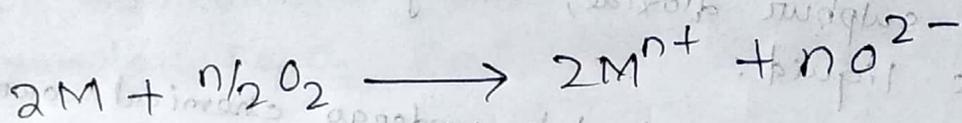
1. Oxidation (loss of electron) takes place at the surface of the metal forming metal ions M^{n+}



2. Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.



3. The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.



Metal + Oxygen \longrightarrow Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is

(i) stable layer:

A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such layer can be of impervious nature (i.e. which cuts-off penetration of attacking oxygen to the underlying metal). Such a film behaves as protective coating in nature thereby shielding the metal surface. The oxide films on Al, Sn, Pb, Cu, Pt etc, are stable, tightly adhering and impervious in nature.

(ii) Unstable oxide layer :-

This is formed on the surface of noble metals such as Ag, Au, Pt. As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) Volatile oxide layer :-

The oxide layer film volatilized as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO_3 is volatile in nature.

(iv) Porous layer :-

The layer having pores or cracks. In such a case, the atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

(*) Pilling - Bedworth ratio (P-B ratio) or rule :-

According to it "an oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal from which it is formed". On the other hand, "if the volume of the oxide is less than the volume of metal, the oxide layer is porous (or non-continuous) and hence, non-protective, because it cannot prevent the access of oxygen to be fresh metal surface below".

Thus, alkali and alkaline earth metal (like Li, K, Na, Mg) form oxides of volume less than the volume of metals. ($V_{\text{oxide}} < V_{\text{metal}}$) Consequently, the oxide layer faces stress and strains, thereby developing cracks and pores in

its structure. Porous oxide scale permits free access of oxygen to the underlying metal surface (through cracks and pores) for fresh action and thus, corrosion continues non-stop.

Metals like Aluminium forms oxide, whose volume is greater than the volume of metal. ($V_{\text{oxide}} > V_{\text{metal}}$). Consequently, an extremely tightly-adhering non-porous layer is formed. Due to the absence of any pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

OR

The P-B ratio is defined as.

$$R_{PB} = \frac{V_{\text{oxide}}}{V_{\text{metal}}} = \frac{M_{\text{oxide}} \cdot f_{\text{metal}}}{n \cdot M_{\text{metal}} \cdot f_{\text{oxide}}}$$

Where:

R_{PB} = Pilling - Bedworth ratio

M = atomic or molecular mass

n = number of atoms of metal per molecule of the oxide

$$f = \text{density} = \frac{M}{V}; \quad V = \frac{M}{f}$$

V = molar volume.

Application

(*) If $R_{PB} < 1$, the oxide coating layer is too thin, likely broken and provides no protective effect (for example Li, K, Na, Mg etc).

* If $R_{PB} > 2$: the oxide coating chips off and provides no protective effect (example Fe).

* If $1 < R_{PB} < 2$: the oxide coating is passivating and provides a protecting effect against further surface oxidation (examples aluminium, titanium, chromium-containing steels).

Corrosion by other gases (by hydrogen):-

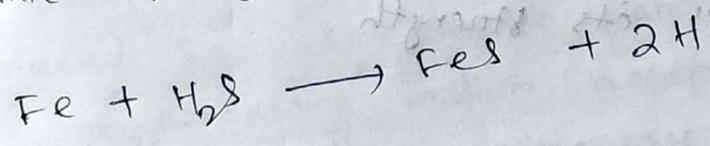
1. What is Hydrogen Embrittlement?

Hydrogen embrittlement (HE) also known as hydrogen assisted cracking (HAC) and hydrogen-induced cracking (HIC), describes the embrittling of metal after being exposed to hydrogen.

Loss in ductility of a material in the presence of hydrogen is known as hydrogen embrittlement.

Mechanism:-

This type of corrosion occurs when a metal is exposed to hydrogen environment. Iron liberates atomic hydrogen with hydrogen sulphide.



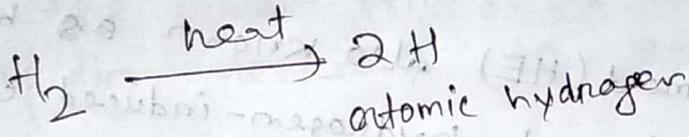
Hydrogen diffuses into the metal matrix in this atomic form and gets collected in the voids present inside the metal. Further, diffusion of atomic hydrogen makes them combine with each other and forms hydrogen gas.



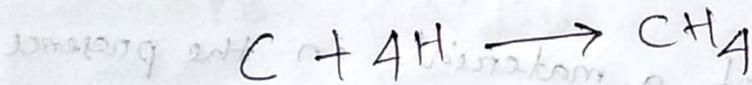
Collection of these gases in the voids develops very high pressure, causing cracking or blistering of metal.

2. Decarburisation:-

The presence of carbon in steel gives sufficient strength to it. But when steel is exposed to hydrogen environment at high temperature, atomic hydrogen is formed.



Atomic hydrogen reacts with the carbon of the steel and produces methane gas.



Hence, the carbon content in steel is decreased. The process of decrease in carbon content in steel is known as decarburization.

Collection of methane gas in the voids of steel develops high pressure, which causes cracking.

Thus, steel loses its strength.

Wet or Electrochemical Corrosion: -

Electrochemical corrosion involves -

- i) The formation of anodic and cathodic areas or parts in contact with each other
- ii) Presence of conducting medium
- iii) Corrosion of anodic areas only and
- iv) Formation of corrosion product somewhere between anodic and cathodic areas. This involves flow of electron-current between the anodic and cathodic areas.

At anodic area oxidation reaction takes place (liberation of free electron), so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc). Hence corrosion always occurs at anodic areas.



M^{n+} (metal ion) \rightarrow Dissolves in solution
 \rightarrow Forms compounds such as oxidation.

At cathodic area, reduction takes place (gain of electrons), usually cathod reactions do not affect the cathode, since most metals cannot be further reduced. So at cathodic part, dissolved constituents in the conducting medium accepts the electron to form some ions like OH^{-} and O^{2-} .

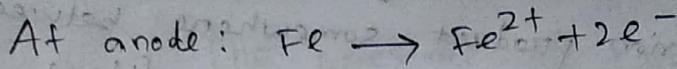
Cathodic reaction consumes electrons, which either by

- a) evolution of hydrogen or
- b) absorption of oxygen, depending on the nature of the corrosive environment.

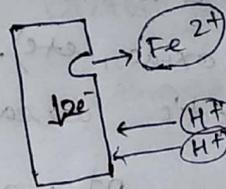
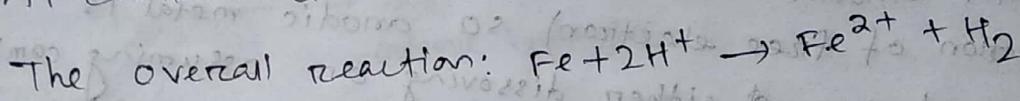
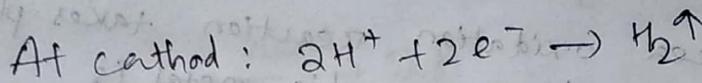
Hydrogen Evolution Type:-

All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

It occurs in acidic environment. Consider the example of Fe.



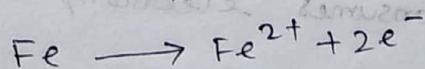
These electrons flow through the metal, from anode to cathode, where H^{+} ions of acidic solution are eliminated as hydrogen gas.



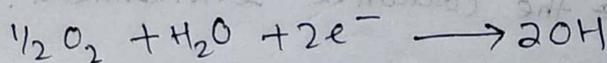
Oxygen Absorption Type:-

Rusting of iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts acts as cathodes.

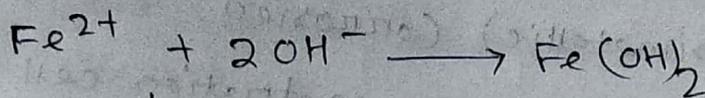
At Anode: Metal dissolves as ferrous ions with liberation of electrons.



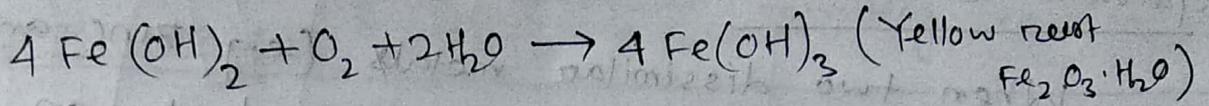
At Cathode: The liberated electrons are intercepted by the dissolved oxygen.



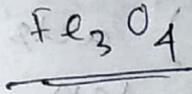
The Fe^{2+} ions and OH^{-} ions diffuse and when they meet, ferrous hydroxide is precipitated. $\text{Fe}^{2+} + 2\text{OH}^{-} \rightarrow \text{Fe}(\text{OH})_2$



(i) If enough oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide.



(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite



* Difference between (dry) chemical and (wet) electrochemical corrosion:

Chemical corrosion

1. It occurs in dry condition.
2. It is due to the direct chemical attack of the metal by the environment.
3. Even a homogeneous metal surface gets corroded.
4. Corrosion products accumulate at the place of corrosion.
5. It is self controlled process.
6. It adopts adsorption mechanism.
7. Formation of mild scale on iron surface is an example.

Electrochemical Corrosion

- It occurs in the presence of moisture or electrolyte.
- It is due to the formation of a large number of anodic and cathodic areas.
- Heterogeneous (bimetallic) surface alone gets corroded.
- Corrosion occurs at the anode while the products are formed elsewhere.
- It is a continuous process.
- It follows electrochemical reaction.
- Rusting of iron in moist atmosphere is an example.

Types of Electrochemical Corrosion

The electrochemical corrosion is classified into the following two types:

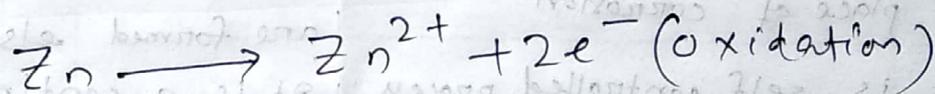
- (i) Galvanic (or Bimetallic) Corrosion
- (ii) Differential aeration or concentration cell corrosion.

Galvanic Corrosion:

When two dissimilar metals (e.g. zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. In this process, the more active metal (with more negative electrode potential) acts as a anode while less active metal (with less negative electrode potential) acts as cathode.

In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series or more noble) acts as cathode.

Mechanism: In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anode metal, zinc to the cathode metal, copper.



Thus it is evident that the corrosion occurs at the anode metal, while the cathodic part is protected from the attack.

- Examples:
- (i) steel screws in a brass marine hardware
 - (ii) Lead-antimony solder around copper wire; ~~(iii)~~
 - (iii) a steel propeller shaft in bronze bearing
 - (iv) steel pipe connected to copper plumbing.

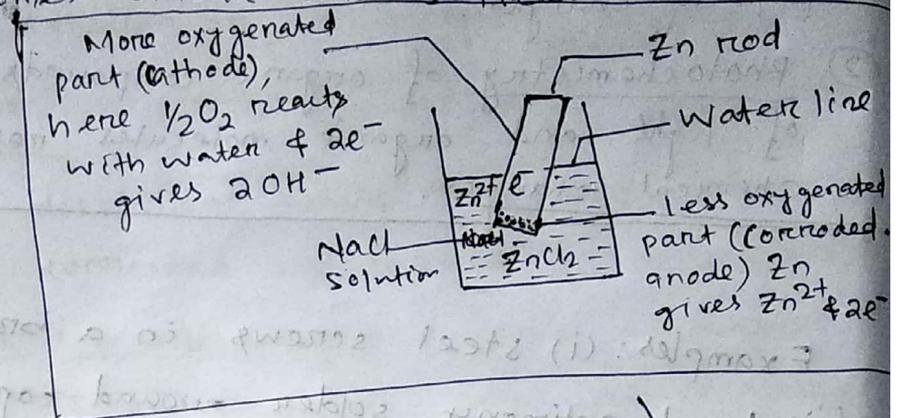
Concentration Cell Corrosion:-

It is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration.

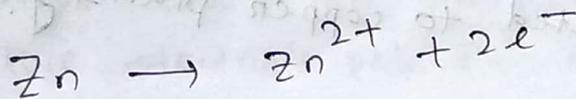
It occurs when one part of metal is exposed to a ~~different~~ different air concentration from the other part. This causes a different difference in potential between differently aerated areas. It has been found experimentally that ~~poor oxygenated~~ poor-oxygenated parts are anodic.

Example: (i) The metal part immersed in water or in a conducting liquid is called water line corrosion.
(ii) The metal part partially buried in soil.

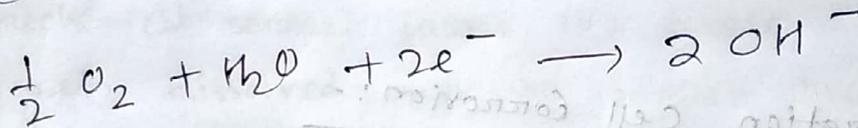
Explanation: - If a metal is partially immersed in a conducting solution the metal part above the solution is more aerated and becomes cathodic. The metal part inside the solution is less aerated and thus becomes anodic and suffers corrosion.



At anode: corrosion occurs (less aerated)



At cathode: OH^{-} ions are produced (more aerated)



Examples for this type of corrosion are

- 1) Pitting or Localized corrosion
- 2) Crevice Corrosion
- 3) Pipeline corrosion
- 4) Corrosion on wire fence.

Pitting Corrosion:

Pitting is a localized attack, which results in the formation of a hole around which the metal is relatively unattacked.

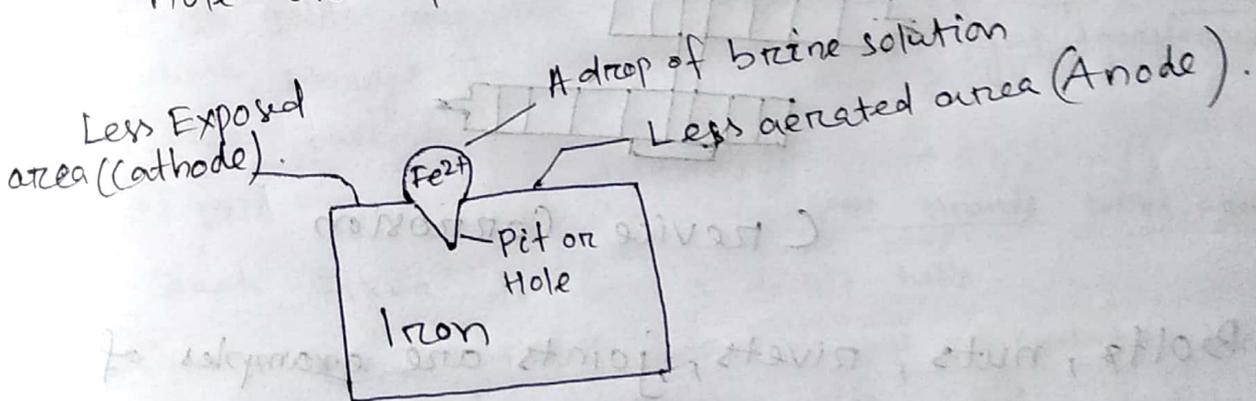
The mechanism of this corrosion involves setting up of differential aeration or concentration cell.

Metal area covered by a drop of water, dust, sand, scale etc. is the aeration or concentration cell.

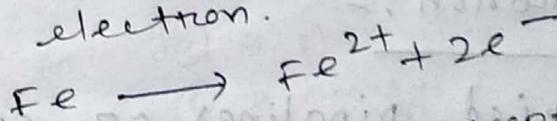
Pitting corrosion is explained by considering a drop of water or brine solution (aqueous solution of NaCl) on a metal surface, (especially iron)

The area covered by the drop of salt solution as less oxygen and acts as anode. This area suffers corrosion, the uncovered area acts as cathode due to high oxygen content.

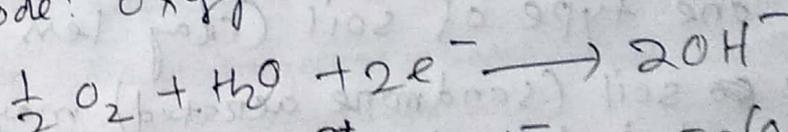
It has been found that the rate of corrosion will be more when the area of cathode is larger and the area of the anode is smaller. Hence there is more material around the small anodic area results in the formation hole or pit.



At anode: Fe is oxidized to Fe^{2+} and releases an electron.



At cathode: Oxygen is converted to hydroxide ion

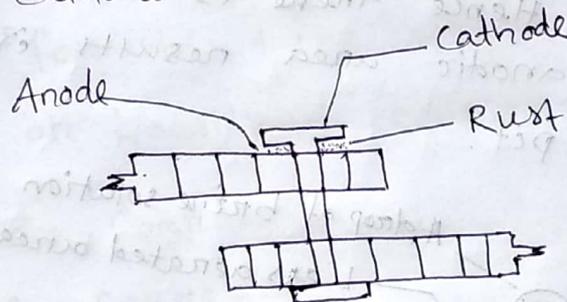


The net reaction is $Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$

The above mechanisms can be confirmed by using ferroxy indicator (a mixture containing phenolphthalein and potassium ferricyanide). Since OH^- ions are formed at the cathode, this area imparts pink colour with phenolphthalein indicator. At the anode, iron is oxidized to Fe^{2+} which combines with ferricyanide and shows blue colour.

Crevice Corrosion: -

If a crevice (a crack forming a narrow opening) between metallic and non-metallic material is in contact with a liquid, the crevice becomes anodic region and undergoes corrosion. Hence, oxygen supply to the crevice is less. The exposed area has high oxygen supply and acts as cathode.



Crevice Corrosion

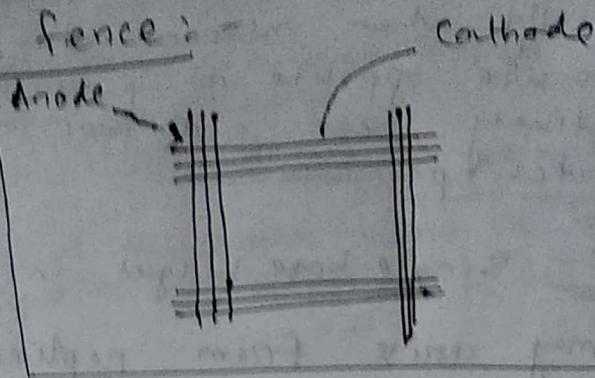
Bolts, nuts, rivets, joints are examples of this type of corrosion.

Pipeline Corrosion: -

Buried pipelines or cables passing from one type of soil (clay less aerated) to another soil (sand more aerated) may get corroded due to differential aeration.

Corrosion in wire fence:

A wire fence is one which the areas where the wire cross (anode) are less aerated than the rest of the fence (cathodic). Hence corrosion takes place at the wire crossing.



Corrosion occurring under metal washers and lead pipeline passing through clay to cinders (ash) are other examples.

Stress Corrosion:

Stress corrosion is another form of corrosion that is important to many fields including civil structures.

Stress-corrosion occurs when a material exists in a relatively inert environment but corrodes due to an applied stress. The stress may be externally applied or residual.

Many alloys can experience stress corrosion, and the applied stress may also be due to a residual stress in the material. An example of a residual stress could be a stress remaining in a material after forming, or a stress due to welding.

Stress corrosion is a form of galvanic corrosion, where stressed areas of the material are anodic to the unstressed areas of the material.

Paradoxically the best way to control stress corrosion cracking is to limit or reduce the stresses a material is under while it is

Protective Coating

Introduction:-

In order to protect metals from corrosion, it is necessary to cover the surface by means of protective coatings. These coatings act as a physical barrier between the coated metal surface and the environment. They afford decorative appeal and impart special properties like hardness, oxidation resistance and thermal insulation.

Classification:-

Protective coatings can be ~~broad~~ broadly classified into two types. They are

1. Inorganic coatings
- 2) organic coating.

Inorganic coatings are further classified into two types. They are

1) metallic coating:

- (i) Hot dipping - Galvanising, Tinning
- ii) Metal cladding
- iii) Cementation - Sherardising, Chromising, Calorising
- iv) Electroplating.

2) Non-metallic coating

- i) Surface coating or chemical conversion coating - chromate coating, phosphate coating and oxide coating.

ii) Anodising

- iii) Enamel coating or vitreous or Porcelain coating.

Organic coatings consists of —

paints, Varnishes, Lacquers and Enamels.

Paints

Paint is a viscous opaque (not clear), mechanical dispersion mixture of one or more pigments (dye) in a vehicle (drying oil).

Requisites of good paint:

- A good paint should have the following properties, it should
- 1) have a high hiding power
 - 2) form a good and uniform film on the metal surface.
 - 3) The film should not crack on drying.
 - 4) give a glossy film.
 - 5) The film produced should be washable.
 - 6) Give a stable and decent colour on the metal surface
 - 7) have good resistance to the atmospheric conditions.
 - 8) be fluid enough to spread easily over the surface.
 - 9) possess high adhesion capacity to the material ~~over~~ over which it is intended to be used
 - 10) dry quickly or in a reasonable duration.
 - 11) The colour of the paint should not fade.

Constituents of paint:-

- a) Pigment
- b) Vehicle or medium or drying oil
- c) Thinner
- d) Driers
- e) Fillers or Extenders
- f) Plasticizers.
- g) Antiskinning agents.

- a) Pigment:- It is a solid substance with which imparts colour to the paint. It is an essential constituent of a paint. Its functions are to
- i) Give opacity (cloudiness) and colour to the film.
 - ii) provide strength to the paint.

(iii) Provide an aesthetical appeal.

iv) Give protection to the paint film by reflecting UV light.

v) Increase weather resistance to the film.

vi) Provide resistance to paint film against abrasion.

The most commonly used pigments in paints and the compounds required are as follows: -

White pigments - White lead, ZnO , $BaSO_4$, TiO_2 , ZnO_2 .

Blue pigments - Prussian blue, Ultramarine blue.

Black pigments: Graphite, carbon black, lamp black

Red pigments: - Red lead, Fe_2O_3 , carmine

Green pigment - Chromium oxide, Chrome green

Yellow pigment: - Chrome yellow, lead chromate.