WHAT IS CORROSION ??

- **Corrosion is defined as the slow and steady destruction of a metal by the environment.**

  It results in the deterioration of the metal to form metal compounds by means of chemical reactions with the environment.

TYPES of CORROSION

1. Uniform, or general attack
2. Galvanic, or two-metal corrosion
3. Crevice corrosion
4. Pitting corrosion
5. Intergranular corrosion
6. Selective leaching, or parting,
7. Erosion corrosion, and
8. Stress corrosion
**9.** Microbial corrosion

Uniform Attack

Uniform attack is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area. The metal becomes thinner and eventually fails. For example, a piece of steel or zinc immersed in dilute sulfuric acid will normally dissolve at a uniform rate over its entire surface. A sheet iron roof will show essentially the same degree of rusting over its entire outside surface.

Galvanic or Two-Metal Corrosion

A potential difference usually exists between two dissimilar metals when they are immersed in a corrosive or conductive solution. If these metals are placed in contact (or otherwise electrically connected), this potential difference produces electron flow between them. Corrosion of the less corrosion-resistant metal is usually increased and attack of the more resistant material is decreased, as compared with the behavior of these metals when they are not in contact. The less resistant metal becomes anodic (anodic part always corrodes) and the more resistant metal acts as cathode.

Galvanic Corrosion
(contact between unlike metals; opposite of cathodic protection)
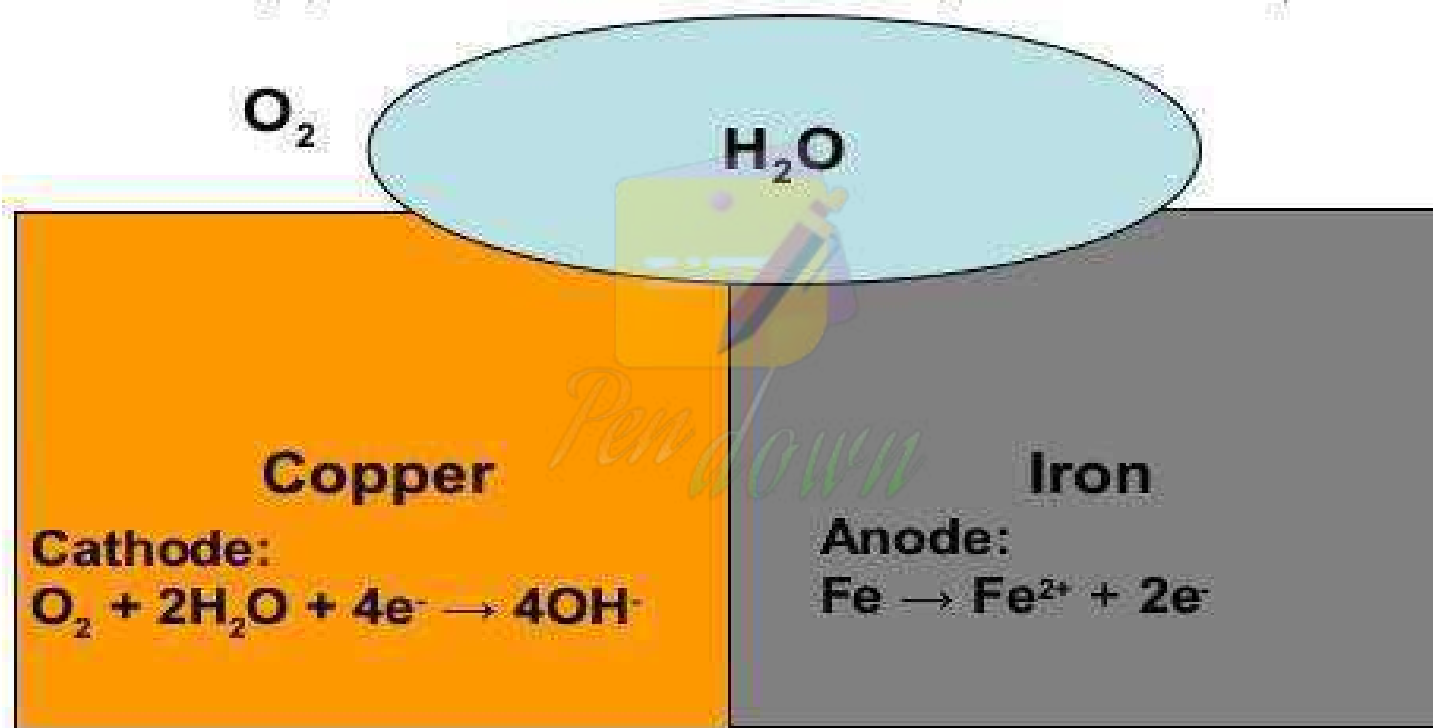
Crevice Corrosion

Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surface deposits, and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion.

Pitting Corrosion

Pitting is a form of extremely localized attack that results in holes in the metal. Pits are sometimes isolated or so close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same as or less than the depth.

Pitting corrosion occurs often due to breaking of the protective oxide film which is invariably always present on the surface of metal. The area where this film gets broken is exposed to corrosive medium and becomes anode.

Intergranular Corrosion

In case of alloys which are a mixture of two or more metals, under certain conditions, grain interfaces are very reactive and intergranular corrosion results. Localized attack at and adjacent to grain boundaries, with relatively little corrosion of the grains, is intergranular corrosion. The alloy disintegrates (grains fall out) and/or loses its strength. Depletion of chromium in the form of CrC (chromium carbide) at the grain-boundary regions results in intergranular corrosion of stainless steels. Impurity acts as anode in general.
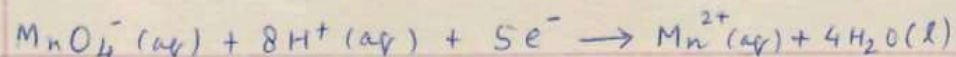
[Stress-corrosion cracking](#)

Stress-corrosion cracking refers to cracking caused by the simultaneous presence of tensile stress and a specific corrosive medium. Many investigators have classified all cracking failures occurring in corrosive mediums as stress-corrosion cracking, including failures due to [hydrogen embrittlement](#) The two classic cases of stress-corrosion cracking are "season cracking" of brass, and the "caustic embrittlement" of steel.

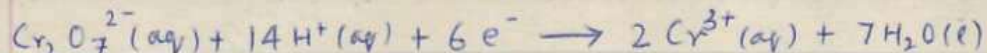# Standard Redn Potentials at 25°C

Reduction Half - Reactions	$E^°(V)$

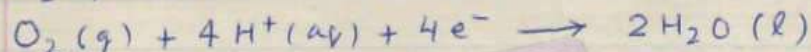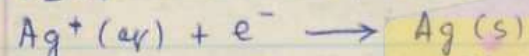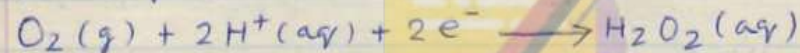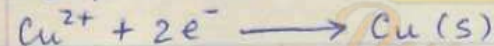$$MnO_4^- (aq) + 8H^+ (aq) + 5e^- \longrightarrow Mn^{2+} (aq) + 4H_2O (l) \qquad 1.51$$

$$Cr_2O_7^{2-} (aq) + 14H^+ (aq) + 6e^- \longrightarrow 2Cr^{3+} (aq) + 7H_2O (l) \qquad 1.33$$

$$O_2 (g) + 4H^+ (aq) + 4e^- \longrightarrow 2H_2O (l) \qquad 1.23$$

$$Ag^+ (aq) + e^- \longrightarrow Ag (s) \qquad 0.80$$

$$Fe^{3+} (aq) + e^- \longrightarrow Fe^{2+} (aq) \qquad 0.77$$

$$O_2 (g) + 2H^+ (aq) + 2e^- \longrightarrow H_2O_2 (aq) \qquad 0.70$$

$$O_2 (g) + 2H_2O (l) + 4e^- \longrightarrow 4OH^- (aq) \qquad 0.40$$

$$Cu^{2+} + 2e^- \longrightarrow Cu (s) \qquad 0.34$$

$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+} (aq) \qquad 0.15$$

$$2H^+ (aq) + 2e^- \longrightarrow H_2 (g) \qquad 0$$

$$Pb^{2+} (aq) + 2e^- \longrightarrow Pb (s) \qquad -0.13$$

$$Ni^{2+} (aq) + 2e^- \longrightarrow Ni (s) \qquad -0.26$$

$$Fe^{2+} (aq) + 2e^- \longrightarrow Fe (s) \qquad -0.45$$

$$Zn^{2+} (aq) + 2e^- \longrightarrow Zn (s) \qquad -0.76$$

$$Al^{3+} (aq) + 3e^- \longrightarrow Al (s) \qquad -1.66$$

$$Mg^{2+} (aq) + 2e^- \longrightarrow Mg (s) \qquad -2.37$$

$$Na^+ (aq) + e^- \longrightarrow Na (s) \qquad -2.71$$

$$Li^+ (aq) + e^- \longrightarrow Li (s) \qquad -3.04$$
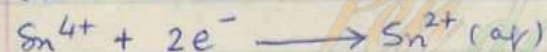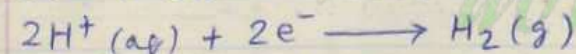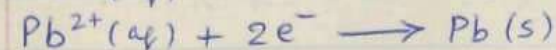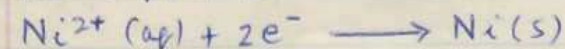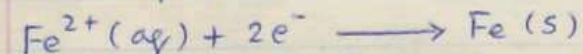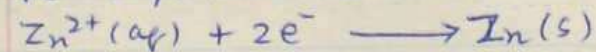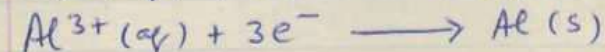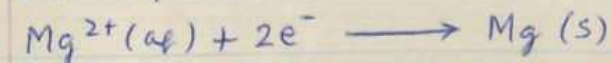
Mechanism of Corrosion By Hydrogen Evolution
(when metal is immersed in dil acid)

$M(s) + H_2O\ (l) \rightarrow M(OH)_2\ (s) + H_2\ (g)$ -----(1)

Oxidation (anodic reaction) $\quad M(s) \rightarrow M^{2+} + 2e^-$ -----(2)

In Solution, $\quad 2H_2O\ (l) \rightarrow 2H^+ + 2OH^-$ -----(3)

Reduction (cathodic reaction) $2H^+ + 2e^- \rightarrow H_2\ (g)$ ----(4)

In Solution, $\quad M^{2+} + 2OH^- \rightarrow M(OH)_2\ (s)$ -----(5)
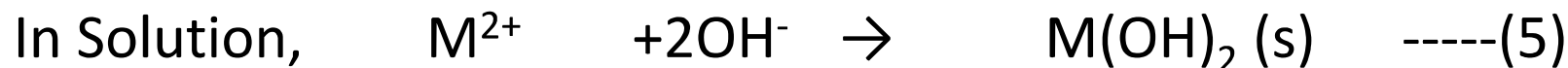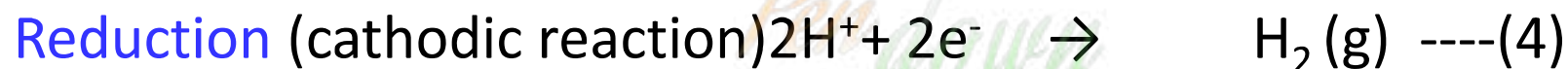
In a simplified form Eq. (1) can be written as
$M(s) + 2H^+ \rightarrow M^{2+} + H_2\ (g)$ -------(6)
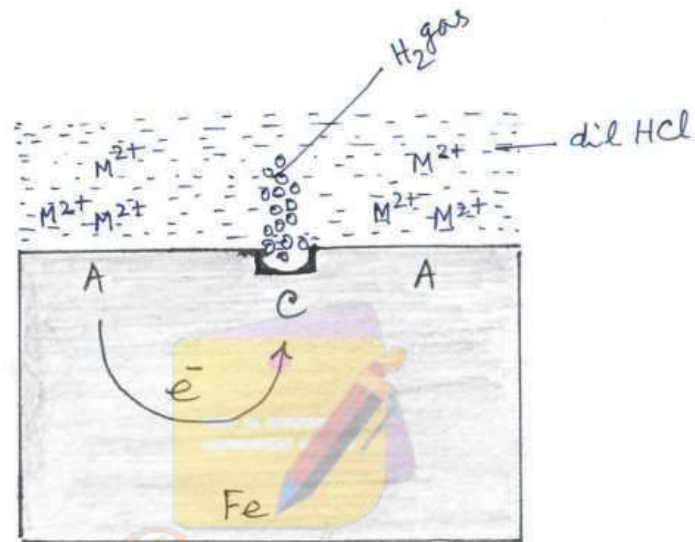
Ist Mechanism

Schematic diagram: Mechanism of Corrosion
By HYDROGEN EVOLUTION
LARGE ANODE — SMALL CATHODE

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \,(s)$$
$$4\,Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4\,Fe(OH)_3 \quad or \quad Fe_2O_3 \cdot x\,H_2O$$
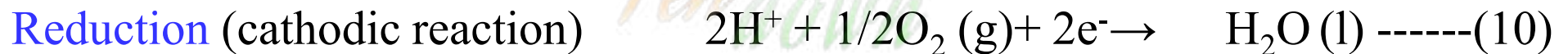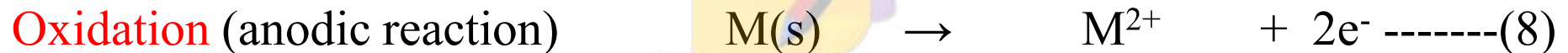Yellow Rust

If O_2 is in low conc. the Corrosion Product is Fe_3O_4 Black
Magnetite

Mechanism of Corrosion By Oxygen Absorption
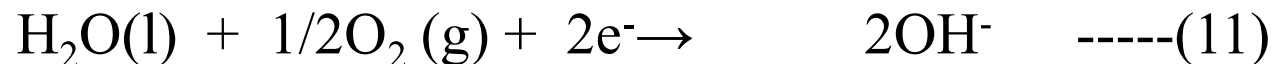## (when metal is immersed in neutral aqueous electrolyte eg. NaCl)

In presence of oxygen the reaction will be

$$M(s) \quad + \quad H_2O \ (l) \ + 1/2O_2 \ (g, air) \quad \rightarrow \quad M(OH)_2 \ (s) ------(7)$$
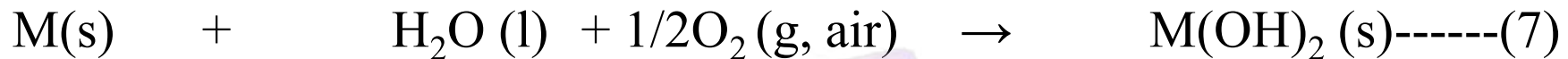
Similarly Eq.(7) can be divided in oxidation and reduction half reactions;

Oxidation (anodic reaction) $\quad\quad M(s) \quad\quad \rightarrow \quad\quad M^{2+} \quad + \ 2e^- -------(8)$

In Solution, $\quad\quad\quad\quad\quad 2H_2O \ (l) \rightarrow \quad\quad 2H^+ \quad + \quad\quad 2OH^- ------ (9)$

Reduction (cathodic reaction) $\quad 2H^+ + 1/2O_2 \ (g) + 2e^- \rightarrow \quad H_2O \ (l) ------(10)$

Or , in alkaline and neutral solutions cathodic reaction will be

$$H_2O(l) \ + \ 1/2O_2 \ (g) + \ 2e^- \rightarrow \quad\quad 2OH^- \quad -----(11)$$

Overall, in Solution,

$$M^{2+} \quad\quad +2OH^- \quad \rightarrow \quad\quad M(OH)_2 \ (s) \quad\quad -----(12)$$

II Mechanism

RUST
$(Fe_2O_3 \cdot x H_2O)$

Neutral Aq.
Electrolyte
NaCl

RUST

Protective
Oxide Layer

C   A   C

e^-

Fe
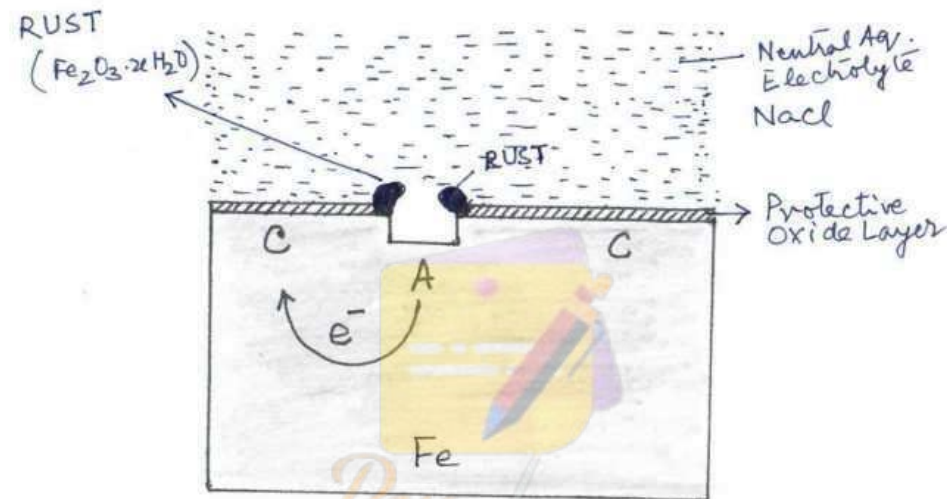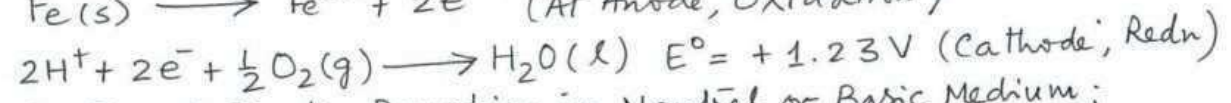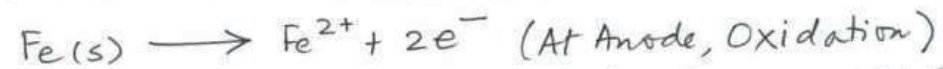
Scheme Diagram : Mechanism of Corrosion
By OXYGEN ABSORPTION
LARGE CATHOD — SMALL ANODE

$Fe_{(s)} \longrightarrow Fe^{2+} + 2e^-$ (At Anode, Oxidation)

$2H^+ + 2e^- + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$ $E° = +1.23V$ (Cathode, Redn)

Another Cathodic Reaction in Neutral or Basic Medium;

$H_2O(l) + \frac{1}{2} O_2(g) + 2e^- \longrightarrow 2OH^-$

$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2(s) \xrightarrow{O_2} Fe(OH)_3$ or $Fe_2O_3 \cdot x H_2O$
(RUST)
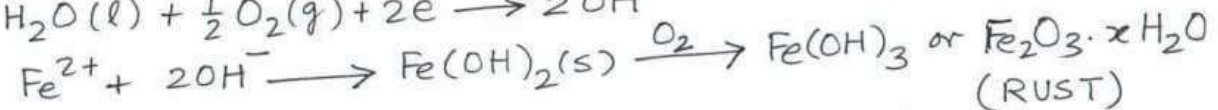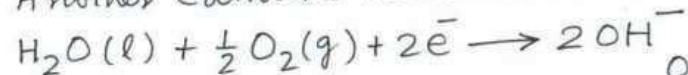
PREVENTION OF CORROSION

The huge annual loss due to corrosion is a national waste and should be minimized

- Materials already exist which, if properly used, can eliminate 80 % of corrosion loss
- Proper understanding of the basics of corrosion and incorporation in the initial design of metallic structures is essential
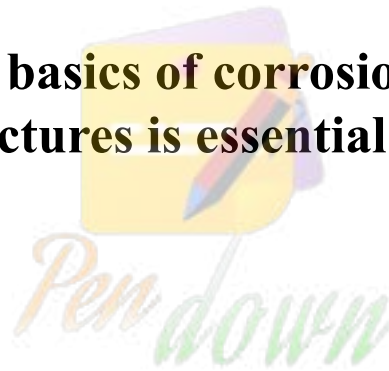
Methods of Corrosion Prevention

- Material selection
- Improvements in material
- Design of structures

By treating the medium

- Alteration of environment

By treating the metal

- Cathodic & Anodic protection
- Coatings

DESIGN OF NEW EQUIPMENTS Or STRUCTURES

- Avoid contact between Two dissimilar metals
- Chose metals not far apart in EMF or Galvanic Series
- Avoid sharp corners or bends
- Complete draining of vessels
- No water retention
- Avoid sudden changes in section
- Weld rather than rivet
- Easy replacement of vulnerable parts
- Avoid excessive mechanical stress

TREATMENT/ALTERATION OF ENVIRONMENT

- Lower temperature and velocity
- Remove oxygen/oxidizers
- Change concentration

USE OF CORROSION INHIBITORS or chemicals which retard corrosion; They may be Anodic or Cathodic, depending upon their action.

- Adsorption type, e.g. Organic amines, azoles
- Hydrogen evolution poisons, e.g. As & Sb
- Scavengers of Oxygen e.g. Sodium sulfite & hydrazine
- Salts of organic acids, e.g. Chromates, nitrates, phosphates, tungstates acts as anodic inhibitors

- Inhibitors are chemicals that interact with a metallic surface, or the environment this surface is exposed, giving the surface a certain level of protection.
- Inhibitors often work by adsorbing themselves on the metallic surface by forming a film

- Inhibitors slow corrosion process by:
  - Increasing the anodic or cathodic polarization behavior (Tafel slopes)
  - Reducing the movement or diffusion of ions to the metallic surface
  - Increasing the electrical resistance to the metallic surface

Passivating (anodic) inhibitors

- Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range.

- There are two types of passivating inhibitors:

    - oxidizing anions, such as chromate, nitrite and nitrate that can passivate steel in the absence of oxygen.

    - nonoxidizing ions, such as phosphate, tungstate and molybdate that require the presence of oxygen to passivate the steel

Cathodic Inhibitors

- Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these area.

- Arsenic, antimony, calcium, zinc, and magnesium are the cathodic inhibitors.

CATHODIC & ANODIC PROTECTION

❖**Cathodic protection**: Make the structure more cathodic by

– Use of sacrificial anodes

– Impressed currents

Used extensively to protect marine structures, underground pipelines, water heaters and reinforcement bars in concrete

❖**Anodic protection**: Make passivating metal; applied only to those metals which show the phenomenon of Passivity

structures more anodic by impressed potential. e.g. 316 s.s. pipe in sulfuric acid plants

Pilling –Bedworth Rule or Ratio

Volume of the Oxide of metal
Volume of metal

If above P-B ratio > 1 (oxide layer protective)

If , P-B ratio < 1 (oxide layer unprotective)

For Cr, Ni, and Mo it ranges from 1.8 – 2.8

Q. At high temperatures, copper reacts with air to form the oxide Cu_2O. Would this oxide be protective according to the Pilling-Bedworth criterion? Densities are: Cu = 8.92 g/cm^3, Cu_2O = 6.0 g/cm^3.

Solution: *The reaction is 2Cu + ½O$_2$ = Cu$_2$O. That is, two moles of copper will form one mole of oxide.*

Volume of 1 mole of oxide =

(2 x 63.55 g/mol of Cu + 15.999 g/mol O) / 6.0 g/cm3 = 23.85 cm^3.

Volume of metal reacted =

2 moles of Cu (2 x 63.55) g/mol / 8.92g/cm^3 = 14.25 cm^3

P-B ratio = 23.85 cm^3 Cu$_2$O / 14.25 cm^3 Cu = **1.67**

Since the *Pilling–Bedworth ratio is greater than one, the oxide should be protective.*
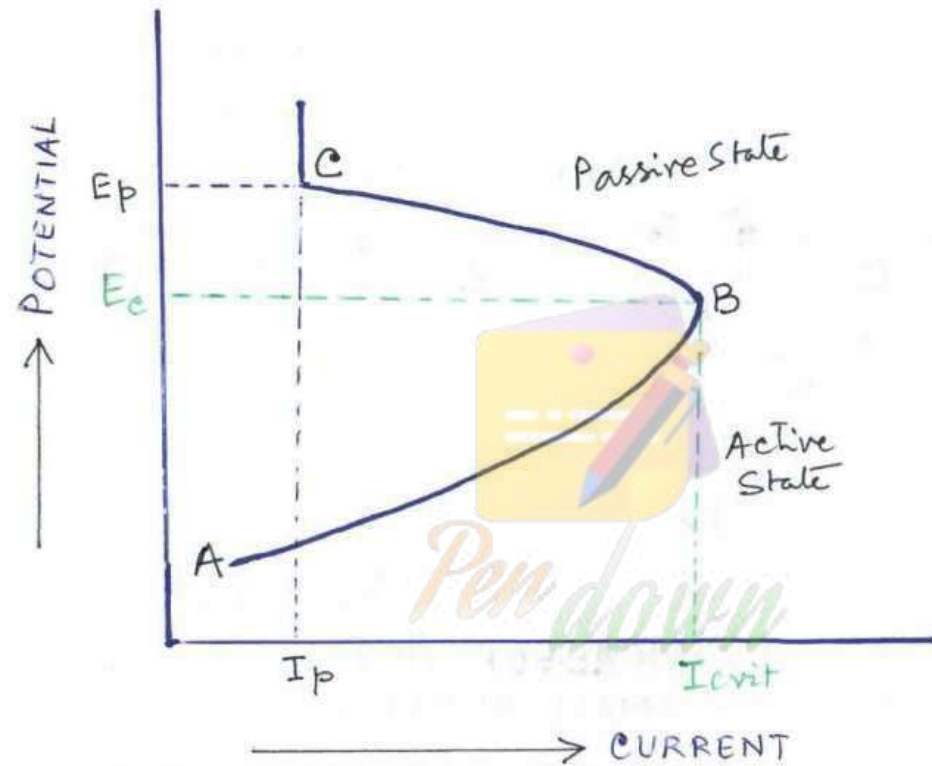
ANODIC PROTECTION

- Simply anodic protection is based on the formation of protection film by external applied anodic current.

- If carefully controlled anodic protection current is applied to Ni ,Fe, Cr, Ti, and their alloys they are passivated and the rate of metal dissolution is decreased.

Anodic Protection *Method*

Anodic protection refers to prevention of corrosion through impressed anodic current. This method of protection tested and demonstrated by Edeleanu in 1954 however can be applied only to metals and alloys that exhibit active-passive behavior (Passivization). The interface potential of the structure is increased to passive domain. If an active-passive alloy such as stainless steel is maintained in the passive region through an applied potential (or current) from a potentiostat, its initial corrosion rate (i_{corr}) can be shifted to a low value at i_{pass}.
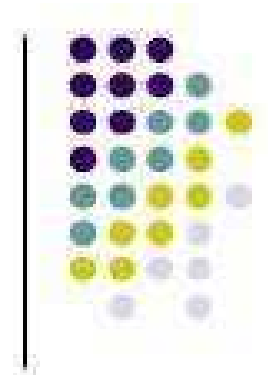
EVAN'S Diagram

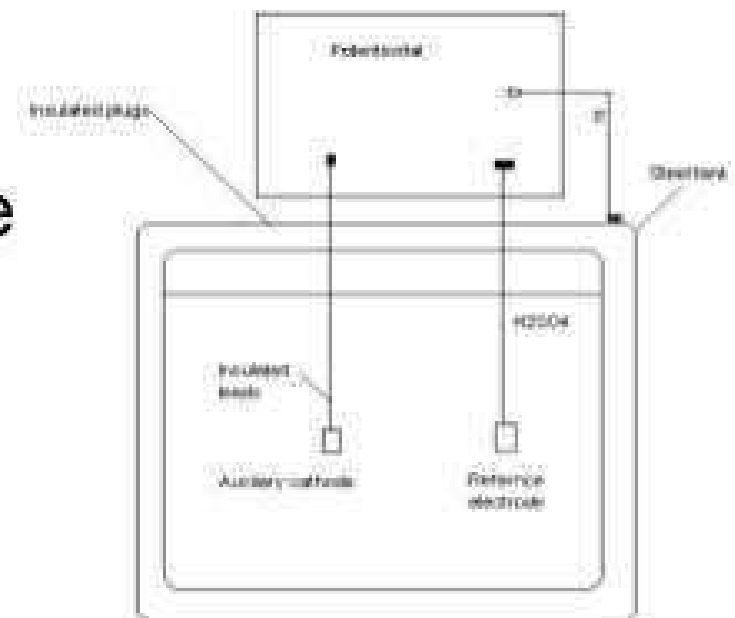$I_p = E_p$ (Passivization Current / Potential)

$I_c = E_c$ (Critical current or Potential)

EVAN'S DIAGRAM

WHAT IS A POTENTIOSTAT?

- How to protect a metal?

- To anodically protect a structure device is required that potentiostat.

- It is an electronic device that maintain a metal at a constant potential either respect to a reference electrode.
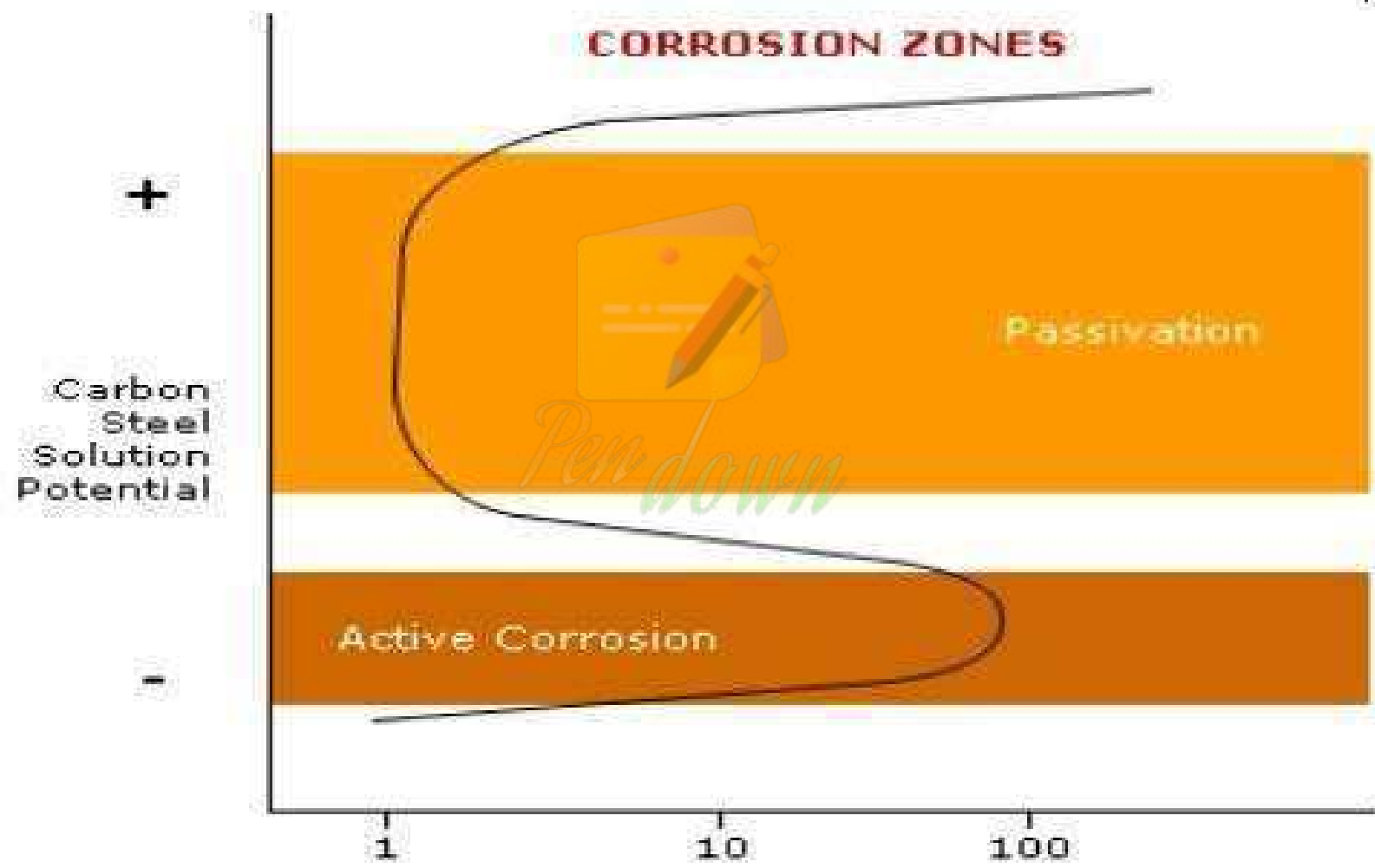
- The figure shows that the potentiostat has the 3 terminals
- one connected to the tank another to the auxiliary cathode and 3rd to the reference electrode.
- In operation the potentiostat remains Constant potential b/w the tank & reference cathode.
- The optimum potential for protection in measured by electrochemical measurements.
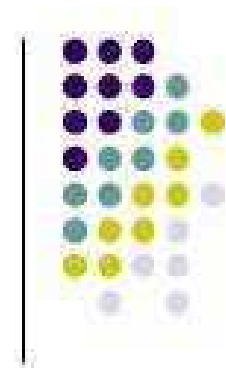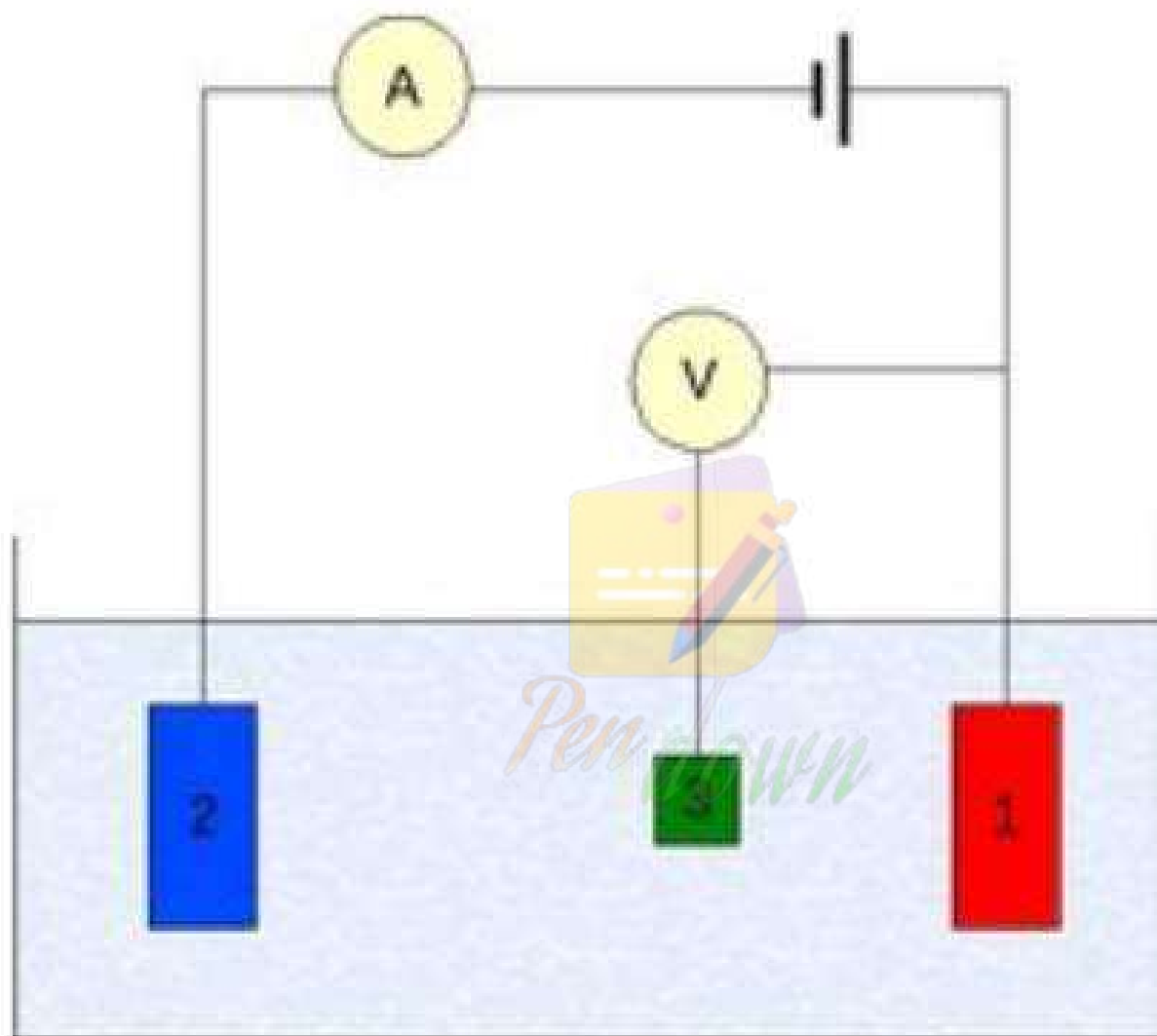
Three-electrode setup: (1) working electrode; (2) auxiliary electrode; (3) reference electrode

CORROSION ZONES

Passivation

Active Corrosion

Carbon
Steel
Solution
Potential

+

−

1   10   100

ADVANTAGES OF ANODIC PROTECTION

- Anodic protection can decrease corrosion rate substantially.

- The primary advantages of anodic protection are its applicability in extremely corrosive environments and its low current requirements.

- Anodic protection has been most extensively applied to protect equipment used to store and handle sulfuric acid.
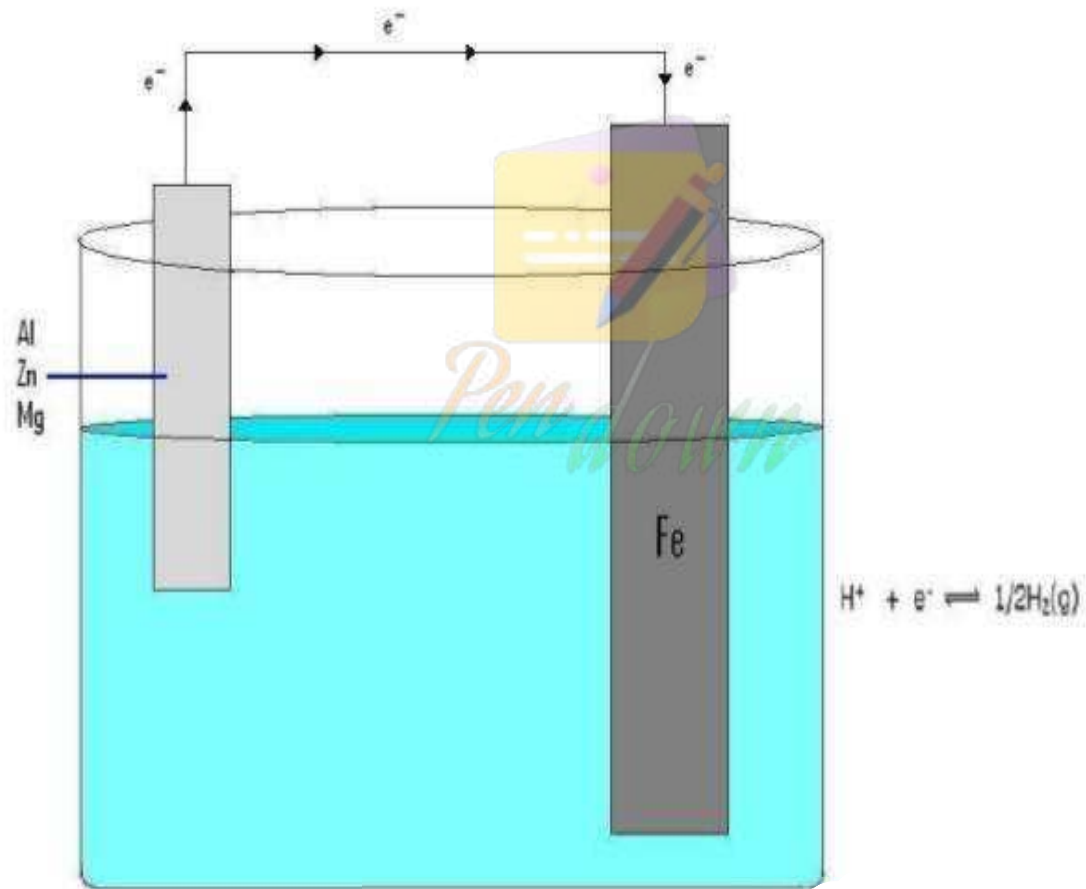
IRON PILLAR OF DELHI

- It is a1600year old pillar. The rusting has been prevented because of the formation of a thin film of oxide of iron on the surface of the pillar.

Cathodic Protection Methods

1. **Sacrificial Anode Cathodic Protection Method**

2. **Impressed Current Cathodic Protection Method**

CATHODIC PROTECTION
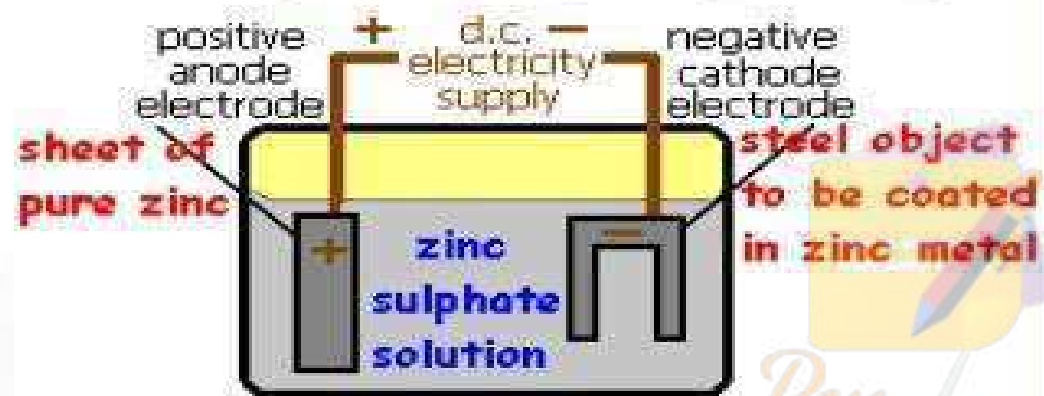

Sacrificial Anode Cathodic Protection

USES:

- Structures that are commonly protected by cathodic protection are the exterior surfaces of:

(i) Pipelines.

(ii) Storage tank bases.

(iii) Steel sheets, tubular and foundation pilings.

(iv) Offshore platforms, floating & sub sea structures.

- Cathodic protection is also used to protect the internal surfaces of:

(i) Large diameters pipelines.

(ii) Ship tanks (product & ballast).

(iii) Storage tanks (oil & water).

(iv) Water circulating systems.
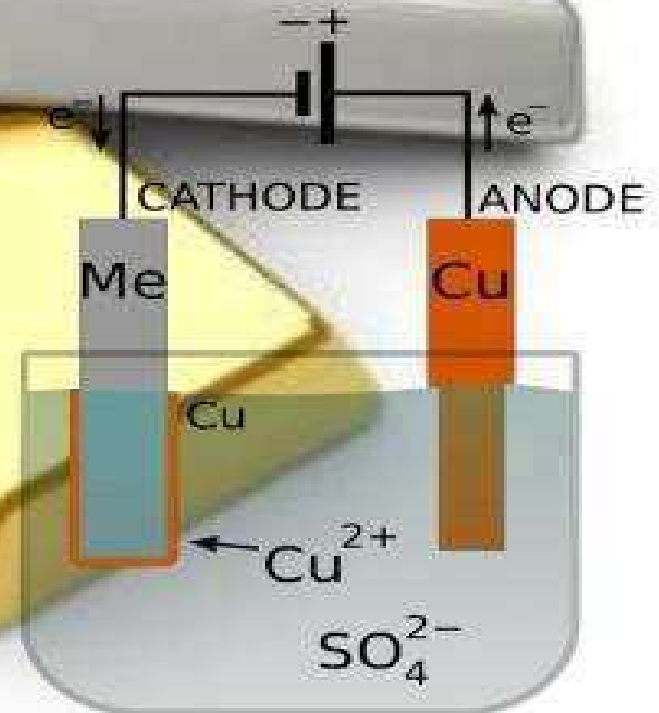
Comparison of cathodic and anodic protection methods

Factors	Cathodic protection	Anodic protection
Suitability	To all metals in general.	Only to those exhibiting active-passive behavior
Environment	Only for moderate corrosion medium	Even aggressive chemical corrosives.
Cost benefit	Low investment, but higher operative cost	Higher investment, but low operative cost
Operation	Protective currents to be established through initial design and field trials	More precise electrochemical estimation of protection range possibe

• Galvanizing

Galvanising a steel object by electrolysis

positive anode electrode
+ d.c. electricity supply −
negative cathode electrode

sheet of pure zinc

steel object to be coated in zinc metal

zinc sulphate solution

• Electroplating

e^- ↓   −+ e^- ↑

CATHODE   ANODE

Me   Cu

Cu

Cu^{2+}

SO_4^{2-}

Anodizing is an electrolytic passivation process used to increase the thickness of the natural oxide layer on the surface of metal parts. The process is called anodizing because the part to be treated forms the anode electrode of an electrolytic cell.