

Module-4 Corrosion

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• Corrosion

- The loss of material (metals or alloys) or its useful properties, by chemical or electrochemical interaction with its environment.

or

"Corrosion is the slow but Spontaneous deterioration of metals by chemical or electrochemical ~~transformation~~ reaction with environment"

• Effects of Corrosion :

(1) loss of material and properties

(2) The porosity of products get affected.

(3) maintenance cost

and

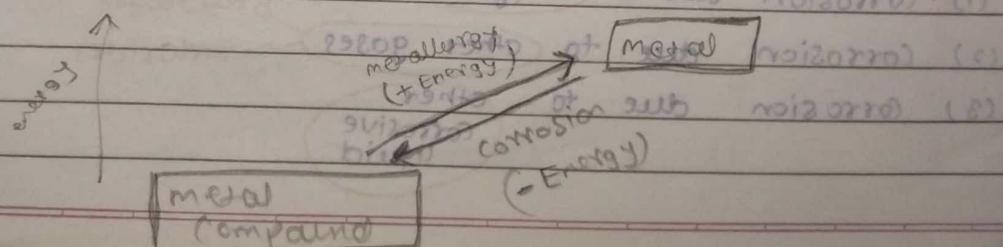
Cost of material increase while
rate of production decrease

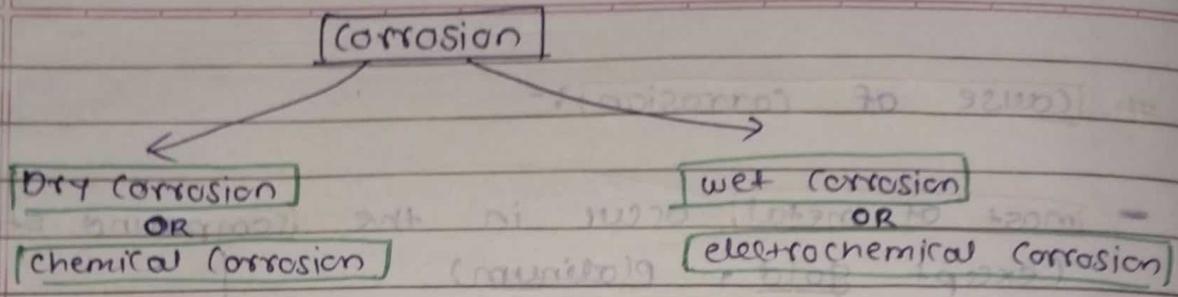
[Cause of corrosion]:-

- most of metal occur in the (Combined state) compound state
(except gold, platinum) (Combined state)
- i.e. in the form of metal compound like (Combined state) oxides, sulphides, carbonates, silicates, chlorides, hydroxide
- Thus it is thermodynamically stable and (Combined state) has lower energy
- In the process manufacturing of metal from their Compound (metallurgy)
 - use add heat or chemical energy and electrical energy
- metal so formed → higher unstable and (Combined state) to attain higher state energy
- Thus it is a nature of any metal (Combined state) to go back to their stable form

Ore Metallurgy
(metal + other chemical) process → Pure Metal (high Reactive) [unstable]
[stable]

Pure metal surrounding → combined state
(corrosion) (Corrode metal)





* (1) Dry corrosion / chemical corrosion :

This type of corrosion occurs to ~~metals~~ -

direct attack of atmospheric gases

(like oxygen, carbon dioxide, sulphur dioxide, halogen, hydrogen sulphide, nitrogen)

with metal surface.

• Rate of this type of corrosion

depends upon Temperature

chemical affinity
by metal and

gas

humidity

moisture in

air

Nature of oxide film

on surface of metal

- It can be classified into

(1) Corrosion due to oxygen

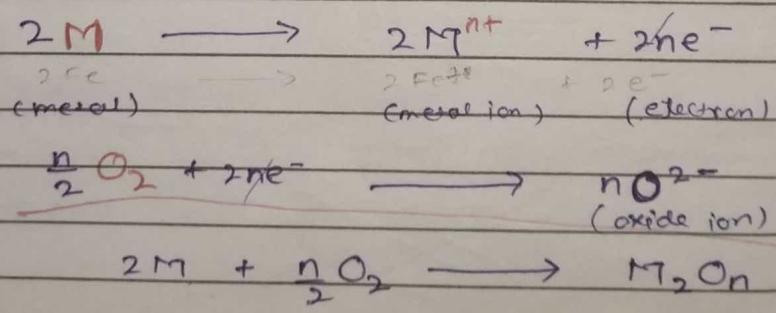
(2) Corrosion due to other gases fluorine

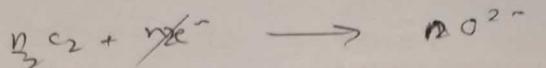
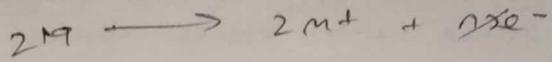
(3) Corrosion due to other
corrosive liquid

Corrosion due to oxygen
(oxidation corrosion)

- → among → The corroding gases oxygen is largest in amount in atmosphere. and it is present everywhere.
 - Oxygen is directly attack on metal surface
① at low as well as high temperature
Temperature
At low temperature
Na, K, Li, Be, Ca
• mg etc are rapidly oxidized
 - At high temperature
all metal except (Ag, Au, pt) are oxidized
 - [After reacting with metal surface]

Mechanism of chemical reaction due to oxidation





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- The extent of corrosion depends upon the types of oxide film formed by metal

- Fe, Cr, Al, Zn forms their corresponding oxide such as Fe_2O_3 , Al_2O_3 , Cr_2O_3 , ZnO . By reacting with oxygen.

- Oxide film formed are classified into three categories

depending on the nature of oxide film.

Nature of oxide film

Play important role in the further corrosion to continue or not

there are three oxide film

(1) Stable oxide film \rightarrow porous

Non-porous

(2) Unstable oxide film

Unstable to moisture

(3) Amorphous oxide film

Stable to moisture

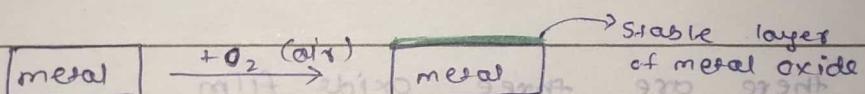
Amorphous \rightarrow 2D layers having strains

Further corrosion depends upon the nature of metal - oxide of scale formed.

Nature of metal oxide layer

Stable Unstable Volatile Porous

- ① **Stable** :- It is tightly adhered to the metal surface.
- Hence, it acts as a protective coating to metal surface.
- Impervious in nature i.e. it does not allow O_2 to reach the underlying metals.
- Reducing rate of further corrosion.
- The extent of corrosion depend upon on its type

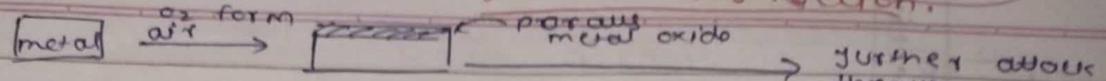


② **Porous**

Porous oxide :- The name itself suggest it has layer pores or cracks.

- In such case, the atmospheric O_2 has access the underlying surface of the metal, through the pores or cracks of the layer.
- This corrosion continues till the entire metal gets completely removed by the action of O_2 .
- Get clear by the example of alkali metal Li, Na, K and alkali earth metal Ca, Mg. These metal forming oxide such as Na_2O , K_2O , MgO etc. where the volume of oxide formed less than, volume of reacted metal.

- Thus, oxide layer is in less quantity and therefore it cannot cover the entire surface of metal block and leads to further destruction.

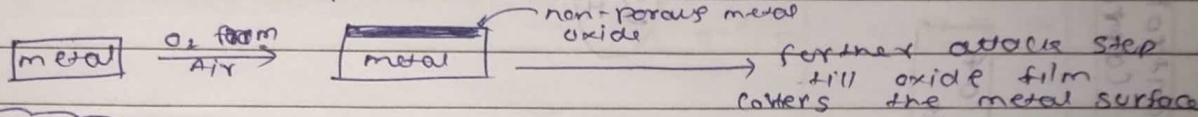


(4) (ii)

Non-porous oxide layer - the rate of corrosion reduces considerably and in most cases, if stop completely, if the nature of film is non-porous in nature

- Metal like Al, Cr etc. Form oxides such as Al_2O_3 , Cr_2O_3
- Volume of oxide film is greater than volume of metal
- Oxide film after its formation covers the entire metal surface (not giving any chance for further attack of oxygen)

- Thus, on metal surface protective layer of oxide (In type of oxide film act as protective layer) and stop further corrosion

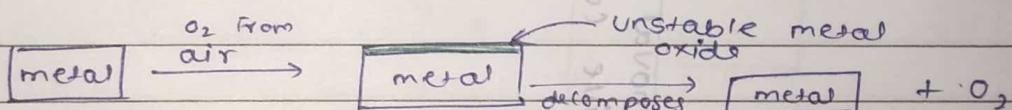


(2)

Unstable oxide film :- This types of film (layer) decomposes back into the metal and oxygen

Molybdenum oxide (MoO_3)

- oxidation corrosion is not possible in such a case
- Thus Pt, Au and Ag don't go under oxidation corrosion



(3)

Volatile oxide film

- As a name suggested volatile mean vaporization

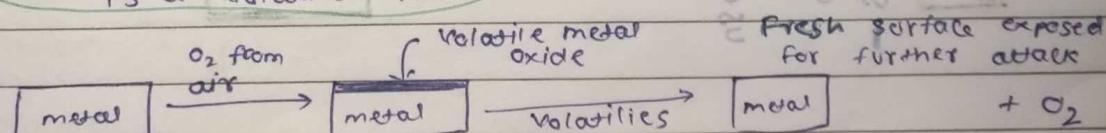
The metal oxide layer vaporizes from metal surface

- The metal is available back to environment

For oxidization - In this case the

ex: Molybdenum oxide (MoO_3) is a volatile film

metal keep depleting



Control of corrosion

By proper Designing

Sharp bends,
corners should
be avoided by
use joints & welding

Modification of environment

Removal of corrosive constituents

Cathodic protection

Protective coating

Use of Inhibitors

**Change of metal
or
modification of properties of metal**

* (2) Wet Corrosion / Immersed Corrosion / Electrochemical Corrosion :

- The corrosion which takes place in the presence of **water or electrolyte** by **electrochemical mechanism** is called **wet corrosion**.
- An electrochemical reaction is the one which result in the transfer of e^- .
- It is observed that when **two different metal** are in **contact with each other through a common liquid.**

* - Metal having

- Higher oxidation potential act as **Anode**
- Lower oxidation potential act as **Cathode**

Anode → undergoes corrosion

Cathode → is protected.

is called **electrochemical corrosion**.

- Electrochemical or wet corrosion take place under two **circumstances**

When a **metal** is in **contact with a conducting liquid**

Two dissimilar metal or alloy are either **immersed or dipped partially in the solution**

- These type of condition are

always suitable → Formation of separate

Anodic area
Cathodic area

area b/w which electric current can flow through the conducting solution

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liberation (oxidation reaction)
of electron take place

- At anode → The destruction of metal occurs (o)

either by dissolving it as metal ion
or by converting it into compound

such as oxide

the absorption of electron take place (reduction reaction)

- At cathode → These reaction do not affect the cathode part.

metal cannot be further reduced

(oxidative part is part of electrolysis)

- Formation of metal ion (M^{n+}) at anode causes dissolution of metal

and free electron are liberated.

thus free electron are consumed in cathodic

reaction

anode to oxidation reaction

from which current flows through the circuit

anode is positive terminal of battery

anode is positive terminal of battery

(a) with the evolution of Hydrogen gas:

- This type of mechanism is generally observed if the metal is exposed to

as the environment is acidic there combined availability of

H^+ ion around metal surface.

acidic environment

① - If the environment is acidic,

there will be availability H^+ in large quantity

② - Generally, Metal tends to lose electron (oxidation)

therefore there is large anodic part

③ - on the same metal surface there can be smaller cathodic part

where this reaction is not taking place

- it can be either because of impurity or

any other reason

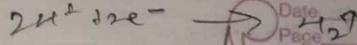
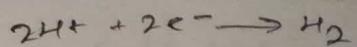
④ - therefore there will be less charge density compared to other part (larger)

- whatever e^- are generated at larger part

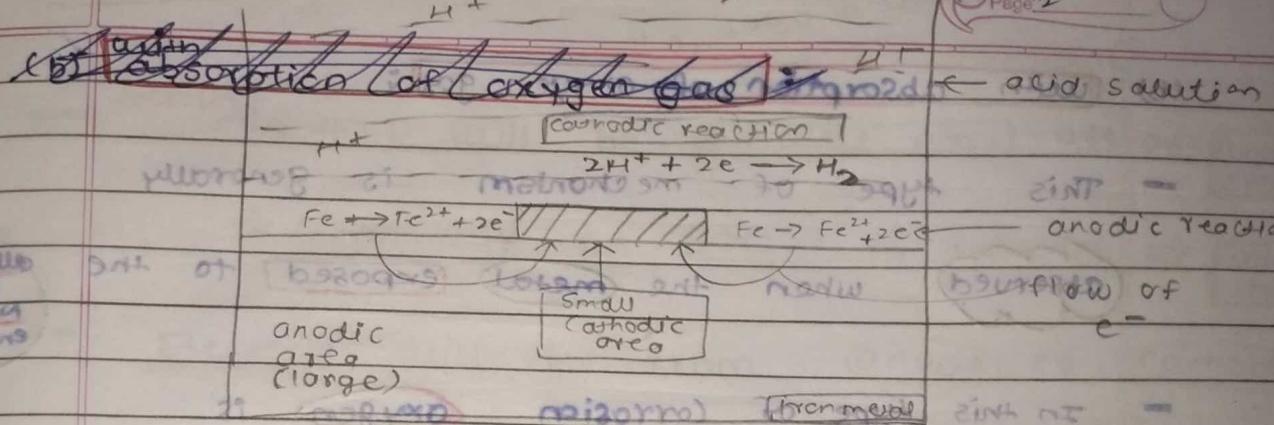
$e^- \rightarrow$ they all will move toward small part

This small area where e^- accumulating

will act as small cathodic area



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- In acidic environment there will be availability H^+ are around this **Smaller port**

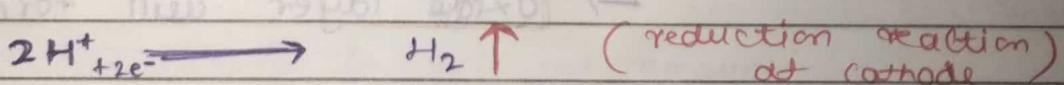
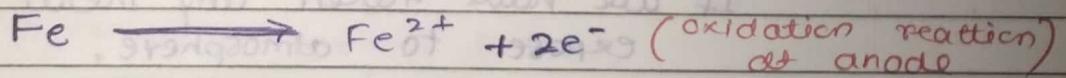
- These H^+ will also attract toward **smaller port**

- At a **smaller port** fluid e^- will absorb by the Hydrogen

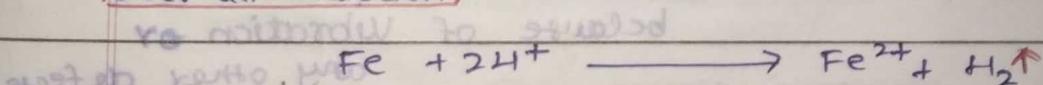
Hydrogen atoms on and get converted into H_2

Electrochemical reactions:

At anode,



Overall reaction:



(i) Iron tank act as **anode** undergoes corrosion

(ii) Fe atoms pass into acidic solution as **Fe²⁺** ions

(iii) Free e^- which are accumulated at **cathode area**.

(iv) e^- one reaction with hydrogen form H_2 gas and simultaneously **evolution of hydrogen**

(v) In this type of corrosion

Anode → large area

Cathode → smaller area

(b) with absorption of oxygen gas:

- This type of mechanism is generally

observed

when the metal exposed to the alkaline or neutral environment

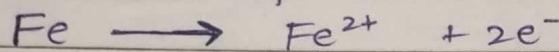
- In this type of corrosion oxygen is

absorbed by the corrosion system

Initially iron reacts with bromine

it will get converted into oxide

brown then finally into hydroxide



- Normally metal \rightarrow have no tendency to lose e^- absorb

- The e^- which are released in above reaction if will absorb O₂ and get convert into oxide

- Suppose

If we have taken any metal, if its exposed to atmosphere,

\rightarrow Oxide layer will form on it

- This oxide layer get broken

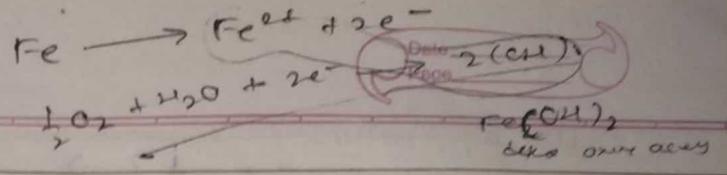
because of vibration or any other defect

- Cracks can be developed. The Cracked Area (smaller part)

behaves anode

In anode area will get oxidized and

release e⁻



therefore

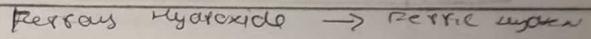
→ there will be **smaller part** act as **anodic area**

→ there will be **larger part** act as **cathodic area**

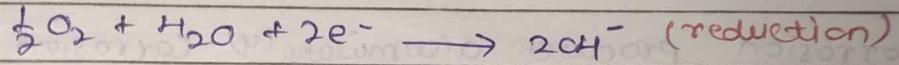
Electron will flow from **anode** to **cathode**

these e^- taken up by the dissolved e^- oxygen in the presence of water.

result take place at cathode is:



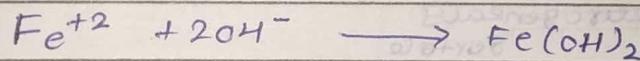
Ferric hydroxide → Ferric oxide



The ferrous ions at the **anode** Fe^{2+}

Hydroxyl ion at the **cathode** 2OH^-

diffuse towards **anode** and then they combine to form **ferrous hydroxide**



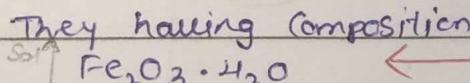
If O_2 is limited amount

At anode

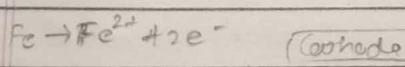
If **O₂ (oxygen)** is in sufficient amount

Ferrous Hydroxide → further oxidized into **Ferric Hydroxide**

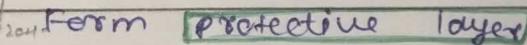
aqueous neutral soil



almost insoluble in water and precipitated as yellow rust.



(Cathode)



Form **protective layer**

on the surface of metal.

and which **decrease corrosion rate**

rust+

metal

most imp

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Chemical/Atmospheric

Electrochemical / Immersed

Dry corrosion

- (1) Dry corrosion it take place in absence of water and in presence of **gasses**.

- (2) It occur through **the chemical environment** of the metal by **direct attack**.

- (3) It can be explained by **absorption mechanism**.

- (4) Corrosion product accumulates at the **same spot** where **corrosion starts**, further corrosion is prevented.

- (5) It is slow process

- (6) It occurs both **homogeneously** and **Heterogeneously** on **Surface**.

- (7) If corrosion is **uniform**

- (8) Rate of corrosion is governed by

Nature of Corrosion Product

Rate of Corrosion

is governed by

Cathodic Product

Wet corrosion

- (1) Wet corrosion it take place in presence of **water** or **electrolytes**.

- (2) It occurs through a large no. of galvanic cells.

- (3) It can be explained by **electrochemical reaction**.

- (4) Corrosion product accumulates at the **Cathodic area**. Hence, further corrosion is occurred.

- (5) It is fast process

- (6) It occurs in **Heterogeneous Surface**.

- (7) Corrosion is **not uniform**

To corrosion ka destruction ho raha hai anode par

→ our metal humara anode hai tha

Hum into karenge ke
Data Page anode te convert koy
denge cartoon main

Cathodic protection :

→ Based principle

metal $\xrightarrow{\text{convert}} \text{(cathode)}$ into

no humara metal Protected raha ga corrosion se

- In this method

protecting metallic object

From corrosion

by making them completely cathodic

and

No area of metallic object

→ is allowed to act as anode

→ is achieved by supplying e^-

to

metal structure to be protected

- There are two types of cathodic protection

By using galvanic
or sacrificial anode
or auxiliary anode method

By using impressed current method

- **disadvantage** of this method

due to application of impressed current

→ anode → deteriorates
it has to be replace from time to time

- **Used** of this method

Protecting

marine structure

tank

Pipeline condenser

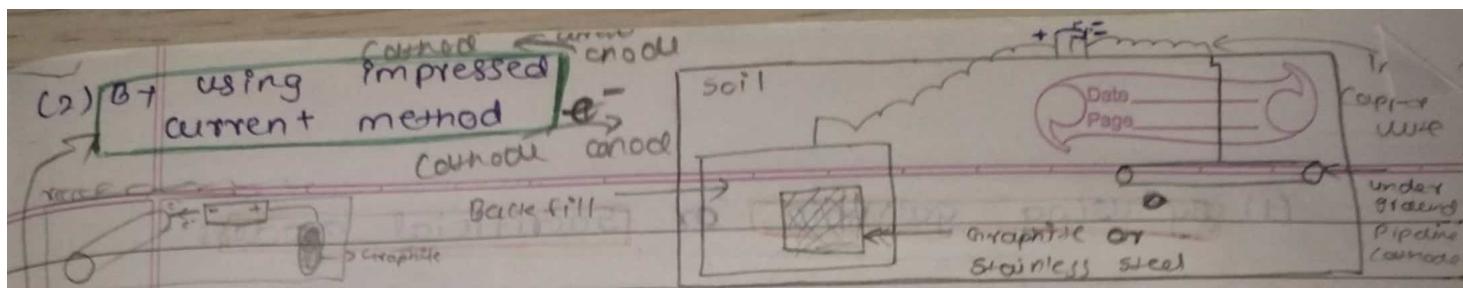
- Single anode
can be used

- many anode
can be used

- This protection is suited

For large structure

For long-term operation



- In this method

the metallic pipeline

is connected to the negative terminal

the connected to the positive terminal

graphite anode

A current is applied to opposite direction to that corrosion current on the iron pipe

- As a consequence

The metal Pipe line

is converted to

cathode

and gets protected

such as

impressed current
can be obtained

by using

dc source

such as

battery 080 dry cell

along with an insoluble anode

such as

platinum

stainless steel

graphite

- The anode ← embedded underground

and to this with help of dc source

impressed current is applied and

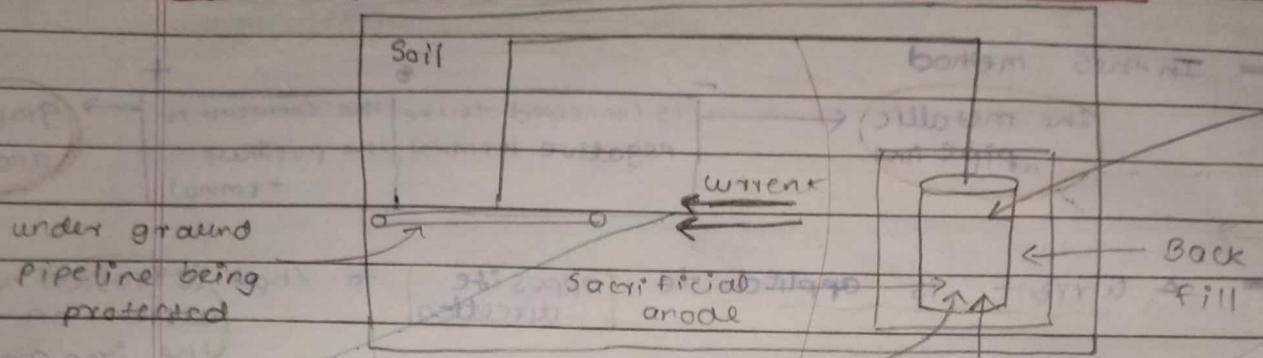
carried out by
cables using wire

The insoluble anode ← are kept inside back fill → which is made up gypsum

→ If the area metallic structure to be protected is small

→ if the area metallic structure to be protected is large

(1) By using galvanic or Sacrificial anode:



- In this method

more active metal
and
their alloy is

→ Connected to →

metal
structure

↓
(to be protected)

- These result in the corrosion of the piece of metal connected
- Since the more active metal → Sacrifices itself

thereby

Saving
the base metal

By undergoing
corrosion

the method name is

Saving the
base metal

Auxilliary
anode

Sacrificial anode

more active
metal

Supply e⁻ to

the metal
structure

By dissolution
of sacrificial
anode

— When this piece of **more active metal** get **Corroded Completely**

*Galv. coating
method puts
Zn, Al, Mg
to give to
longer life
replace*

— It can be simply **replaced** by **Fresh new piece**

The metal normally used
or **Mg, Zn and Al**

Used of this method

↳ protect **buried steel pipelines**,

industrial water tanks

protect **cable or iron pipeline** → By connected them to **Mg-Block**

In case protect **marine structure, ship** → By using **Zn-plates**
(as sacrificial anode)

Boiler, water tanks → By using **Zinc metal**

If requires **low installation cost**, **minimum maintenance** and **short term protection**

~~most imp~~

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Cathodic Protection

(1) This method is applicable to all **metals**

(2) Al, Mg, Zn etc.

(3) Installation cost is **lower**

(4) operating cost is **higher**

(5) useful for **weak** or **moderate**

(6) Applied current can't give any indication of corrosion

(7) It can provide **steady, consistent protection**

Protection for long duration

Anodic Protection

(1) This method applicable to only those metals, which show active-passive behaviour.

(2) Steel, Stainless Steel, Fe, Ti, Al and Cr

(3) Installation cost is **Higher**

(4) operating cost is **lower**

(5) More corrosive environment can be handled.

(6) Applied current gives an indication of **corrosion rate**.

(7) It may not provide **steady protection**.

But if system goes out of control, rate of corrosion increase suddenly

Factor affecting the rate of corrosion

(i) Factor related to metal:

(i) Nature of oxide film :-

If a protective

Non-porous oxide film → formed → is strongly adhered to metal surface

⇒ then it will protect a metal surface

But

if the film → formed is loosely adhered to metal surface.

⇒ then most probable to further corrosion

(ii) Relative areas of anode and cathode :

If two dissimilar metal are in contact

one forming anode and

while another forming cathode

then

the corrosion of is directly proportional to the ratio of area occupied by the cathodes and anod

$$\text{Corrosion at anode} = \frac{\text{Area of Cathodic part}}{\text{Area of Anodic part}}$$

(iii) Solubility of corrosion product

The corrosion product formed is soluble → rate of corrosion will then be faster.

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The corrosion product formed in
Eros

The corrosion product formed on insoluble → rate of corrosion will in turn be decreased.

(2) Factor related to environment:

(i) Temperature:

The rate of the reaction is accelerated with rise in temperature.

- The rate of dry corrosion increases ↑ with increase in temperature ↑
- The rate of wet corrosion increases slightly ↑ with increase in temperature ↑

(ii) presence of moisture:

The rate of corrosion → increase rapidly ↑ → in presence of moisture

(iii) Effect of pH of moisture:

Acidic medium are more corrosive
then Neutral or alkaline medium

(A) Anodic Coatings :

(1) - coating with more active metal.

(2) - If the active metal → whose electrode potential are higher than that of base metal → form anodic coating

(3) - e.g. zinc, aluminium, Cadmium on iron or steel

(4) - If any portion of coating is broken

a galvanic cell is formed

(5) ^{case of} The ^{1st} galvanized zinc, coating part act as Anode and base metal acts as Cathode
Zn → act as Anode
Fe → act as Cathode
- Coating part ^(metal) act as Anode, undergoes corrosion
- Base metal act as Cathode, undergoes protected

(6) Anodic coating will be good under all condition and protect base metal from corrosion

irrespective whether coating is porous or non-porous

therefore,

galvanic cell set up are protected the base metal and cathodic coating are not protected the base metal and corrosion occur faster than anodic coating

(B) Cathodic coatings :

(1) — Coating with less active (more noble) metal.

(2) — If the less active more noble metal → whose electrode potential is lower than that of the base metal

form cathodic coating

(3) — e.g. Sn and Cu on Iron or steel

(4) — If any portion of coating are broken

- The coating metal act as cathode.

- Base metal act as anode & undergoes corrosion

Therefore,

Anodic coating

more preferred coating

Cathodic coating

less preferred coating

• Anodic coating

(1) Coating with more active metal

(2) Coating metal

is higher place in

[EMF series] than Base metal

(3) Base metal remain safe

as long as Coating metal present on the base metal

If Coating ruptured

(4) e.g. Galvanization

(5) more preferred coating

• Cathodic coating

(1) Coating with more noble metal

(2) Coating metal

is lower place in

[EMF series] than Base metal

(3) Base metal undergoes fast corrosion

If Coating are ruptured or crack

(4) e.g. Tinning

(5) less preferred coating