

# unit - 3

## corrosion

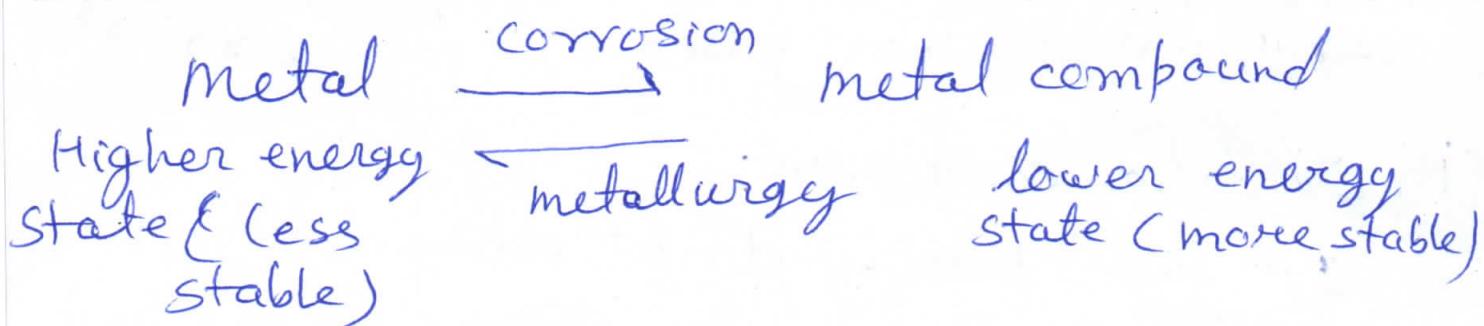
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### Definition :-

Corrosion is destruction or deterioration of metal or alloy by means of some chemical reaction starting at its surface due to the attack of natural environment.

### Reason of corrosion :-

Metals have tendency to acquire lower energy state so they react with surrounding compounds to form stable state that is lower energy state



### Consequences or effects of corrosion

- 1) loss of efficiency
- 2) Increase cost of maintenance
- 3) Decrease in efficiency of machine may decrease production rate
- 4) Increase chances of accident in iron work
- 5) Causes leakage of harmful gases and toxic products
- (6) Metal loses their useful properties, it is also an economical loss.

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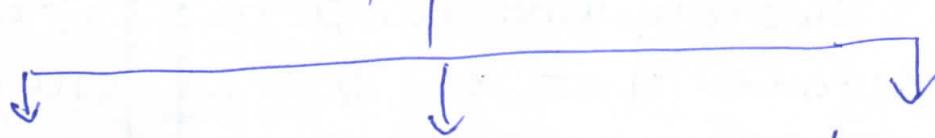
## Types of corrosion (Three types)

- 1) Dry / chemical corrosion
- 2) Electrochemical / wet corrosion
- 3) Acid / carbonate ~~corrosion~~ Formation

### (i) Theory of Dry/chemical corrosion

It occurs due to the direct action of atm. gases like  $O_2$ ,  $CO_2$ ,  $H_2S$ ,  $SO_2$ ,  $N_2$  etc. and halogens etc. on the surface of metals.

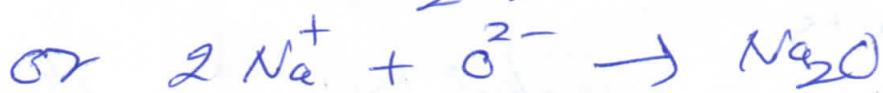
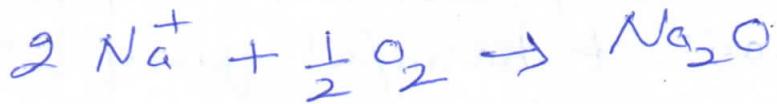
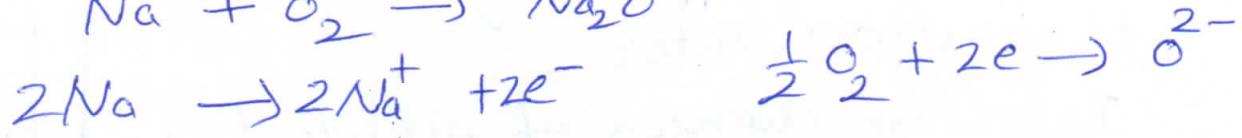
Dry/chemical corrosion is of 3 types



- i) oxidation corrosion
- ii) corrosion by other gases
- iii) Liquid metal corrosion

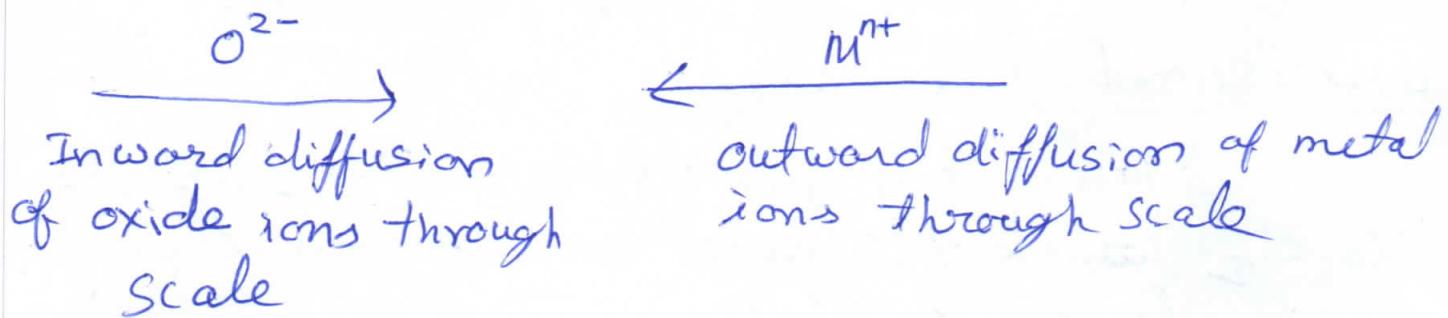
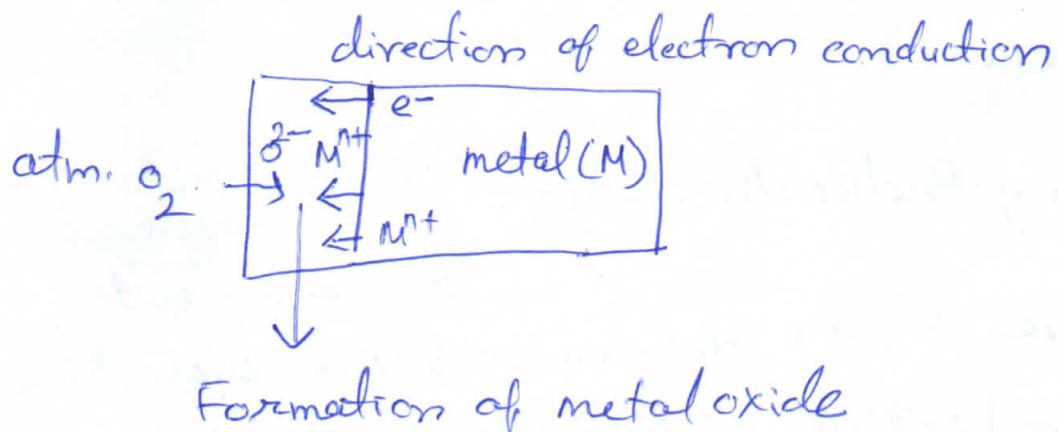
### (i) Oxidation corrosion:-

It takes place by direct action of oxygen on metal surface in the absence of moisture. Generally alkali & alkaline earth metals are rapidly oxidised at low temperature due to their low ionisation potential.



## Mechanism of oxidation corrosion

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metal oxide scale forms a barrier for further oxidation, In such conditions, oxidation is continuous under two cases:

- i) Metal diffuses outwards through the scale to the surface
- iii) Oxygen diffuses inwards through the scale to the underlying metals:

outward diffusion of metal ions is faster due to smaller size of metal ions which are more mobile than oxide ions.

### Pilling Bedworth Rule

If the volume of metal oxide is equal or greater than the metal consumed, the oxide layer is tightly adhering, non-porous,

and hence protective (e.g.  $\text{Al}_2\text{O}_3$ ), on the other hand if the volume of oxide layer is less than the metal consumed, the layer is porous and hence non-protective (e.g. oxides of alkali metals) (4)

Pilling-Bedworth ratio =  $\frac{\text{Vol. of metal oxide formed}}{\text{Vol. of the metal consumed}}$

Significance : - It determines the protective or non protective coating of oxides.

### (2) Corrosion by other gases :-

other dry gases like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{F}_2$  and  $\text{Cl}_2$  attack the metal and forms their compounds on surface.

e.g.  $2\text{Ag} + \text{Cl}_2 \rightarrow \text{AgCl}_2$  (non porous; hence decrease further corrosion)

$\text{Sn} + \text{Cl}_2 \rightarrow \text{SnCl}_2$  (porous and whole metal is destroyed)

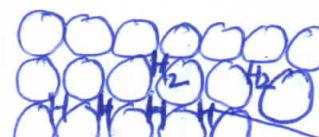
### (3) Corrosion by hydrogen:-

Hydrogen attacks metal and causes blisters and fissures at the metal surface is known as Hydrogen embrittlement

e.g.  $\text{Fe} + \text{H}_2\text{S} \rightarrow \text{FeS} + 2\text{H}$

This atomic hydrogen diffuse into metal, absorbed or collected in the voids and finally converted into molecular hydrogen ( $\text{H}_2$ )

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 metal crystal

 Hydrogen captured in voids

When pressure increases in these voids, it causes blisters or fissures and weakens the metal.

#### (4) liquid metal corrosion:

- It occurs due to chemical action of the flowing liquid metals over solid metal or alloy at high temp. due to → Dissolution of solid metal by the liquid metal

→ Internal penetration of the liquid metal ions into the solid metal.

e.g. Liq. Na is used as heat transfer medium in nuclear reactors.

#### Electrochemical Theory or Wet corrosion

This type of corrosion occurs at a solid-liquid interface when the metal are in contact with the moist air or any liquid medium

#### Different types of wet corrosion

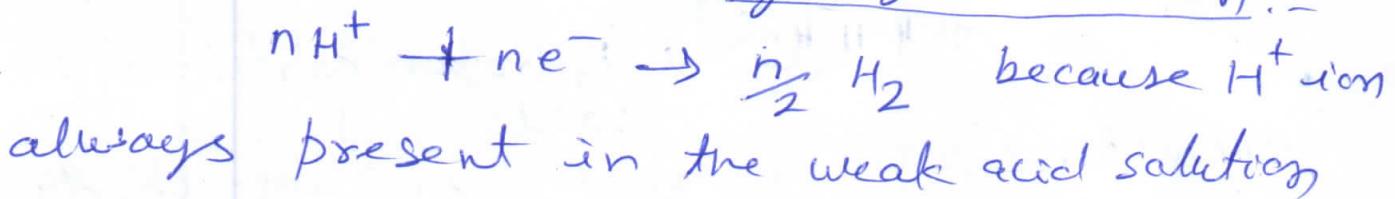
#### Mechanism of wet/electrochemical corrosion

In this corrosion, electric current flows between anodic area & cathodic areas.

At Anode : - Dissolution of metal to form ions  $M \rightarrow M^{n+} + ne^-$

At Cathode : - Two different reactions take

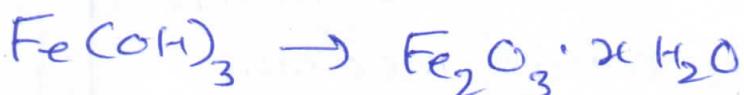
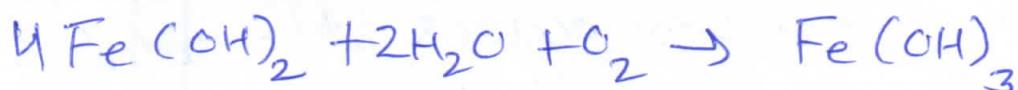
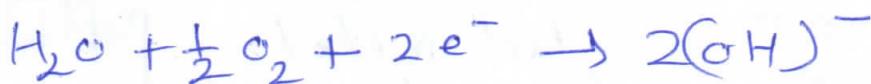
place, depending upon the nature of  
corrosive medium - (1) Hydrogen evolution:-



(2) Oxygen absorption. - Electrons flow through  
the iron from anode area to cathode area.  
As oxygen is also present in the solution,



overall reaction



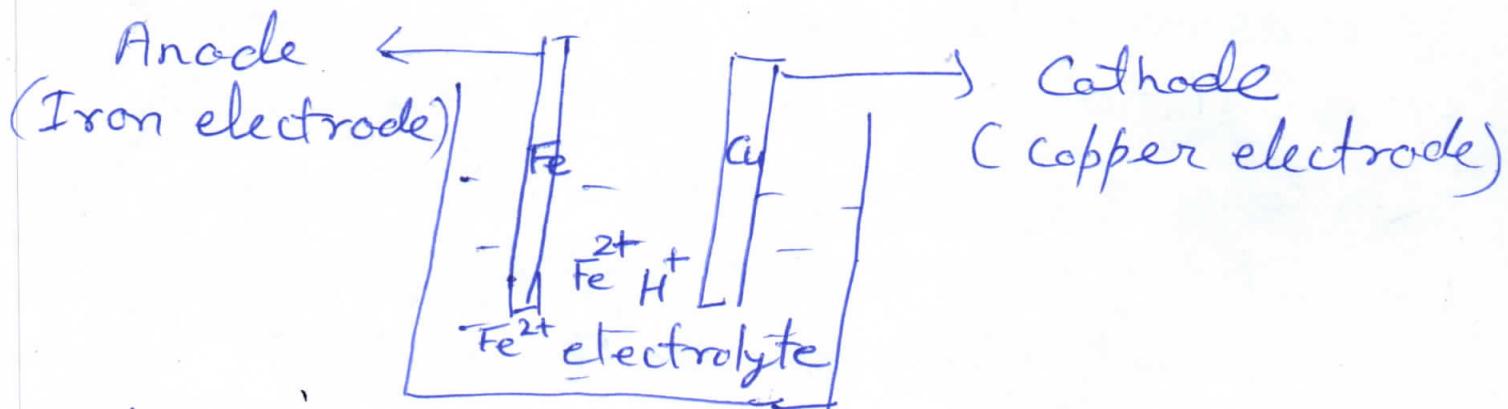
Different form of Wet corrosion

- (1) Galvanic corrosion
- (2) Concentration corrosion
- (3) Pitting "
- (4) stress "
- (5) Intergranular "

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## Galvanic cell (corrosion): -

When metals having different electrode potential are electrically connected and are exposed to a neutral or acidic environment in presence of oxygen, "the metal of lower electrode potential oxidise while other metal with higher value of electrode potential get reduced. The oxidised metal is said to be corroded"



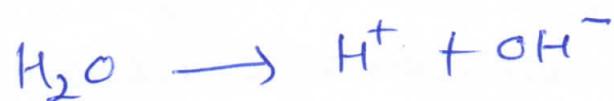
At Anode



Surplus ion flows to copper electrode

At Cathode

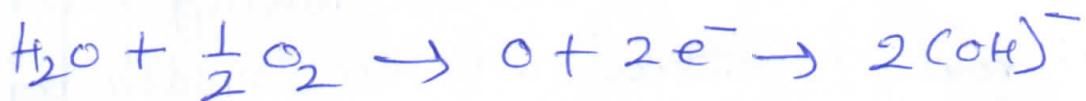
$\text{H}^+$  takes up the  $\text{e}^-$  which is produced by dissociation of  $\text{H}_2\text{O}$



Now  $\text{OH}^-$  ions are available at cathode



The oxygen dissolved in water, results in another reaction at cathode ⑧



So the presence of oxygen in water increase the rate of reaction and corrosion will be faster.

### Concentration cell corrosion :-

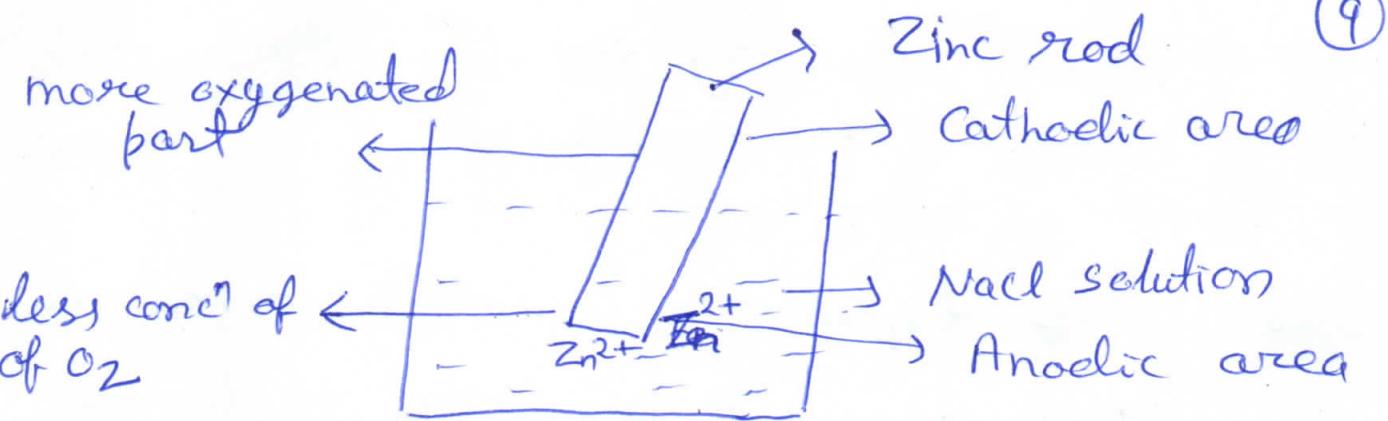
This type of corrosion takes place due to dissimilarity of a solution when a solution may involve high concentration of oxygen at one point of the metal and low at the other.

The electrons are released from the place where the concentration of oxygen is lower and becomes the Anode. From the anode, the electrons flow towards the area where concentration of dissolved oxygen is higher and becomes a cathode. And the medium becomes an electrolyte.

It may takes place in two ways

(i) Differential ~~are~~ aeration corrosion ,

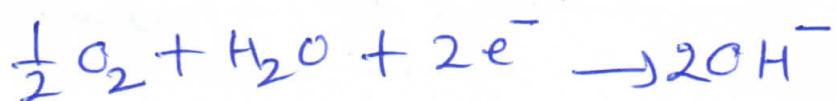
It occurs when metallic surface is partially immersed in electrolyte and other part is exposed to air



The part of  $Zn$ , immersed to depth has lesser oxygen concentration and becomes anode

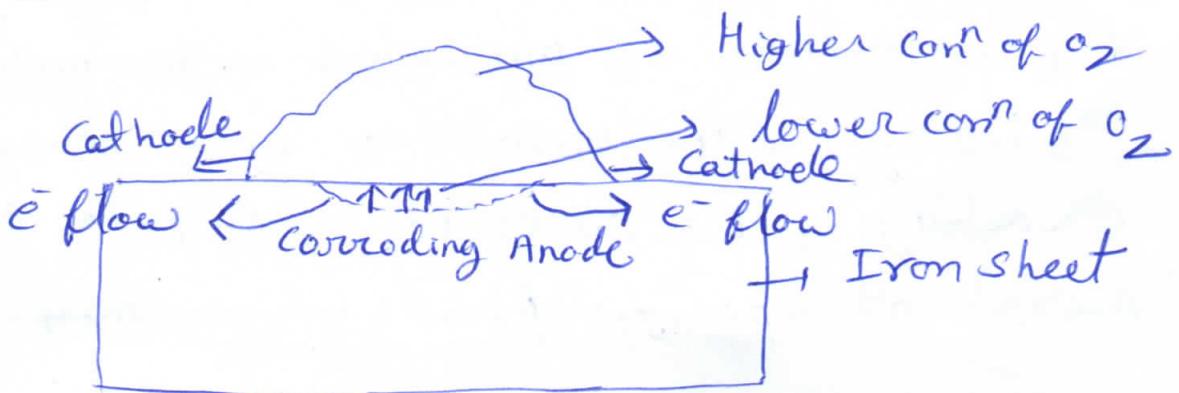


Cathode



(ii) Drop corrosion:- When a large drop of water or an electrolyte is placed on the surface of a clean sheet of iron, the conc' of  $O_2$  will be lower at the centre of the wetted surface as compare to the outer portion of the wetted surface, which is more accessible to the oxygen.

The centre area will act as an Anode & outer area will act as a cathode.

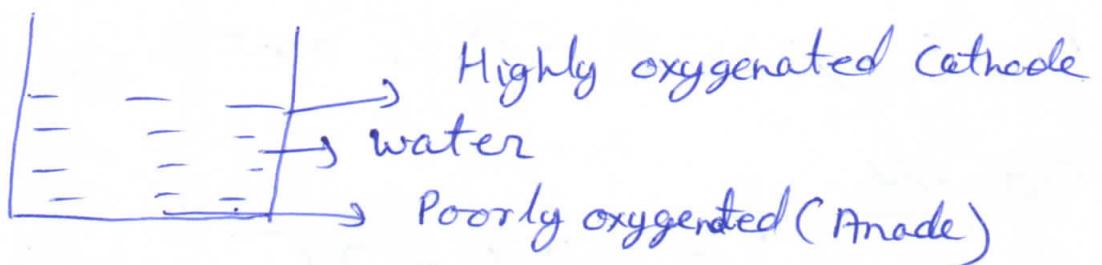


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So it is not necessary for dissimilar metals to be in contact for corrosion but may occur in same metal.

### Example of differential aeration corrosion

It is observed in water tanks due to different  $O_2$  concentration



Pitting Corrosion :- It occurs in passive metals

passivity of metal - metals or alloys having higher position in electrochemical series shows corrosion resistance behaviour due to formation of very thin protective layer on the surface which is invisible, insoluble, non porous.

Pitting corrosion occurs due to the accelerated attack, which results in the formation of pits, cavities and pin-holes in the metal

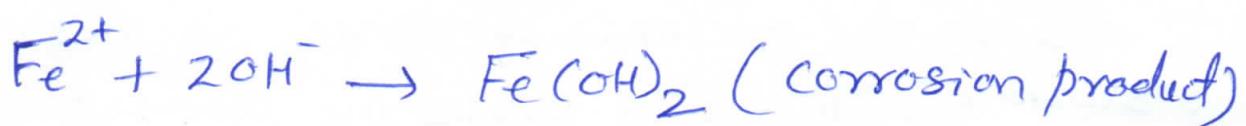
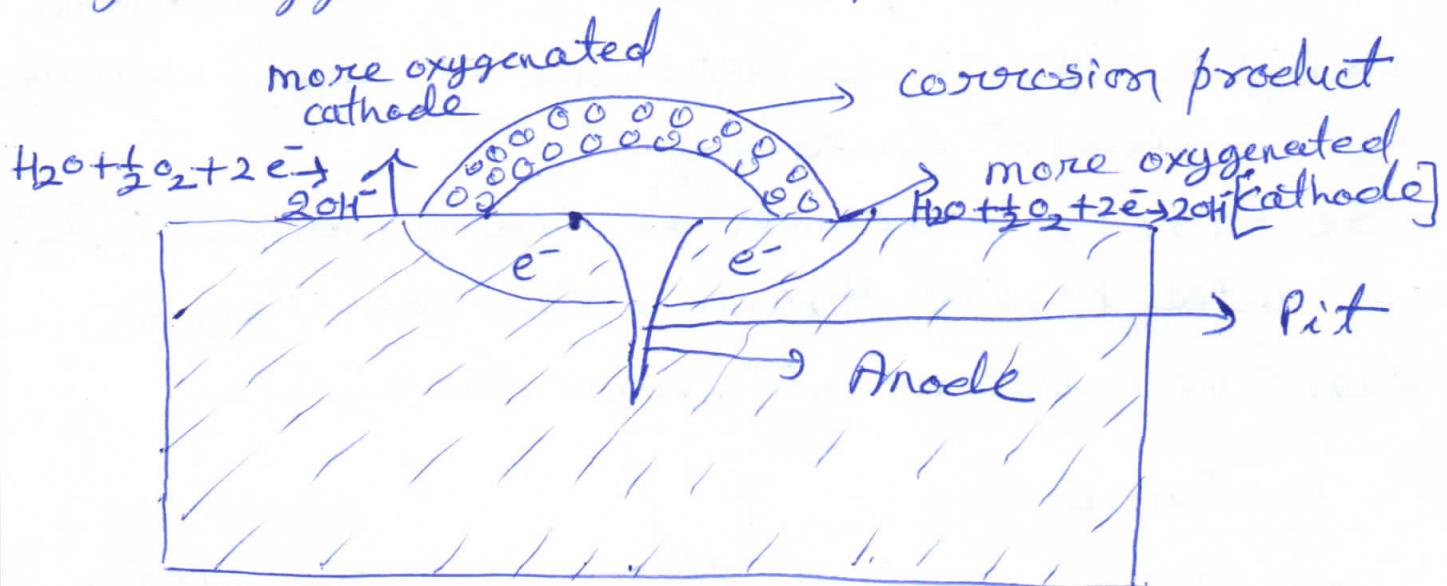
Pitting is the result of breakdown or cracking of the protective film on the metal at specific points which may be

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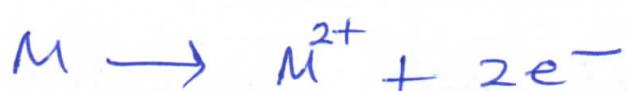
Caused by -

- 1) Surface roughness
- 2) Scratches
- 3) Local straining of metal due to non uniform stresses and chemical attack.
- 4) Extra deposition of impurities or drop of salts.

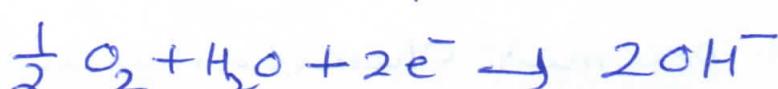
The small ~~part~~ metal part, which is covered by impurities or drop of salt has low oxygen concentration and thus acts as an ele. Anode and undergoes corrosion & whereas the surrounding large uncovered metal surface acts as cathode due to high oxygen concentration.



At Anode



At Cathode



Formation of large cathodic area and small anodic area set up differences of potential at localised spot or pits. Thus the potential difference between anodic and cathodic area produces corrosion current. Once a small pit is formed, the rate of corrosion will be increased. e.g. stainless-steel, Al, Ni etc.

### Stress corrosion:

The corrosion which is caused by the presence of stress at metal surfaces is called stress corrosion.

Internal stress may be due to manufacturing defects, fabrications or heat. External stress develops due to heavy working or insufficient annealing.

So stress corrosion is the "combined effect of static tensile stresses and the specific corrosive environment (corrosive agents)

### Mechanism

- In stress corrosion, there is some strain due to the presence of stress on the metal surface. This will cause the formation of localised zones.
- The point under stress behaves as ~~Anode~~ and becomes chemically active and attacked

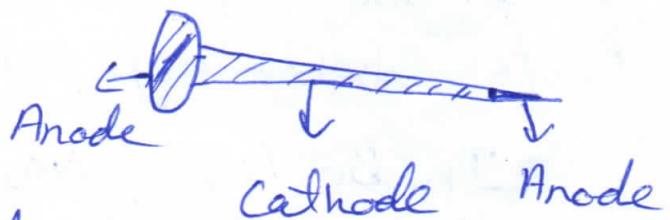
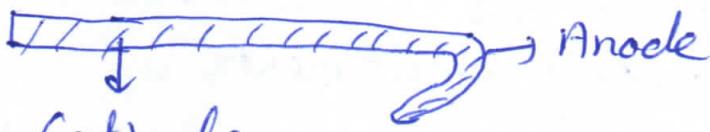
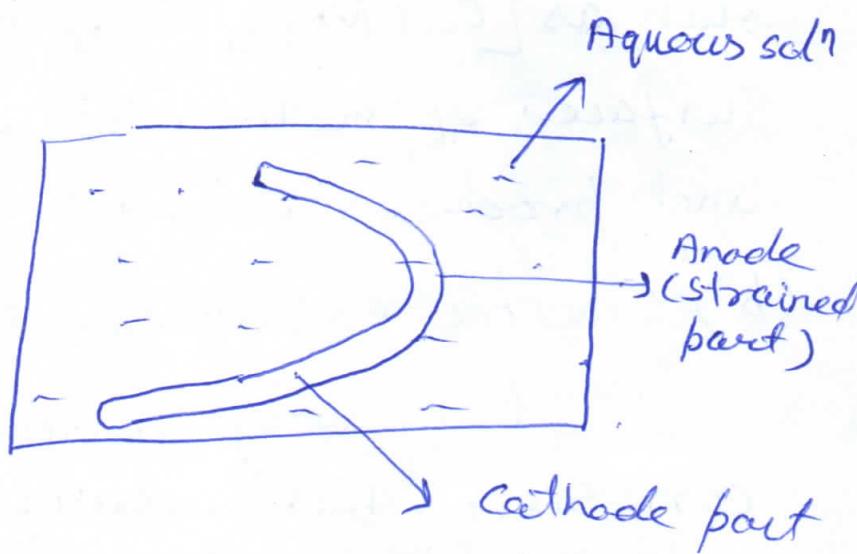
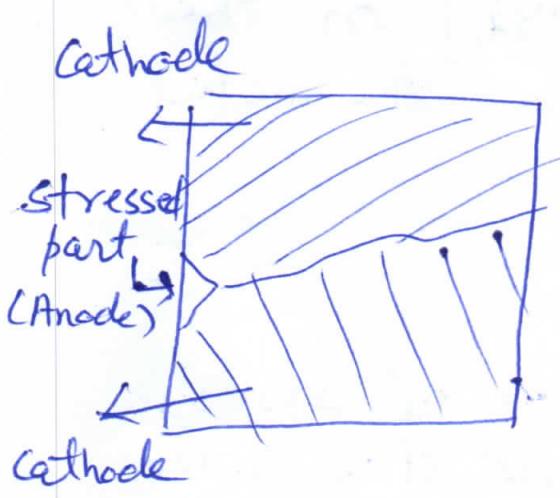
by mild corrosive agents

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e.g. Head and point of a nail

(c) The large stress free surfaces acts as cathode

(d) However potential differences between anodic and cathodic area is very small but the path of the stress is very narrow, hence corrosion is concentrated in a narrow path which is Anode with large cathodic surface, It helps to open up cracks which widens due to stress



There are two types of stress corrosion:

- Season's cracking
- Caustic embrittlement

(a) Season cracking :-

It occurs mainly in copper alloys like brass ( $Cu + Zn$ ). Pure copper is immune to stress corrosion but presence of small amount of  $Zn$  or ( $P, As, Al$  etc) cause season cracking.

For example,

Alpha-brass ( $Cu + Zn$ ), in presence of Ammonia or Amines, forms complex ions such as  $[Cu(NH_3)_4]^{2+}$  or  $[Zn(NH_3)_6]^{2+}$  on the surfaces of metal. It dissolves the metal and produces cracks.

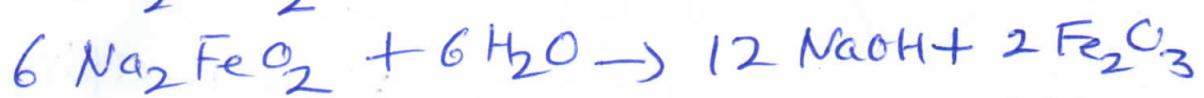
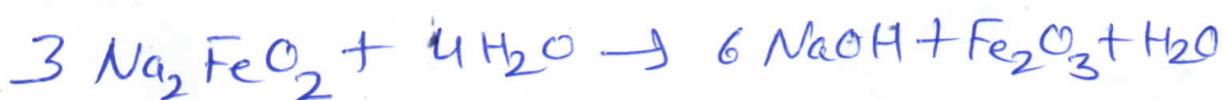
(b) Caustic embrittlement:

It is very serious form of stress corrosion which occurs in mild steel, when mild steel exposed to alkaline solution at a high temp. and stress. It occurs in steam boiler and heat transfer equipments in which water shows high alkalinity.

In Boilers,  $Na_2CO_3$  is added as softening agent for internal treatment. At high temp.  $Na_2CO_3$  gives the following reaction



NaOH makes water alkaline and enters (15) into minute hair cracks. In boilers, water evaporates continuously but left behind NaOH in the cracks. As the con<sup>n</sup> of NaOH increases, it reacts with iron of boiler and forms hypoferroite ( $\text{Na}_2\text{FeO}_2$ ) making metal in stressed condition.



Above reactions show the regeneration of NaOH which continue the reaction with iron.

#### Prevention of caustic embrittlement

- 1) Use of softening agents like  $\text{Na}_2\text{SO}_4$  and in place of  $\text{Na}_2\text{CO}_3$ .
- 2) Use of Tannin or lignin to fill up minute hair cracks.
- 3) Maintain the PH of water.

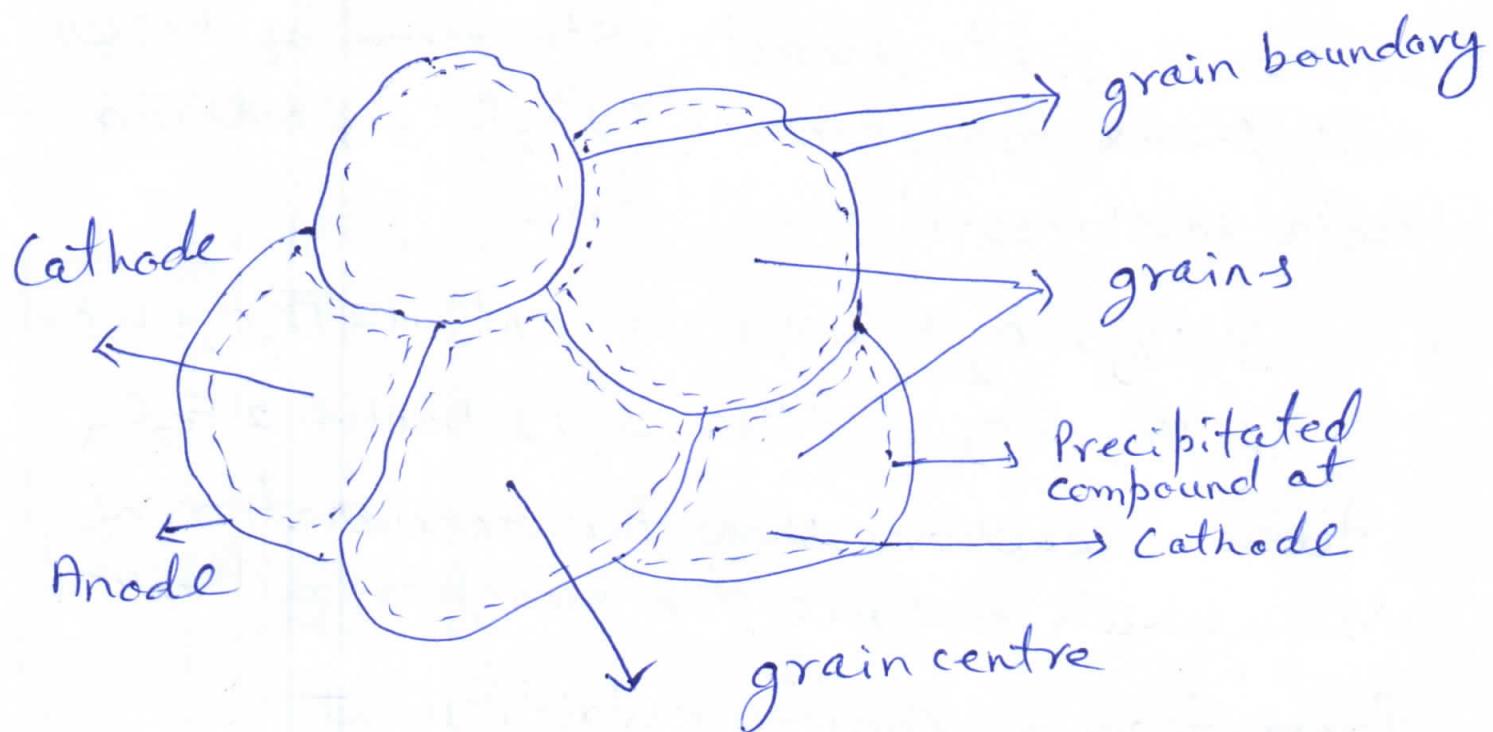
#### Intergranular corrosion (grain boundary corrosion) -

metal grains boundaries have higher energy than the centre of grain. So grain boundary have high potential as compare to rest of the metal crystal. As a result metal boundary act as Anode and grain

centre serves as cathode.

Under corrosive conditions, a galvanic cell is formed causing corrosion of boundary

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### Intergranular corrosion

Due to abnormalities of structure and composition, Anodic attack takes place at grain boundaries.

Fine grains have higher corrosion rate as compare to coarse grained metals. This is due to the fact that area of grain boundaries is much more in fine grained metals and the fine grained metal have higher potential than the coarse grained metals.

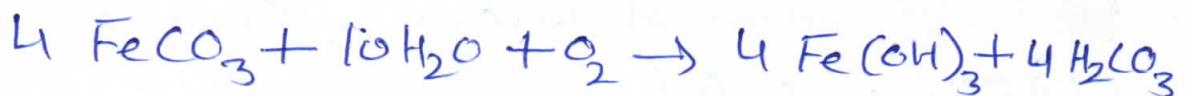
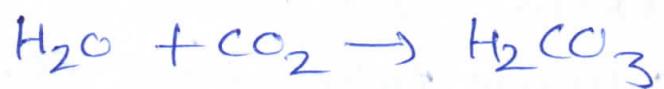
Examples: - Intergranular corrosion occurs due to precipitation of some ~~metal~~ material at grain boundaries which shows electrode potential more anodic as compare to centre.

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During the welding of stainless-steel, (alloy of Fe, Cr, C), chromium carbide ( $\text{Cr}_3\text{C}$ ) is precipitated at the grain boundaries and the region just adjacent to grain boundary becomes depleted in Cr-concentration and is more Anodic as compare to centre part which is in rich Cr-concentration.

### Acid or Carbonate Formation

According to this theory, traces of an acid is necessary for the corrosion to occur. Acidic oxides gases like ( $\text{CO}_2, \text{SO}_2, \text{NO}_2$ ) reacts with metal in the presence of water. Even  $\text{CO}_2$  dissolved in water is sufficient for corrosion because carbonic acid ( $\text{H}_2\text{CO}_3$ ) is formed.



Iron is converted into soluble  $\text{FeCO}_3$  which is further oxidised to basic ferric carbonate and converted into hydrated ferric oxide (rust).

$\text{H}_2\text{CO}_3$  is regenerated and responsible for further attack, Excess  $\text{O}_2$  promotes

corrosion and other gases like  $H_2S$ ,  $SO_2$  or  $Cl_2$  may also react with Iron.

The Factors influencing / affecting the rate of electrochemical corrosion:-

- (1) Nature of metal
- (2) Nature of environment

### Nature of metal

#### 1) Position in Galvanic cell series:-

The metal which is placed at high position in galvanic series is more active towards corrosion. If the distance between two metals is more, the rate of corrosion is faster.

#### 2) Oversvoltage:-

Oversvoltage is the difference between potential of a metal at which the electrolysis actually takes place continuously and theoretical decomposition potential for the same solution is known as oversvoltage. e.g.

Electrolysis of  $H_2SO_4$  with Pt occurs at 1.70 volts whereas theoretical potential is 1.229 volts. So difference is 0.471 volts, which is oversvoltage. It means that if oversvoltage of a metal is higher, rate of corrosion gets decreased.

### ③ Relative area of Anode & Cathode

Small Anodic & high Cathodic area causes more corrosion. Reason behind this is that the current density at small surface of Anode is high and demand of these electrons by large cathode is only fulfilled by high corrosion rate at small anode.

### (4) Purity of metal :-

Rate of corrosion is slower in pure metals. Because presence of impurities in metals cause non-homogenous surface and creates electrochemical cell. So corrosion is faster due to presence of impurities.

### (5) Physical state of metal :- Physical states like grains size, crystal orientation, stress etc. determines the rate of corrosion. Smaller grain size gives high corrosion.

### (6) Nature of surface film (Protective layer)

If the protective layer is non porous, hard, and tightly adhering, rate of corrosion is lesser.

The nature of film (protective layer) depends on volume ratio -

$$\text{Specific vol. ratio} = \frac{\text{Vol. of metal oxide}}{\text{Vol. of metal consumed}}$$

Higher the value of sp. vol. ratio, lower will be the corrosion rate.

#### (7) Passive character of metal:-

Some metals like Al, Cr, Mg, Ni etc. show passivity due to formation of a thin, non porous protective film on surface which is self healing nature. So passivity decrease rate of corrosion

#### (8) Solubility of corrosion product:-

Rate of corrosion will be intensified if corrosion product is soluble in electrolyte medium.

#### (9) Volatility of corrosion product:-

Volatile corrosion product cause high corrosion because it leaves exposed surface of the metal in environment.

### Nature of environment

1) Temp. : - Rate of corrosion is higher at high temp. due to increase rate of diffusion.

2) Humidity of air : - Humidity acts as electrolyte for  $\text{CO}_2$  &  $\text{O}_2$  etc. Rain water washes oxide film and exposes metal surface for further corrosion.

### (3) Presence of impurities in atm. :-

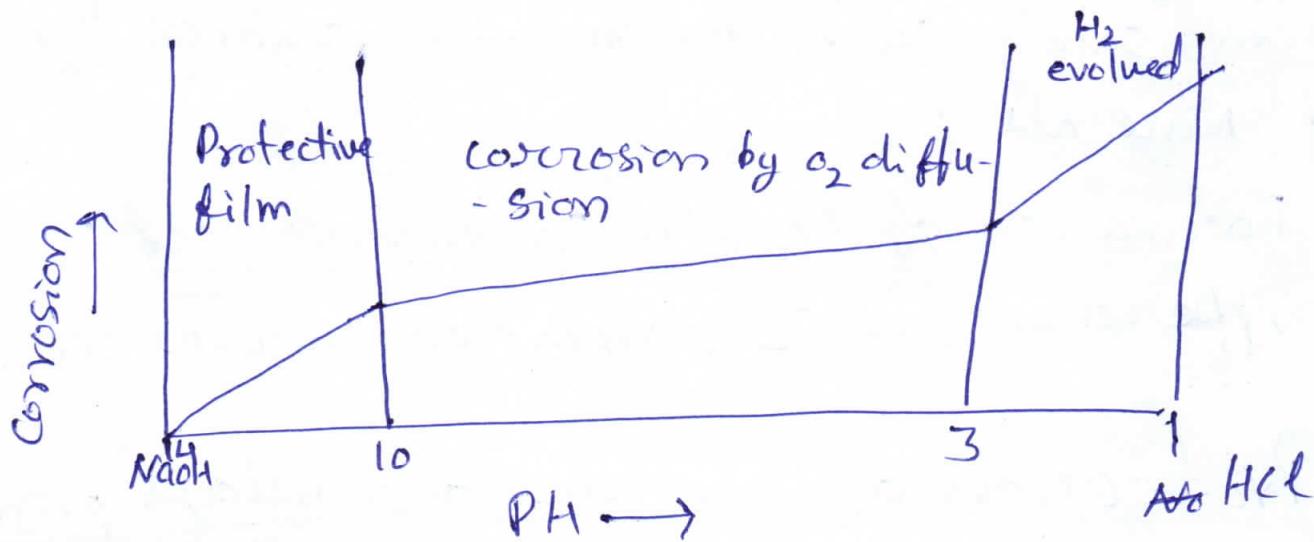
Presence of gases like  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{HCl}$  etc. in atm, increases acidity and responsible for more corrosion

### (4) Presence of suspended particles :-

Active particles like  $\text{NaCl}$ ,  $(\text{NH}_4)_2\text{SO}_4$  are absorbed by moisture and behave like an electrolyte and give high corrosion.

### (5) Effect of PH :- High PH creates low concn of $\text{H}^+$ ion and decrease rate of corrosion.

Degree of corrosion of metals immersed in solution may be influenced by PH of medium involving different concentration of  $\text{H}^+$  or  $\text{OH}^-$  ions.



Degree of corrosion against PH of solution in contact with steel .

If the sample is kept in alkaline solution, it is observed that a certain amount of protective film formations will occur. So degree of corrosion is restricted above PH-10. Between PH, 3-10 presence of oxygen is responsible and corrosion will proceed only by  $O_2$  diffusion method. Below PH 3, no longer necessary of  $O_2$ ,  $H_2$  gas is evolved.

(6) Nature of ions :- Various ions present in environment affect corrosion in different ways. If silicates ions are present, they form insoluble reaction product silica gel, which inhibits corrosion whereas  $Cl^-$  and  $NH_4^+$  ions destroy protective layer and increase corrosion

(7) Conductance of conducting medium :-

corrosion is higher in mineralized soil than sandy soil due to more conductivity of minerals.

(8) Formation of oxygen concentration cell :-

Difference in  $O_2$ , promotes corrosion.

Protection of metals and Alloys from corrosion

- (1) Protective coating - galvanisation & tinning,
- (2) Cathodic protection (3) Sacrificial Anode
- (4) Modification of design .

## (1) Protective Coating:-

### Galvanisation - (Hot dipping) -

The metal can be coated mechanically by dipping them in a bath of molten metal whose coating is to be made. A thin layer of the protective metal is found adhering which prevents corrosion of Base metal.

Iron articles are galvanised with zinc coating. First of all, iron articles are cleaned by dil. HCl. Acid dissolves all the scale and rust deposited on the surface. After washing & drying, these articles now dipped in the bath of molten zinc and withdrawn after sufficient time.

A coating of zinc is deposited on the surface which in due course of time converts into  $ZnO$ , which is hard and protective and prevents further corrosion.

Tinning :- When a protective layer of Tin is coated over iron metals, It is known as tinning. The process of tinning is similar to galvanisation.

(2) Cathodic Protection:- It is the most important method to control corrosion of machine parts immersed in the soil and

dipped in water.

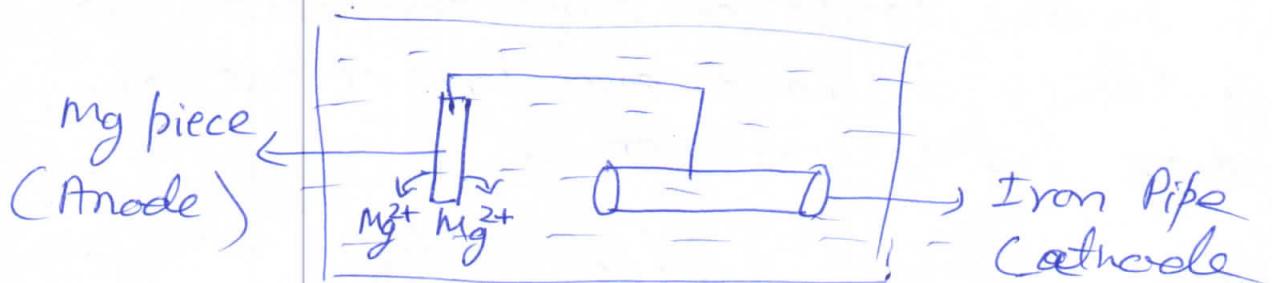
(24)

In this process Anodic metal is converted into cathodic metal which is not corroded.

It is of two types

(a) Sacrificial anodic protection:-

In this method, the metallic part which is to be protected is connected with a more anodic metal. So all the corrosion is concentrated at a more anodic metal and protected metal acts as Cathode, ~~so~~ Cathode is saved from corrosion. The more active metal which is used as anode is known as sacrificial metal. e.g. Mg, Al and Zn etc. are most commonly used.



The metal used for anode is to be replaced time to time.

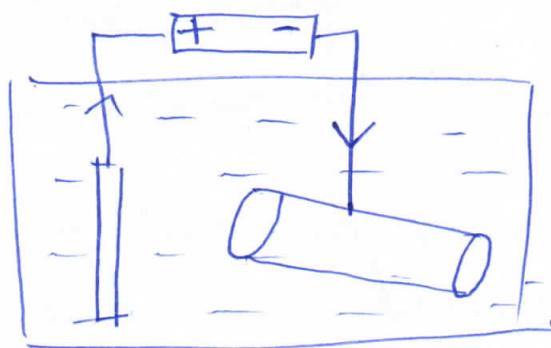
- e.g. - For protection of buried pipe line of water and oil
- Protecting marine & ships parts
- Protecting domestic tanks & pipes

## (b) Impressed current Protection

In this method protecting metal is connected to external DC source with its negative terminal. The positive terminal is connected to a insoluble anode like graphite or Pt or scrap Iron. D.C. source supply current in the opposite direction of the corrosion current produced by ~~metal~~ protecting metal.

The insoluble anode is kept in such a way that a uniform potential is developed over the surface of metal.

Impressed current of D.C. source nullify the corrosion current as the protecting metal gets electrons and become cathode. The anodic material should be replaced time to time.



Impressed current cathodic Protection

Uses/Applications:- Burried pipelines, water tanks, Transmission tower, Marine pipes

## Modification of Design

corrosion can be reduced by appropriate designing of equipments which reduce the contact of metal with surrounding.

The following points should be considered

- 1) Two dissimilar metal should not be connected to avoid formation of galvanic cell.
- 2) If two dissimilar metals are present, then Anode should be larger area and cathode should be smaller area
- 3) Two metals should be close in electrochemical series because more diff' in potential promotes galvanic cell formation
- 4) Anode should not be painted, because any damage in coating will lead to high corrosion
- 5) If two metals are required, then they should be connected by insulator.
- 6) Crack or cavities should be avoided.
- 7) Sharp corners and recesses should be avoided.
- 8) Free circulation of air promotes corrosion, therefore equipment should be rested on stands.

The end.