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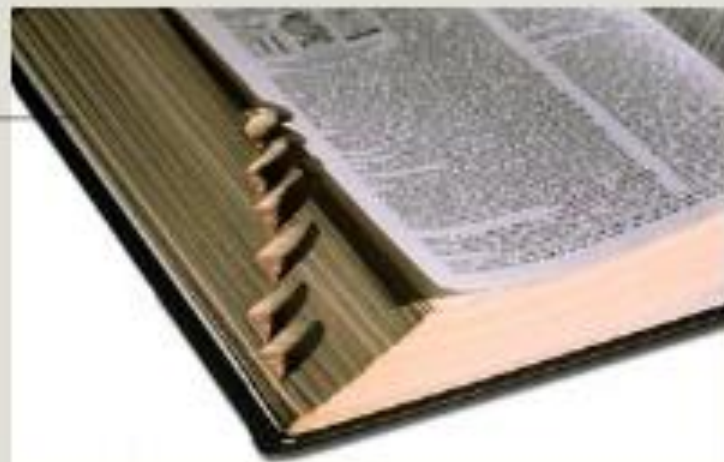
# Introduction to Corrosion

- ❑ The serious consequences of the corrosion process have become a problem of worldwide significance.
- ❑ In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive overdesign.
- ❑ It can also jeopardize safety and inhibit technological progress.

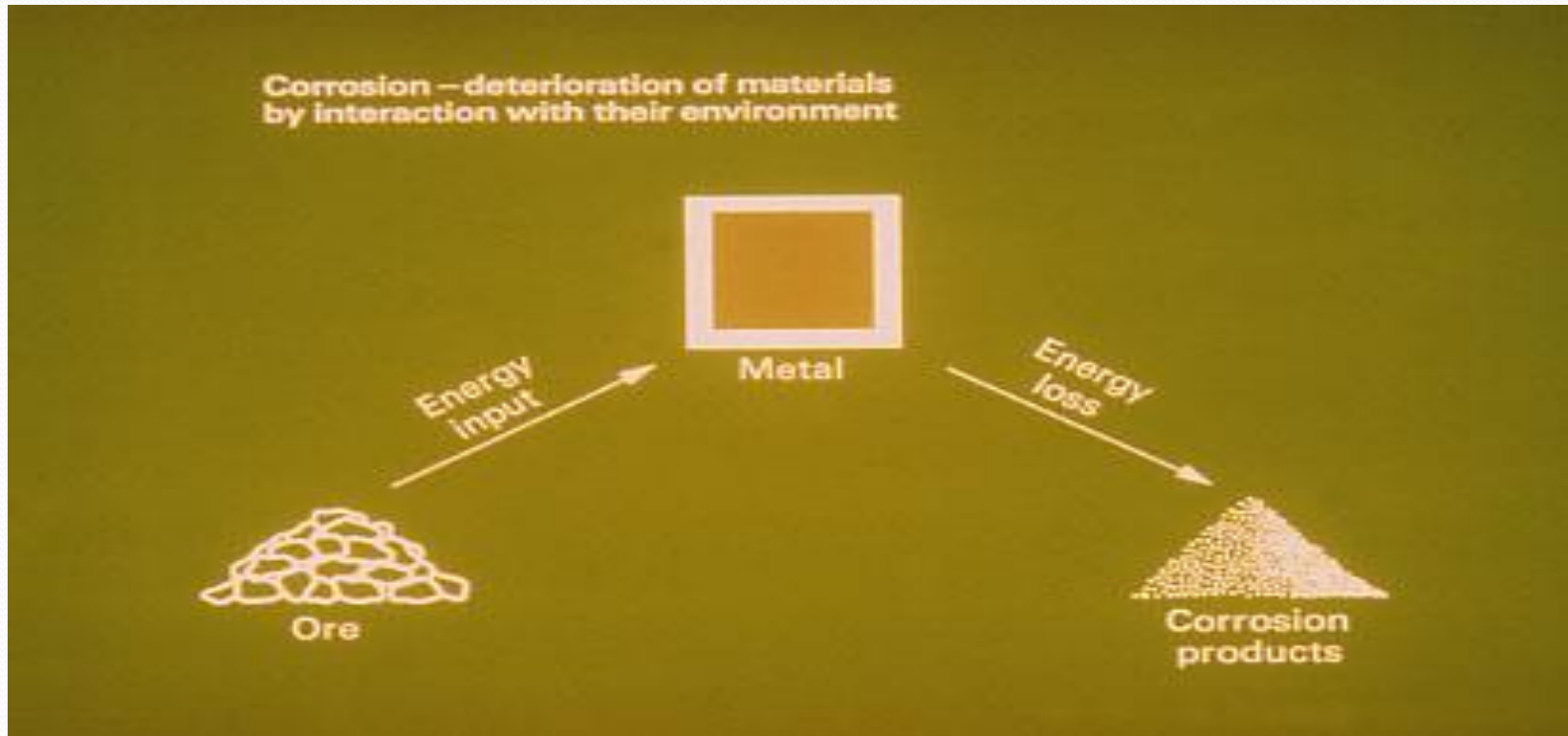
# What is Corrosion

## Corrosion (n)

- The chemical or electrochemical reaction between a material and its environments that produces a deterioration of the material and its properties.



# Definition of Corrosion



Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes also applied to the degradation of plastics, concrete and wood, but generally refers to metals.

# Corrosion

Humans have most likely been trying to understand and control corrosion for as long as they have been using metal objects. The most important periods of prerecorded history are named for the metals that were used for tools and weapons (Iron Age, Bronze Age). With a few exceptions, metals are unstable in ordinary aqueous environments.

Metals are usually extracted from ores through the application of a considerable amount of energy. Certain environments offer opportunities for these metals to combine chemically with elements to form compounds and return to their lower energy levels.

# Corrosion

- Corrosion is the primary means by which metals deteriorate.
- Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes, and other solid and liquid chemicals.
- Metals will also corrode when exposed to gaseous materials like acid vapors, formaldehyde gas, ammonia gas, and sulfur containing gases.

# Dry corrosion

# Wet corrosion

- dilute, acidic or alkaline) on metal through electrochemical reactions.
- The moisture and oxygen are also responsible.

• This type of attack of dry gases (Air and Oxygen) on the metal (corrosion is quite common).

through chemical reactions. As a result an oxide layer is formed over the surface.

# Corrosion

- ❑ Corrosion specifically refers to any process involving the deterioration or degradation of metal components.
- ❑ The best known case is that of the rusting of steel.
- ❑ Corrosion processes are usually electrochemical in nature.
- ❑ When metal atoms are exposed to an environment containing water molecules they can give up electrons, becoming themselves positively charged ions, provided an electrical circuit can be completed.



# Mechanism

- All metals exhibit a tendency to be oxidized, some more easily than others. A tabulation of the relative strength of this tendency is called the galvanic series.
- The mechanism involves the formation of a galvanic cell by diff metals or in diff areas on same piece of metal.
- When galvanic cells are formed on diff metals, the galvanic corrosion.

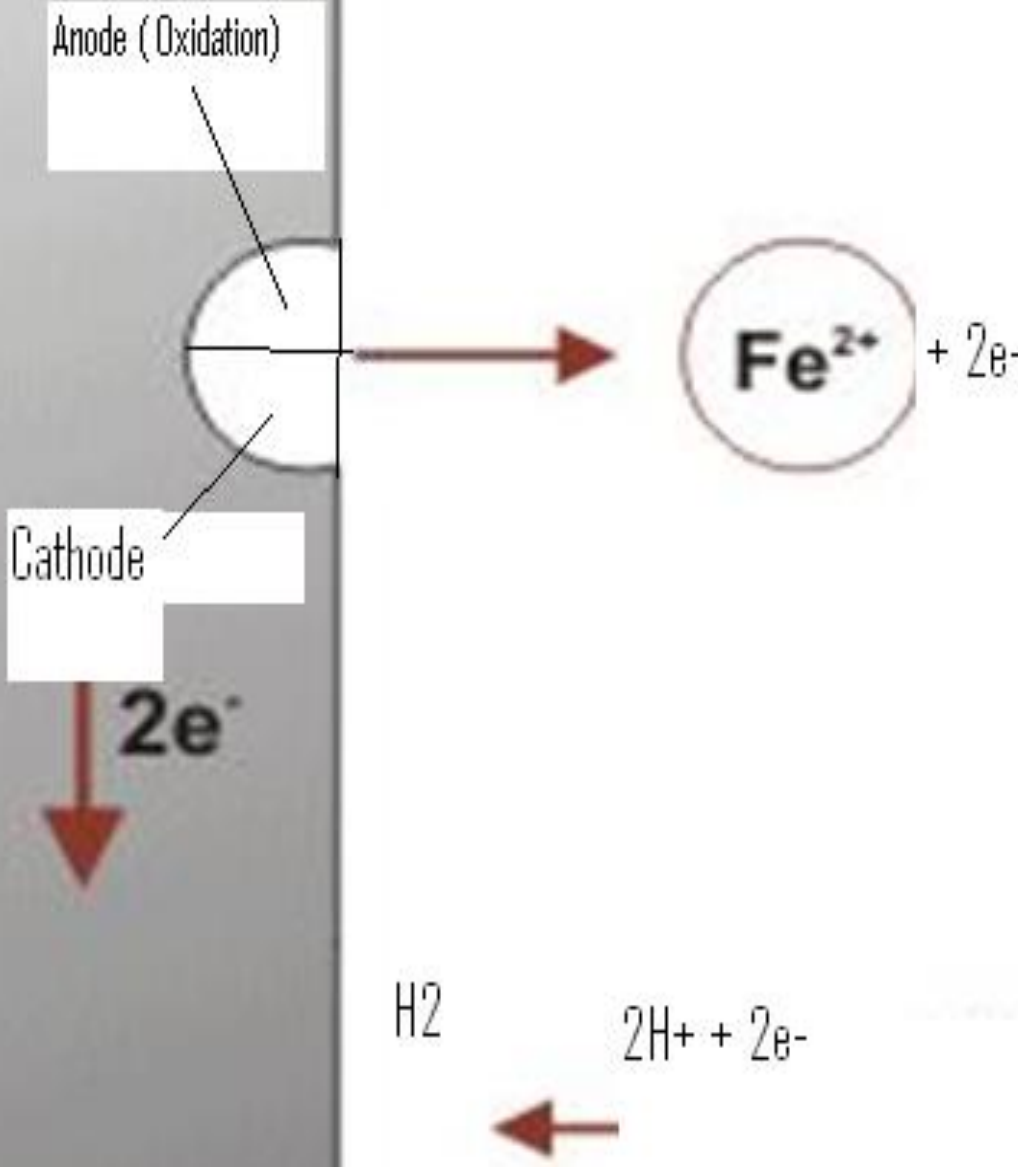
# Mechanism

- The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons that are consumed by a secondary process (cathodic reaction).
- These two processes have to balance their charges. The sites hosting these two processes can be located close to each other on the metal's surface, or far apart depending on the circumstances.

# Corrosion Reaction on Single Metal

- Electrochemical reactions are illustrated by considering the corrosion on a piece of iron in hydrochloric acid.
- Anodic and Cathodic areas are formed on the surface of iron, owing to surface imperfection (localized stresses, grain orientation, inclusions in the metals ) or due to variations in the environment.
- Numerous tiny reactions may occur.

# Mechanism



# Corrosion Mechanism

- Corrosion is the destructive attack, or deterioration, of a metal by chemical or electrochemical reaction with its environment.
- Corrosive attack of metals is an electrochemical process.
- In a galvanic cell, two dissimilar metals (e.g., iron and copper) are placed in electrical contact in the presence of oxygen and moisture.
- Separate chemical reactions take place at the surfaces of the two metals, creating a flow of electrons through the connecting wire.

# Reaction at anode

- Oxidation takes place with the release of electrons.
- Positively charged iron atoms get detached from the solid surface and enter in to solution (electrolyte) as positive ions.
- At Anode:  $\text{Fe} \longrightarrow \text{Fe}^{++} + 2 \text{e}^-$  (indicating rough surface)
- The released free electrons pass round the external circuit.

# Reaction at cathode

- Reduction of constituents occurs with the taking up of electrons.
- The free electrons reach the cathode and react with some positively charged species such hydrogen ions in the electrolyte solution.
- In the absence of acid, water itself dissociates to generate H<sup>+</sup> ions.
- At Cathod :  $2 \text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$  (indicating by formation of bubbles at the surface)

# Galvanic Cell

## Reactions

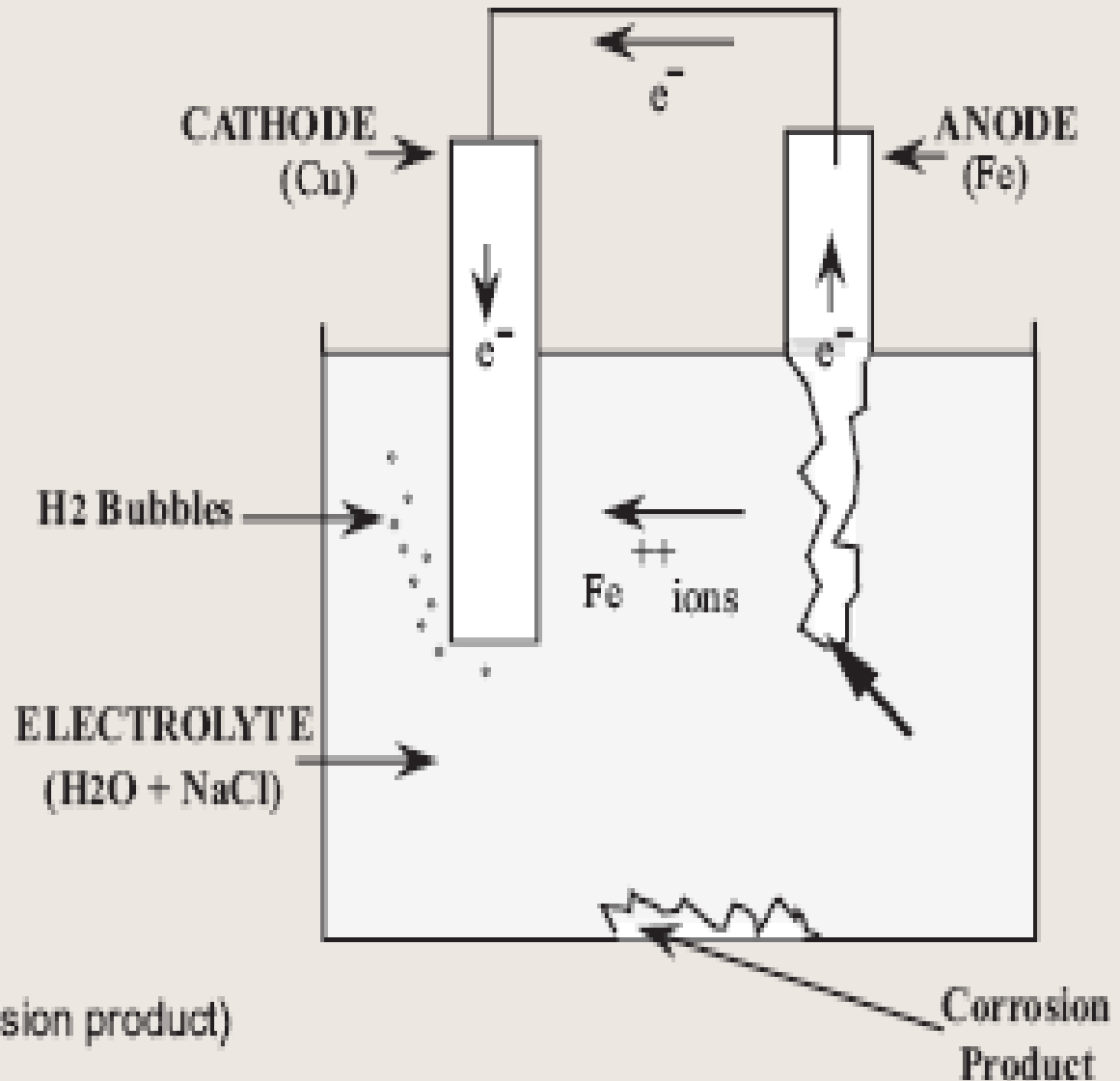
### At the Anode:



### At the Cathode:



### In the Electrolyte:





- The amt of metal (iron) which is dissolved in the electrolyte is proportional to the number of electrons flowing, which in turn is dependent upon the resistance of the metal.

- The overall Reaction :  $\text{Fe} + 2\text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})_2 + \text{H}_2$

Red brown rust.

- High evolution of  $\text{H}_2$  accompanies rapid corrosion such as hydrogen embrittlement.
- Depletion of hydrogen also enhance corrosion.
- In moderate conc of  $\text{H}_2$ , corrosion slows down.

- The actual loss of metal involved in the process takes place at the anode.
- The iron atoms are transformed to ferrous ions ( $\text{Fe}^{++}$ ) which dissolve in the solution around the anode.
- They may diffuse and combine with the hydroxyl ions ( $\text{OH}^-$ ), with the precipitation of ferrous hydroxide [ $\text{Fe}(\text{OH})_2$ ] in accordance with the following net redox reaction:
  - $2\text{Fe} + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}(\text{OH})_2$ .
- The hydrous ferrous oxide formed ( $\text{FeO}\cdot\text{H}_2\text{O}$ ) is further oxidized to form hydrous ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ ), which is rust.

# Corrosion Reaction between Metals

- Galvanic corrosion result from the flow of current from a more active metal (anode) to a less active metal (cathode).
- For example, zinc dissolves and forms an anode, while copper forms the cathode.
- These two metals form two electrons electrodes and their presence in an electrolytic solution forms galvanic cell.
- Spontaneous reaction can occur when two electrodes are connected through an external wire.

- At Anode :  $\text{Zn} \longrightarrow \text{Zn}^{++} + 2\text{e}^-$  (indicated by rough surface)
- At Cathode :  $2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2$  (indicated by formation of bubbles at the surface)
- The corrosion current flows at the expense of the anode metal, which gets corroded continuously, whereas the cathode metal is protected.
- In some cases, evolution of the hydrogen gas is slow.
- The accumulation of hydrogen on the cathode surface slows down the corrosion.
- This is called cathodic polarization.
- It forms an insulating layer that slows down or stops the electrochemical reaction.

# Corrosion Involving Oxygen

- The oxygen dissolved in an electrolyte can react with accumulated hydrogen to form water.
- Depletion of hydrogen layer allows corrosion to proceed.
- At cathode:  $O_2 + 2H_2 \longrightarrow 2H_2O$
- Corrosion proceeds due to depletion of Hydrogen.
- Above reaction take place in acid media.
- When the corrosion media is alkaline or neutral, oxygen is absorbed. The presence of moisture promotes corrosion.
- The effective conc of oxygen in water adjacent to cathode depends upon the degree of aeration, temp &

# Factors influencing corrosion

- Solution pH.
- Oxidizing agent.
- Temperature.
- Velocity.
- Surface Films.
- Other Factors.

# Solution pH

- Metals such as iron dissolve rapidly in acidic solution. In the middle pH range (4 to 10), the conc of  $H^+$  ions is low. Hence, the corrosion rate is controlled by the rate of transport of oxygen.
- Certain amphoteric metals dissolve rapidly in either acidic or basic solution. E.g. Al and Zn.
- Noble metals are not affected by pH. E.g. gold and platinum.
- $H^+$  ions capture electrons and promote anodic corrosion.

# Oxidizing agents

- Oxidizing agents accelerate the corrosion of one class of materials, whereas retard another class.
- Oxidizing agents such as oxygen react with hydrogen to form water. Once hydrogen is removed, corrosion is accelerated. E.g. copper in NaCl
- Oxidizing agent retard corrosion due to formation of surface oxide films, which makes the surface more resistant to chemical attack.
- Thus a balance between the power of oxidizing agent to preserve the protective layer and their tendency to destroy the protective film determine the corrosion of metal.



# Temperature

- Rise in temp increase rate of corrosion.
- Increase in temp reduce the solubility of oxygen or air. The released oxygen enhances the corrosion.
- Increase in temp induces phase change, which enhance the rate of corrosion. At high temp organic chemicals are saturated with water. as temp decreases, water gets condensed.
- Oxygen is needed for maintaining iron oxide film. In the absence of O<sub>2</sub> corrosion of S.S. increases.
- Copper based alloys do not depend on oxide film for corrosion.

# Velocity

- High velocity of corrosive medium increases corrosion.
- Corrosion products are formed rapidly, because chemicals are brought to the surface at a high rate.
- The accumulation of insoluble film on the metallic surface is prevented. So corrosion resistance of these films decreases.
- The corrosion products are easily stirred and carried away, thereby exposing the new surfaces for corrosion.

# Surface Films

- The oxide films are formed on the surface of S.S. these films absorb moisture, which delay time of drying and hence increases the extent of corrosion.
- Insoluble salts such as carbonates and sulphates may be precipitated from hot solution on the metal surfaces. These protect the metal surfaces.
- If the film is porous (e.g. ZnO) corrosion continues. Nonporous films (CrO on iron) prevent further corrosion.
- Oil and grease films may occur on the surface either intentionally or naturally. These films protect surface from direct contact with corrosive substance. E.g. metals submerged in sewage .

# Other factor

- The conc of corrosive chemicals. In distillation columns, evaporators, the conc can change continuously, so difficult to predict the corrosion rate.
- The presence of moisture that collects during cooling can turn innocuous chemicals into dangerous corrosives.

# Type of Corrosion

Four Type of corrosion

- 1. Fluid corrosion, General
- 2. Fluid corrosion, Localized
- 3. Fluid corrosion, Structural
- 4. Fluid corrosion, Biological.

# 1. Fluid corrosion, General

- When corrosion is generally confined to a metal surface, it is known as general corrosion.
- It occurs in uniform fashion over the entire exposed surface area.
- Two type general corrosion
  - 1. Physicochemical corrosion
  - 2. electrochemical corrosion

# 1. Fluid corrosion, General

Physicochemical  
corrosion

Electrochemical  
corrosion

- point of metallic surface.
- Metallic surface.
- The effect of surface type is swelled in organic acids, cracking, softening and porosity e.g.

corrosion of non metal plastic & metal

# General Corrosion Control

- Eliminate oxygen
- Eliminate chloride ion
- Maintain pH levels
- Prevent stagnation
- Chlorinate





## 2. Fluid corrosion, Localized

- It is most commonly observed on different locations.

Four types

1. Specific site corrosion
2. Stress induced corrosion
3. Liquid flow related corrosion
4. Chemical reaction related corrosion


# A) Specific site corrosion

- Mechanically weak spots or dead spots in a reaction vessel cause sp site corrosion.


Three type

1. Inter-granular corrosion
2. Pitting corrosion
3. Crevice corrosion

## a) Inter-granular corrosion

- Selective corrosion that occurs in the grain boundaries in a metal/alloy is called as inter-granular corrosion.
- When it is severe it causes loss of strength and ductility.
- E.g. Austenitic S.S +  $\text{HNO}_3$   grain boundary ppt.
- S.S is stabilized by adding niobium/titanium (less than 0.03 %).

## b) Pitting corrosion

- In this type pits and cavity develops.
- They range from deep cavities of small diameter to shallow depression.
- E.g. alloy of Al/S.S + Aq. Solution  Cavities.

Pitting occur when there is break in protective oxide layer and imperfections on the underlying metal.

## c) Crevice corrosion

- Here, corrosion take place in crevices bcz solutions retained at this place and takes longer time to dry out.
- When this occurs, the severity of attack is more severe at crevices.
- Crevices are formed bcz of the metal contact with another piece of the same or other metal or with a nonmetallic material.
- Corrosion in crevice is due to deficiency of  $O_2$ , Acidity changes, Depletion of inhibitor.

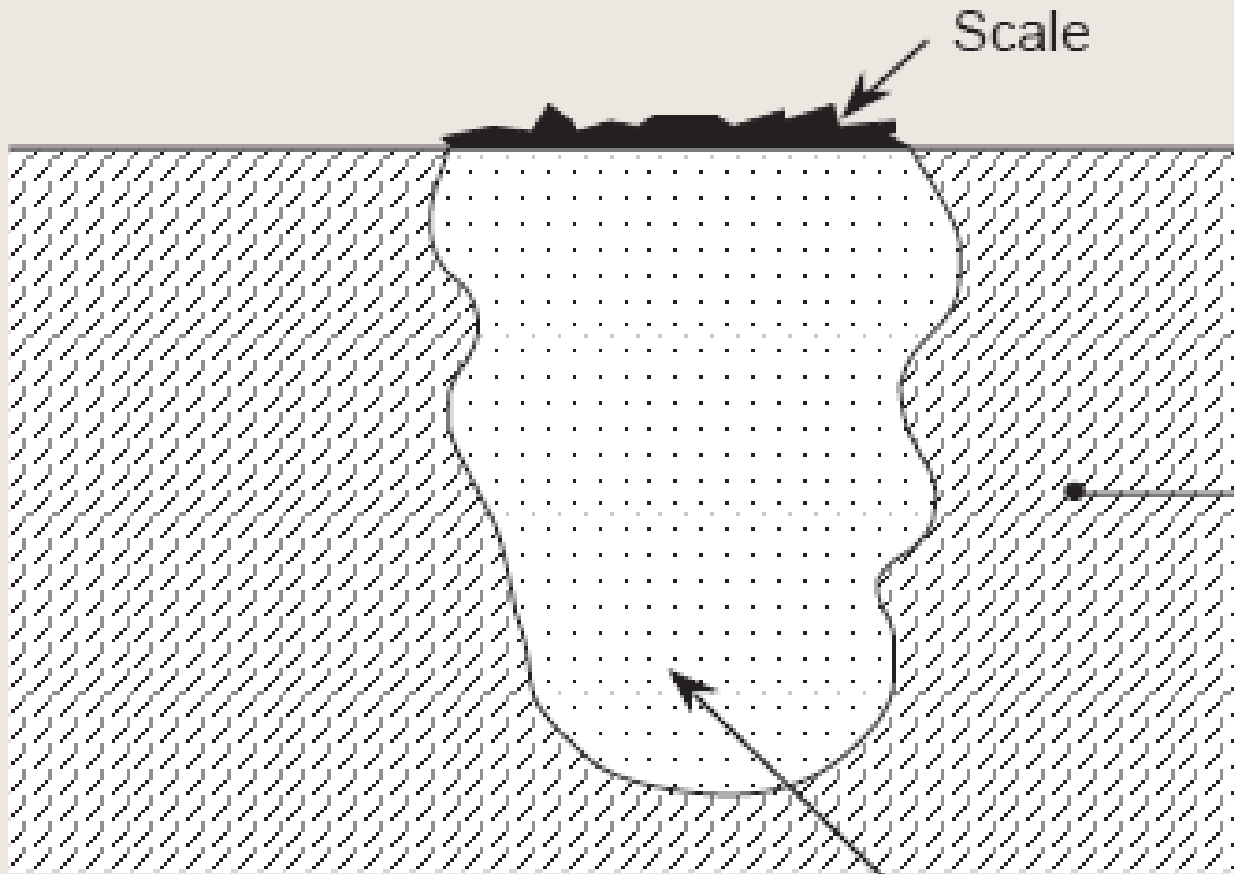
# Pitting and Crevice Corrosion

Electrolyte ( $H_2O$  plus dissolved oxygen)

Scale

Metal

Region where pit will form



## B) Stress induced corrosion

- Residual internal stress in metal external applied stress accelerate the corrosion.
- Residual internal force is produced by:
  - ❑ Deformation during fabrication
  - ❑ Unequal rate of cooling from high temp.
  - ❑ Internal stress rearrangement involving volume changes
  - ❑ Stress induced by rivets, bolts and shrink fits.

Eliminating high stress areas prevent this type of corrosion.

# a) Stress Corrosion Cracking

- At the surface, if the tensile stress is equal to or more than yield stress, the surface develops crack is known as stress corrosion cracking.
- E.g. cold formed brass develops crack in the environment of ammonia.
- Embrittlement of cracking of steel is observed in caustic solution.





## **b) Corrosion fatigue**

- Corrosion fatigue is the ability of metal surface to withstand repeated cycle of corrosion. The metal surface is stressed and simultaneously attacked by the corrosive media.
- Pits indicating corrosion are formed initially, which further develops in to cracks.
- The protective surface oxide film reduces corrosion. Under cycling or repeated stress conditions, rupture of protective oxide films takes place at a higher rate than at which new protective films can be formed. So the rate of corrosion is

## c) Fretting corrosion

- Fretting corrosion occurs when metals slide over each other and cause mechanical damage to one or both.
- During relative movement of metals, two processes may occur, (i) frictional heat is generated, which oxidizes the metal to form oxide films. (ii) removal of the protective films resulting in exposure of fresh surface to corrosion attack.
- This can be avoided by using harder materials, minimizing friction by lubrication or by proper designing of the equipment.

# C) Flow related corrosion

- Liq. Metals can cause corrosion.
- The driving force is the tendency of the liq. To dissolve solids or penetrating the metal along the grain boundaries at place of wetting.
- E.g. mercury attack on Al alloy
- Molten Zinc on S.S.

## a) Impingement corrosion

- Also referred as erosion corrosion or velocity accelerated corrosion.
- It is accelerated by removal of corrosive products, which would otherwise tend to stifle the corrosion reaction.

## b) Erosion corrosion

- Erosion is the destruction of metal by abrasion and attrition caused by the flow of liq./gas.

Factors that influence erosion

1. Alloy content of the steel (e.g. Cr, Cu, Mn)
2. Pipe system design and component geometry.
3. Water and steam composition (especially pH and oxygen content).

The use of harder metals and changes in velocity or environment are used to prevent erosion.

## c) Cavitation corrosion

- Formation of transient voids or vacuum bubbles in a liq stream passing over a surface is known as cavitation.
- The bubble may collapse on the metal surface thereby causing severe impact or explosive effect.
- So considerable damage and corrosion is observed.
- Cavitation corrosion is also observed around propellers, rudder in pumps etc.

## D) Chemical Reaction related corrosion

- Corrosion involves chemical reactions such as oxidation and reduction.
- Galvanic corrosion
- Oxygen conc cell
- Hydrogen embrittlement

## a) Galvanic corrosion

- It is associated with the flow of current to a less active metal from a more active metal in the same environment.
- Coupling of two metals, which are widely separated in the electrochemical series, generally produces an accelerated attack on the more active metal, zinc.



## b) Oxygen conc cell

- It is due to the presence of oxygen electrolytic cell.
- i.e. diff in the amt of oxygen in solution at one point exists when compared to another.
- Corrosion is accelerated when the  $O_2$  is least, for example, under gasket, stuffing boxes etc.

## c) Hydrogen embrittlement

- hydrogen can penetrate carbon steel and react with carbon to form methane.
- The removal of carbon result in decreased strength.
- Corrosion is possible at high temp as significant hydrogen partial pressure is generated.
- This cause a loss of ductility, and failure by cracking of the steel.
- Resistance to this type of attack is improved by allowing with chromium / molybdenum.

## c) Hydrogen embrittlement

- Hydrogen damage can also result from  $H_2$  generated by electrochemical corrosion reaction.
- The result is failure by embrittlement, cracking, and blistering.
- This is observed in solution of sp weak acids such as hydrogen sulphide and HCN.

# 3. Fluid corrosion: Structural

- Here, the strength is reduced on account of corrosion.
- This may occur when one component of the alloy is removed or released into solution.
- The corrosion pdt may retain in the plant.
- E.g. Graphite corrosion
- Dezincification

# a) Graphite corrosion

- Graphite is allotropy of carbon.
- Graphite corrosion may occur in gray cast iron.
- Metallic iron is converted in to corrosive pdts leaving a residue of intact graphite mixed with iron corrosive pdts and other insoluble constituent of cast iron.
- When the layer of corrosion is impervious corrosion will cease.
- If layer is porous corrosion will be greater.

# a) Graphite corrosion

- When carbon steel is heated for prolonged periods at temp greater than 455 C, carbon may segregated, which is then transformed in to graphite. So the structural strength of the steel is affected.
- Employing killed steels of Cr and Molybdenum or Cr and Ni can prevent this type of corrosion.

## b) Dezincification :

- It is seen in brass containing more than 15 % zinc.
- In brass the principle pdt of corrosion is metallic copper, which may redeposit on the plant.
- Another mechanism involves the formation of zinc corrosion pdts.
- Corrosion may occur as a plug filling pits or as a continuous layer surrounding the unaffected core of brass.
- It can be reduced by addition of small amt of arsenic, antimony or phosphorus to the alloy.

# 4. Fluid corrosion : Biological

- The metabolic action of M.O. can either directly or indirectly cause deterioration of a metal. Such a process is called as a biological corrosion.

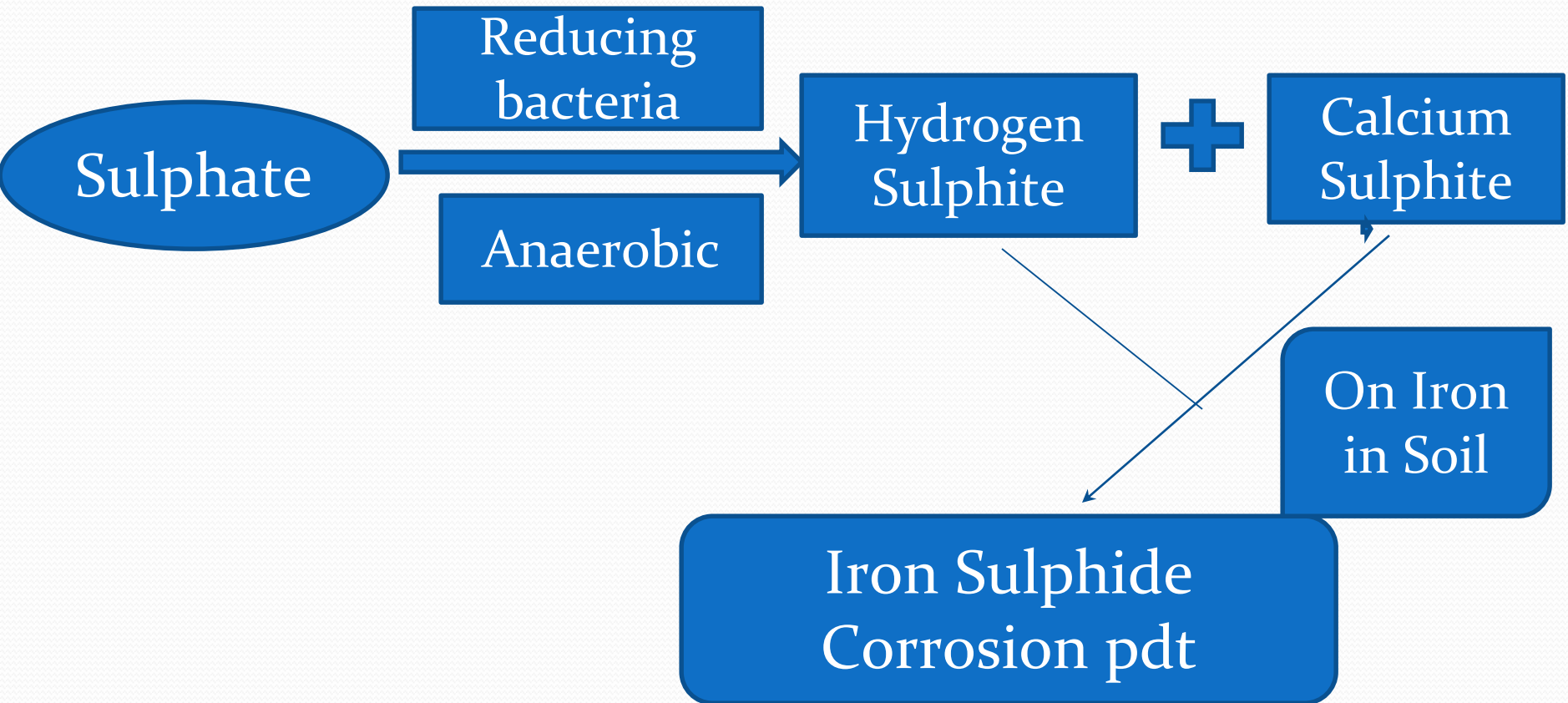
The cause of biological corrosion are:

1. Producing corrosive environment or altering environment composition.
2. Creating electrolyte conc cells on the metal surface.
3. Altering resistance to surface films.
4. Influencing the rate of cathodic/ anodic reaction.



# 4. Fluid corrosion : Biological

- The role of biological corrosion may be explained by sulphate reducing bacteria in slightly acidic or alkaline soils.



# Prevention and control

The corrosion may be prevented or controlled by following ways:

1. Selection of proper material
2. Proper design of equipment
3. Coating and lining
4. Altering environment
5. Inhibitors
6. Cathodic protection
7. Anodic protection

# 1. Selection of proper material

- Corrosion should not be permitted in fine wire screen, orifice and other items in which the dimensions are critical and change is not permitted.
- In some cases, non metallic materials will be more economic and have good performance. It should be considered if their strength, temp and design is satisfactory.
- The corrosion characteristics of chemicals and limitation of construction material can be considered.
- The processing conditions should also be considered.

## 2. Proper design of equipment

- In the design of equipment, the number of fittings like, baffles, valves and pumps should be considered.
- Corrosion can be minimized if the equipment design facilitates
  - ❑ Elimination of crevices
  - ❑ Complete drainage of liquids
  - ❑ Ease of cleaning
  - ❑ Ease of inspection and maintenance
- A direct contact between two metal is avoided, if they are separated widely in electrochemical series.

# 3. Coatings and Linings

- Nonmetallic coatings and linings can be applied on steel and other materials of construction in order to combat corrosion.
- Coating methods: electroplating, cladding, organic coating.
- The thickness of lining is important.
- Effective linings can be obtained by bonding directly to substrate metal or building multiple layers.
- Organic coatings can be used in tanks, piping and pumping lines.

### 3. Coatings and Linings

- A thin non-reinforced paint like coating of less than 0.75 mm thickness should not be used in services for which full protection is required.
- The cladding of steel with an alloy is another approach to this problem.
- Sp glass can be bonded to steel so that the liner is 1.5 mm thick which is impervious.
- Piping and equipment lined in this manner are used in severely corrosive acid services.

## 4. Altering Environment

Corrosion can be reduced by employing following conditions:

1. Removing air from boiler feed water prevents the influence of water on steel
2. Reducing the temp
3. Eliminating moisture
4. Reducing the velocity of turbulence
5. Shortening the time of exposure
6. Pumping the inert gas into solutions
7. Reducing aeration.

# 5. Inhibitors

The corrosion inhibitors are added to the environment to decrease corrosion of metals. This form protective films.

1. Adsorption type, e.g. adsorbed on metal
2. Scavenger phase type, e.g. remove corrosion agent
3. Vapor phase type, e.g. sublime and condense on metal surface.

Inhibitors are generally used in quantities less than 0.1 % by weight.



# 5. Inhibitors

e.g. of inhibitors

1. Chromate, Phosphates & Silicates protect iron and Steel in aq solution.
2. Organic sulphide and Amines protect iron and Steel in acidic solution.
3. Copper sulphate protects S.S in hot diluted solution of  $H_2SO_4$ .

# 6. Cathodic protection

- It is based on the galvanic action between the metals of the anode and cathode suspended in the solution.
- The metals to be protected is made a cathode.
- Electrons are supplied , there by dissolution of metal is suppressed.
- It can be achieved by:
  - 1. Sacrificial anode method
  - 2. Impressed emf method

# Sacrificial anode method

- In this method, anodes are kept in electrical contact with the metal to be protected.
- The anodes are sacrificed, since it goes into solution.
- E.g. for the protection of iron and steel tanks, the metals such as Zinc, Al, Mg and their alloy are used as sacrificial anodes.
- These are used in limited pH range.
- Anode metal is selected from electrochemical series.
- The anodes should not be poisonous and not detrimental to the products.

# Impressed emf method

- It is also known as applied current system, i.e., external voltage is impressed between tank and electrodes.
- The negative terminal of power is connected to the material to be protected.
- So the natural galvanic effect is avoided and the anode is maintained positive.
- Since anode is not consumed, metal or non corrodable material can be used.

# Advantages

- This method is used for large tanks to store mild corrosive liquors. In these cases, mild steel is used with negligible corrosion.
- Cathodic protection method is simple and the most effective.
- It is inexpensive. It enables the use of cheaper material for plant construction.
- **Dis-advantage:** Corrosion can not be reduced to zero.

# 7. Anodic Protection

- In this method, a predetermined potential is applied to the metal specimen and the corresponding current changes are observed.
- During the initial stage, the current increases indicating the dissolution of the metal.
- When the current reaches a critical point, passivation occurs, i.e., the oxide layers set in a suitable oxidizing environment. The potential at the critical point is called passivating potential.
- Above this passivating potential, the current flow decreases to a very small value called passivating current.

## 7. Anodic Protection

- The passivating current is defined as the minimum protective current density required to maintain passivisation.
- At this stage, an increase in potential will not corrode the metal since the latter is in highly passive state.
- E.g. in case of S.S. titanium becomes easily passive and can not offer cathodic protection.



- **Advantages :**

- The anodic protection method is utilized in the transportation of conc  $\text{H}_2\text{SO}_4$ .

- **Dia-advantages:**

- Corrosion can not be reduced to zero.

- This method cannot be applied for metals, which do not passivate.



# Application of Corrosions

Dies & punches

Milling equipment

- obtained for  
the time
- size  
reduction.  
Corrosion  
does not  
affect the  
material but  
the surface  
punches  
imperfectio  
should  
in order to  
the time
- Proper rust  
& cleaning  
corrosio

Chemical processing  
reactors

Fermentors

Storage  
containers

- During fermentation the release of these metals from the fermentors may have deleterious effects on enzyme and metabolic pathway of organism.
- Maintenance of hygiene, need for sterility and prevention of contamination are important considerations in the construction of fermentors.



**THANK YOU**