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CORROSION AND CORROSION CONTROL: Introduction. Types of corrosion. Causes of corrosion. Theories of corrosion- Direct chemical attack or dry corrosion. Electrochemical theory or wet corrosion. Differential Aeration or concentration cell corrosion. Factors influencing corrosion- nature of the metal- nature of the environment. Corrosion control. sujithkv@payyanurcollege.ac.in

Corrosion is the gradual destruction of materials (usually metals) by chemical reaction with their environment.

eg. Tarnishing of silver (AgS), rusting of iron (hydrated ferric oxide), green scales formed on copper vessels (basic cupric carbonate) etc.

- Destruction or deterioration of metal surface : CORROSION - Cancer to metals (Decay of metals)

- Metallic destruction either by direct chemical attack (by environment) or by electrochemical attack (similar to Daniell cell).

CORROSION : "Any process of deterioration (or destruction) and consequent loss of metallic material, through an unwanted (or unintentional) chemical or electrochemical attack at its surface."

Rusting of Iron ($Fe_2O_3.H_2O$, Fe_3O_4), Tarnish of Silver & Copper (Ag_2S, $AgCl$) & [$CuCO_3$+$Cu(OH)_2$]

CORROSION : REVERSE OF EXTRACTION OF METALS
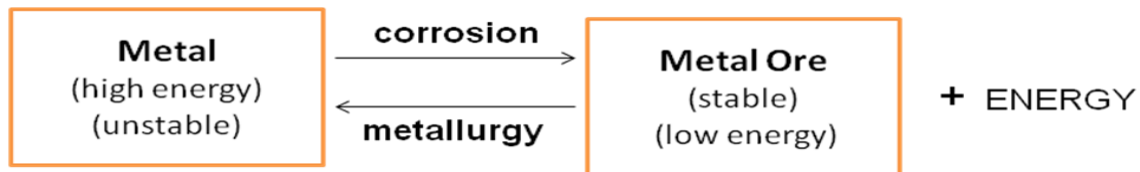
Naturally metals are in combined forms of their oxides, carbonates, sulphides, chlorides etc. These are reduced to metallic state supplying energy through extraction.

<u>**Corrosion Science and Engineering.**</u>

Corrosion engineering is the application of science to prevent or control corrosion economically and safely.

Involves ..

- principles of corrosion,
- metallurgy,
- corrosion environment,
- chemical, physical & mechanical properties of material
- designing and fabrication by engineers.

Economic aspects of corrosion - Global and Indian situations.

Corrosion: India losing Rs 1.52 lakh crore annually *in various sectors, including infrastructure, utility services, production & manufacturing, and defence.*

…….. amounting to between Rs 75,000 crore and Rs 80,000 crore, could be saved annually by proper monitoring and timely evaluation.

- Loss of valuable products
- Maintanance and operating cost
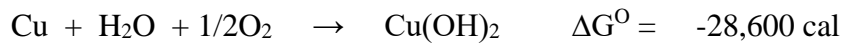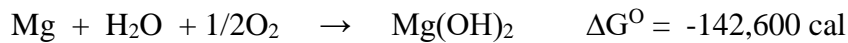- Safety and reliability

Causes of corrosion-

1. Environment, 2.Temperature, 3. Metal nature, 4. Electrochemical series, 5. Gibbs free energy,
   6. Electrode potential, 7. Passivity.

Change in Gibbs free energy.

$$\Delta G = - nFE$$

Gibbs free energy ΔG : Measures the tendency for the chemical reaction.

- More negative the value of ΔG , greater is the tendency for reaction (including corrosion reaction)
- Eg.

$$Mg + H_2O + 1/2 O_2 \rightarrow Mg(OH)_2 \qquad \Delta G^O = \text{-142,600 cal}$$
$$Cu + H_2O + 1/2 O_2 \rightarrow Cu(OH)_2 \qquad \Delta G^O = \text{-28,600 cal}$$

- The reaction (corrosion) tendency of Cu in aerated water is less compared to Mg.

PILLING–BEDWORTH RATIO.

The **P–B ratio**, in corrosion of metals, is the ratio of the volume of the elementary cell of a metal oxide to the volume of the elementary cell of the corresponding metal (from which the oxide is created).

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

where:

R_{PB} is the Pilling–Bedworth ratio,

M – the atomic or molecular mass,

n – number of atoms of metal per one molecule of the oxide

ρ – density, and V – the molar volume.

Meaning:

- An oxide is protective or non-porous if volume of oxide is great as volume of metal from which it formed
- Eg Alkali and Alkaline earth metals form less volume of oxides. Hence the metal oxides face stress & strain thereby developing cracks & pores, permit the underlying metal for free access of O_2 and corrosion continues . .

- Metal like Al form more volume of oxide than vol. of Al, hence tightly adhering non-porous layer formed, which decreases rate of corrosion to zero.
- $R_{PB} < 1$: the oxide coating layer is too thin, likely broken and provides no protective effect (for example magnesium)
- $R_{PB} > 2$: the oxide coating chips off and provides no protective effect (example iron)
- $1 < R_{PB} < 2$: the oxide coating is passivating and provides a protecting effect against further surface oxidation (examples Al, Ti).

TYPES OF CORROSION

- 1. DRY or CHEMICAL CORROSION
- 2. WET or ELECTROCHEMICAL CORROSION

1. DRY CORROSION : by direct chemical attack of atmospheric gases like O_2 , SO_2 , halogens, hydrogen sulphide etc. on the metal surface. Since this is observed in the absence of moisture or conducting electrolyte, it is called dry corrosion. it is further of following types:
- (a) Corrosion by O_2 or Oxidation corrosion.
- (b) Corrosion by other gases.

a. Oxidation Corrosion
- It is due to chemical attack of O_2 on the metal resulting the formation of ***metal oxide layer*** as:
- Metal + Oxygen --------$\rightarrow$ Metal oxide (layer over the surface)
- At low temp. alkali and alkaline-earth metals are oxidised. At high temp. almost all metals (except Ag, Au, Pt) are oxidized.
- This theory is called **Wagner's Theory.**

Mechanism:
- Metal + Oxygen --------$\rightarrow$ Metal oxide (layer over the surface)

$$M \rightarrow M^{n+} + ne^- \quad (\text{loss of e-})$$
$$nO_2 + ne- \rightarrow nO^{2-} \quad (\text{gain of e-})$$
$$M^{n+} + nO^{2-} \rightarrow \text{Metal oxide}$$

- Oxidation occur first at the surface of metal
- formed Metal oxide scale/layer forms a barrier, restricting further oxidation.
- To continue oxidation, either metal must diffuse outwards through scale or O_2 must diffuse inwards
- Outward diffusion of metal is more rapid, due to small size and higher mobility of metal ion than oxygen.

**Nature of Metal oxide layer :** $\quad \text{Metal oxide} \rightleftharpoons \text{Metal} + \text{Oxygen}$

(1) **Stable:** It acts as a barrier between metal and O_2, So prevents further corrosion. (oxide films on Al, Cu, Sn)

(2) **Unstable:** It decomposes back to metal and O_2. Ag, Au, Pt are protected by this manner.
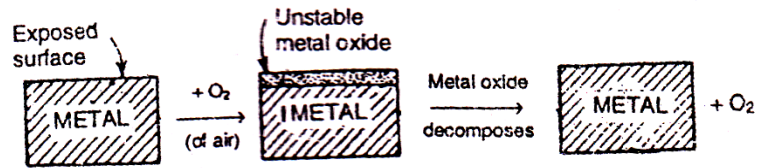
 (3) **Volatile:** Layer volatalises and metal exposed for further corrosion. (MoO_3)
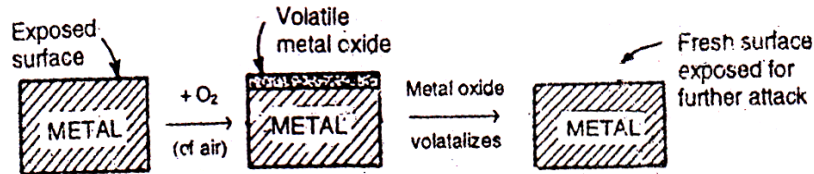
(4) **Porous**: Corrosion occur through pores or cracks and continues till entire metal gets corroded.
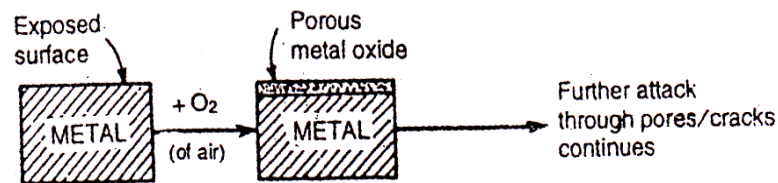
Pilling Bedworth Rule: If the volume of oxide layer formed is equal or greater than the volume of the metal, the oxide layer is protective. However if the oxide layer formed has volume lesser than that of the metal, then the oxide layer is non-protective.

b. Corrosion By Other Gases

- Corrosion is also caused by some other gases like Cl_2, H_2S, CO_2, SO_2 etc. This type of corrosion depends on chemical affinity between metal and gas.
- Degree of attack depends on the formation of protective or non-protective films on the metal surface.

2. WET CORROSION : This type of corrosion occurs when a liquid medium is involved. One part behaves as anode and undergoes oxidation and other part acts as cathode and undergoes reduction. Corrosion occurs due to separate anodic and cathodic areas between which current flows through conducting solution.

- At anode, oxidation (lose of electrons) takes place.
- *So anodic metal is destroyed.*
- *Corrosion always occurs at anodic areas.*

    $M \rightarrow M^{n+} + ne^-$ Oxidation (loss of e-)

- *At Cathode, reduction (gain of electrons) takes place. These can be of the following two type*

- It is further of two types:

    (a) Evolution of H_2 type corrosion

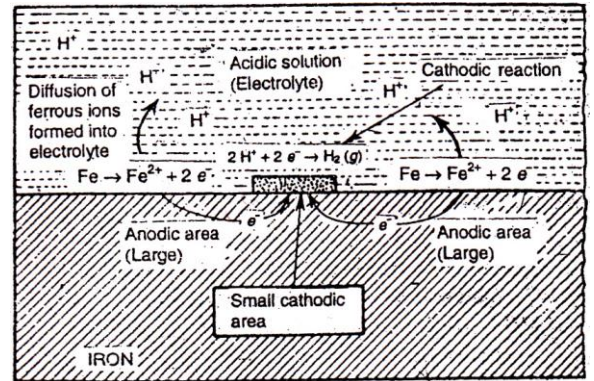   (b) Absorption of O_2 type corrosion

[This Explains THEORY OF ELECTROCHEMICAL CORROSION or ELECTROCHEMICAL MECHANISM]

a) Evolution of H₂ type corrosion

- It occurs in the acidic environment.

    At anode   :   M--------$\rightarrow$ M^{n+} + ne-   (oxidation)

    At cathode : $2H^+$ + 2e- -----$\rightarrow$ H_2 (reduction)

Mechanism Of Wet Corrosion By Hydrogen Evolution:

- All metals above hydrogen in the electrochemical series

    have a tendecy to get dissolved in acidic medium.

- The anode ara are usually large, and cathodes are small areas.

b) Absorption of O₂ type corrosion

- E.g. Rusting of iron
- If the layer of iron develops some cracks, this damaged surface acts as anode while the other intact metal behaves as cathode. Presence of moisture acts as electrolyte.
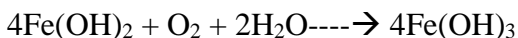
Mechanism Of Wet Corrosion By Hydrogen Evolution

The reactions occuring are:

- Anode   Fe ------> Fe^{+2} + 2 e- (oxidation)
- Cathode O_2 (g) + $2H_2O$ + 4e⁻ ------> 4OH⁻ (rdn)

    $2Fe^{+2}$ + 4OH⁻ --------$\rightarrow$ $2Fe(OH)_2$

Fe^{+2} (from anode) and OH⁻ (from cathode) diffuse to form
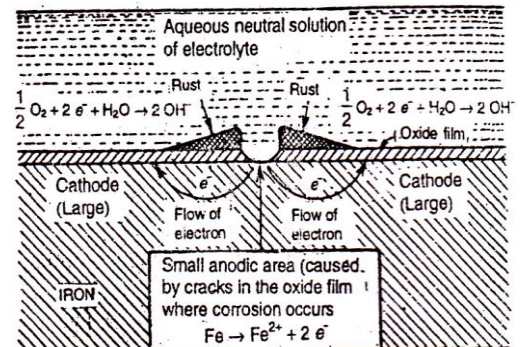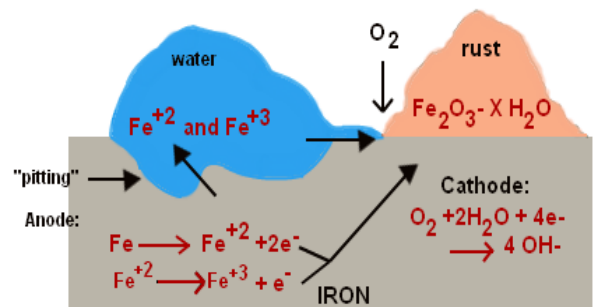
ferrous hydroxide precipitate

In the presence of excess oxygen, $Fe(OH)_2$ oxidises to $Fe(OH)_3$ as:

    $4Fe(OH)_2$ + O_2 + $2H_2O$----$\rightarrow$ $4Fe(OH)_3$

This ferric hydroxide formed decomposes to hydrated ferric oxide

    $Fe(OH)_3$ ---------$\rightarrow$ $Fe_2O_3.xH_2O$

                    (Yellow) Rust
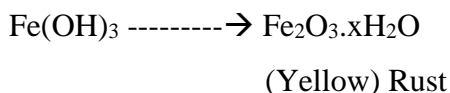
If O_2 supply is limited, pdt will be black anhydrous magnetite, Fe_3O_4.

OTHER TYPES OF CORROSION

- 1. Differential metal corroaion. (Galvanic Corrosion)
- 2. Differential aeration corrosion (Waterline Corrosion)

- 3. Pitting Corrosion

1. **Galvanic Corrosion**

- *This type of corrosion occurs when two dis-similar metals are connected to each other in the presence of an electrolyte.*
- This constitutes a galvanic cell in which a metal with lower reduction potential undergoes corrosion.

- metal with lower electrode potential acts as anode and undergoes corrosion.

  (e.g metals like Zn, Mg)

- The less active metal with higher electrode potential acts as cathode.

- Higher the difference in potential, higher the rate of corrosion.

- When two metals are in contact, galvanic cell is set up and current flows.

- Metals acting as anode (as per electrochemical series) undergoes corrosion.

electro-chemical series

|		
Potassium	-2.92	
Calcium	-2.87	metal activity increasing
Sodium	-2.71	
Magnesium	-2.37	
Aluminium	-1.66	
Zinc	-0.76	
Iron	-0.44	
Tin	-0.14	
Lead	-0.13	metal oxide activity increasing
Hydrogen	0.00	
Copper	+0.34	
Silver	+0.80	
Mercury	+0.85	
Gold	+1.68	
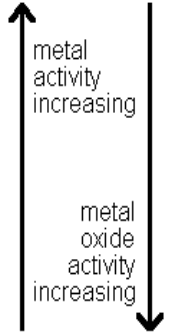
Galvanic Effec
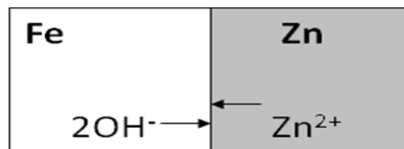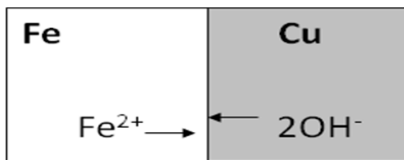
e.g. when Zn and Cu are connected to each other then Zn having lower reduction potential i.e. -0.76V acts as anode and is corroded while Cu with more reduction potential i.e 0.34V acts as cathode and remains protected.

2. **Differential aeration corrosion**

- When metal surface exposed to different air or O_2 concn.
- Part exposed to (high concentration) air is cathodic region
- Part exposed to low concentration of air is anodic region
- Poorly oxygenated region undergoes corrosion.
- Anode (less O_2 concentration)
- $M \rightarrow M^{n+} + 2e^-$ (Oxidation)
- Cathode (high O_2 concentration)
- $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Reduction)
- Eg. For differential aeration corrosion is water-line corrosion.
- It is seen in steel water storage tanks, floating ships etc.
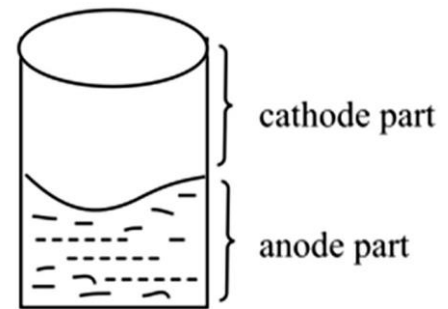
Water storage steel Tank

Waterline corrosion:

- When water is stored in a metallic tank,
- The area above water is more oxygenated, acts as cathode.
- Area below water is less oxygenated, acts as anode.
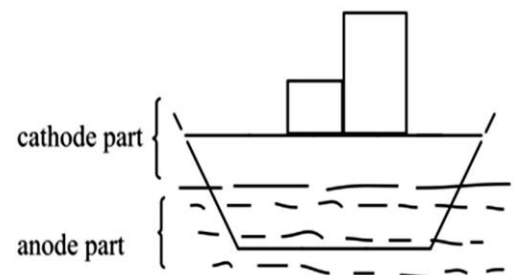
Ship in sea

- Therefore area below Water is corroded and area above water is protected.
- This type of corrosion is observed in the water tanks where water remains collected for a long time. **It is found just below the line of water, so called waterline corrosion.**

3. Pitting Corrosion

- This type of corrosion occurs due to cracking of protective film from the surface of metal. It results in the formation of pits or holes on the metal, so called pitting corrosion
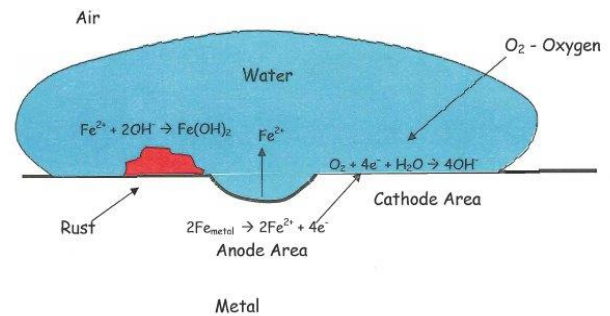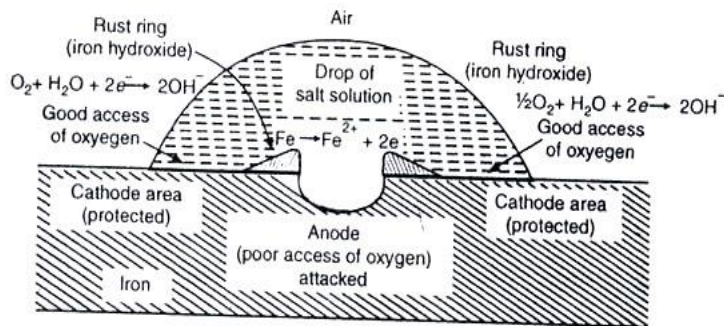
- initiated by the presence of the impurities like sand, dust, scale or due to the breaking down of the protective films on the metal surface.
- The area of the metal below the deposit is exposed to less oxygen concentration hence acts as anode.
- Where as the uncovered region acts as cathode. So the area below the deposit undergoes corrosion leading to small pinholes.
- Because of small anodic and large cathodic area corrosion becomes faster leading to pits.

Factors influencing corrosion

1. Nature of metal (Primary Factor) : Primary Factors (due to metals)
2. Nature of corrosive environment (Secondary Factor) : Secondary Factors (due to environment)

Nature of Metal: (Primary factors)

(1)*Purity of metal:* Impure the metal, more is the rate of corrosion. This is because impurities act as "**minute electrochemical cells.**"

(2) *Physical state of metal:* Physical state of metal like grain size, stress affects the corrosion rate. Stressed areas undergo more corrosion.

(3) *Electode Potential :* Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum, silver. Where as metals with lower electrode potentials, readily undergo corrosion.e.g. metals like, Zn, Mg, Al.
More Potential difference, higher the rate of corrosion.

Eg: Potential difference between Fe and Cu is 0.78 V. Potential difference between Fe and Sn is 0.3 V. So Fe corrodes faster in contact with Cu.

(4) *Position in Galvanic series:*More the oxidation potential i.e if metal is higher in the galvanic series, it is more anodic and hence more is the rate of corrosion.

(5) *Nature of Oxide layer*: if it is stable, insoluble, and non porous. If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium. If it is unstable, porous, and soluble, it further enhances corrosion.

(6) *Passive nature of metal:* Some metals like Ti, Al, Cr show more corrosion resistance than expected from their position in the electrochemical series. These are called **passive metals.** This is due to formation of thin protective layer on metal surface.

(7) **Nature of corrosive products:** If the corrosion products are soluble or volatile in nature, then corrosion increases.

(8) **Relative area of anode and cathode**: smaller the anodic area, more is the corrosion rate because oxidation of anode occurs at faster rate. (and liberated electrons are rapidly consumed at larger cathode)

(9) **Polarization** will decrease the rate of corrosion.

Nature of corroding environment: *(Secondary Factors)*

  (1) *Temperature***:** Rate of corrosion increases with increase in temperature.

  (2) *Moisture:* More the moisture, more is the rate of corrosion.

  (3) *pH of the medium:* In general rate of corrosion is higher in acidic pH

  (4) *Humidity :* Corrosion rate increases with increase in humidity in the medium Presence of moisture in atmosphere provides the conducting medium for formation of galvanic cell, facilitating the corrosion rate.

  (5) *Nature of electrolyte*: Presence of salts in the electrolyte increases the rate of corrosion.

  (6) **Presence of impurities in atmosphere**: Impurities increase the rate of corrosion. Corrosion is more in industrial areas and sea. This is because of presence of gases like CO_2, H_2S, SO_2

  (7) **Effect of oxygen:** Oxygen plays an important corroding medium. If the metal is exposed to different concentration of oxygen, differential aeration corrosion takes place.


Theory of cathodic protection.

It is a technique of protecting a metal from corrosion by converting it to cathode. It can be done by,

  1. sacrificial anodic method
  2. Impressed voltage method

- In this metal to be protected is converted into cathode by connecting it to more active metal.

- The active metal acts as auxillary anode. (Metals like zn, Mg, Al generaly used as auxillary anodes.)

- Anode being more reactive undergoes corrosion, where as the metallic structure is unaffected.

- Since anode is sacrifised to prevent corrosion of anode, It is called sacrificial anode method.

1. Sacrificial anodic method

- A magnesium block connected buried oil storage tank acts as sacrificial anode, and prevents the tank from corrosion.

- When Magnesium blocks are connected to the sides of the ship, it acts as anode, prevents ship from corrosion.

- Magnesium blocks connected to buried pipelines prevents structure from corrosion, by acting as anode.
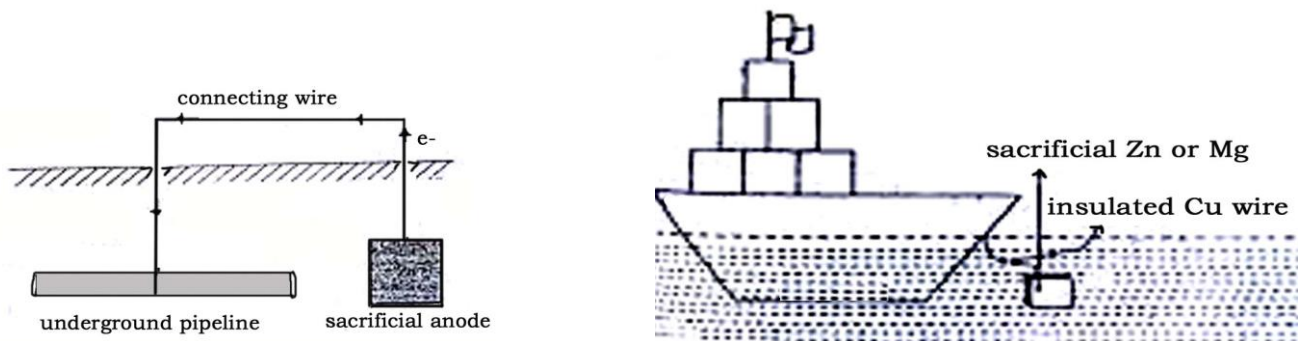
2. Impressed voltage method:

- In this method electrons are supplied from external source to the metallic structure to be protected.

- Metal to be protected is connected to the negative terminal of D.C source so that it is cathode.

- A rod made up of inert graphite or palladium is connected to positive terminal as anode.

- The electrons are released from anode prevents the basic structure from corrosion.
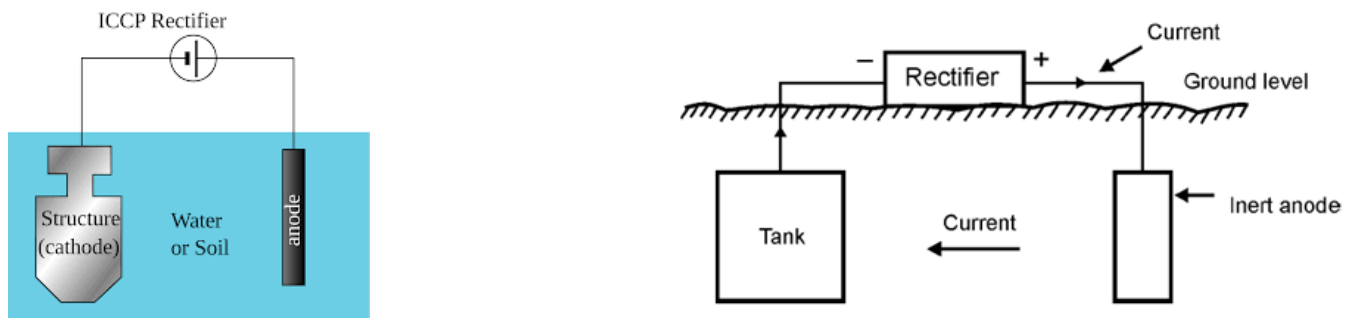
Corrosion control

There are varios ways by which corrosion can be controlled.

1. Design and Selection of materials

2. Protective coatings

3. Cathodic Protection

4. Anodic Protection

5. Corrosion Inhibitors

1. Design and Selection of materials: Differential metal corrosion can be reduced by metals far away in galvanic series.

- anode material must be large as possible and cathode as small.
- Similarly reduce joints and stress in the materials. Also use proper designed smooth materials in equipments.

The Area Effect

- In a galvanic cell, the anode/cathode area ratio is an important factor for severity of corrosion attack
- A large cathode causes severe attack on a small anode
- If we cannot avoid situations for galvanic corrosion, we may reduce thinning by making the anode material of large surface area and cathode of smaller area.

Eg. Copper plates with steel rivets in seawater Steel rivets severely attacked (Large cathode/small anode). Steel plates with copper rivets in seawater- Tolerable corrosion of steel plate (Small cathode/large anode).

2. Protective coatings

a) Metal coatings – anodic and cathodic

b) Inorganic coatings – anodizing and phosphate coating

c) Organic coatings – Paint and enamels

3. Cathodic protection: protecting a metal from corrosion by converting it to cathode. It can be done by,

a) sacrificial anodic method:

In this metal to be protected is converted into cathode by connecting it to more active metal; from galvanic series.

b) Impressed voltage method:

In this method electrons are supplied from external source to the metallic structure to be protected. Metal to be protected is connected to the negative terminal of D.C source so that it is cathode.

4. Anodic protection:

Prevention of corrosion by anodic current is called anodic protection. It involves deposition of oxide film on metal by applying anodic current in an oxidizing environment.

5. Corrosion Inhibitors

These are the chemical substances added in small amounts to the corrosive medium to decrease the corrosion rate. Such as Anodic corrosion inhibitors and cathodic inhibitors.