Wet / Electrochemical Corrosion

- 1. Anodic reaction: Metal undergoes oxidation (corrosion) with release of electrons
- **2. Cathodic reactions:** These reactions are dependent on the constituents of the corrosion medium.

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}$$

If the solution is aerated and almost neutral, oxygen is reduced in presence of H₂O to OH⁻ ions.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

If the solution is deaerated and almost neutral, H₂ is liberated along with OH⁻ ions.

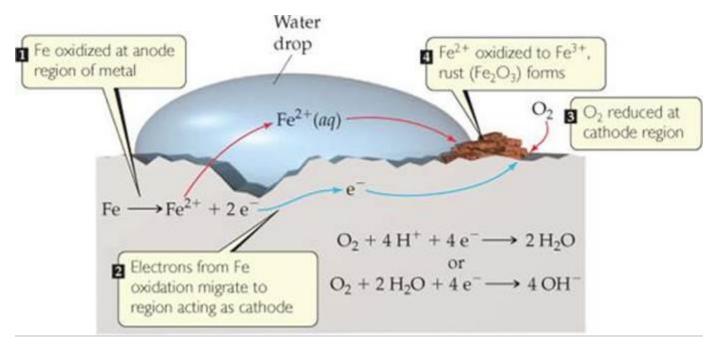
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

If the solution is deaerated and acidic, H⁺ ions are reduced to hydrogen gas

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$$

Wet corrosion (Electrochemical theory of corrosion)

 Metal comes in contact with a conducting liquid or when two dissimilar metals are immersed dipped partly in a solution.



The metal ions formed at the anode combine with hydroxyl ions and form the corresponding metallic hydroxide Fe(OH)₂, which further gets oxidized to hydrated ferric oxide [rust].

$$2\text{Fe}^{2+} + 4\text{OH}^{-} \rightarrow 2\text{Fe}(\text{OH})_{2}$$

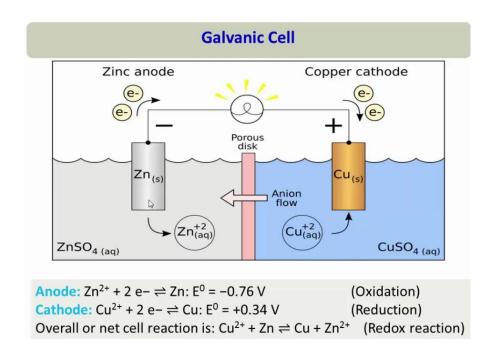
 $2\text{Fe}(\text{OH})_{2} +_{1/2}\text{O}_{2} + (x - 2)\text{H}_{2}\text{O} \rightarrow \text{Fe}_{2}\text{O}_{3} \cdot x\text{H}_{2}\text{O}$
(Rust)

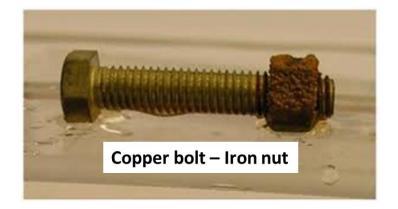
Types of Wet corrosion / Electrochemical corrosion

- 1. Differential metal corrosion (Galvanic corrosion)
- Differential aeration corrosion (concentration cell corrosion / Water-line corrosion)
- 3. Pitting corrosion
- 4. Inter-granular corrosion
- 5. Soil corrosion
- 6. Stress corrosion cracking
- 7. Crevice corrosion

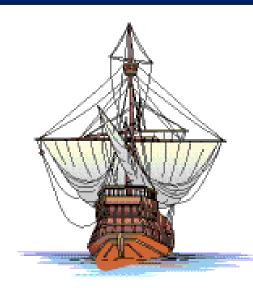
1. Differential Metal Corrosion (Galvanic Corrosion)

When two dissimilar metals are in contact in corrosive environment, metal with lesser standard reduction potential will act as anode and will undergo oxidation (corrosion). Metal with higher standard reduction potential will act as cathode and it will provide surface for reduction of oxygen.





Galvanic Corrosion



One of the earliest documented incidences of serious galvanic corrosion occurred in the eighteenth century on the Royal Navy's frigate, H.M.S. Alarm. This vessel had its wooden hull covered by copper sheathing, which was in turn attached by iron nails.

One of the purposes of this copper covering was to limit marine biofouling, plaguing many materials immersed in sea water. Reduced speed and maneuverability of ships are consequences of such growths. Copper generally acts as a biocide, limiting such fouling.

Not surprisingly, the iron fasteners in contact with the copper were subject to rapid galvanic corrosion and led to detachment of some sheathing.

Other examples of differential metal corrosion (galvanic corrosion) include

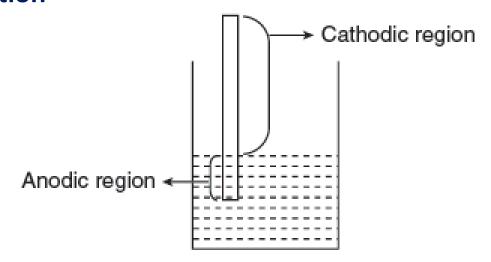
- 1. Buried iron pipeline connected to zinc bar.
- 2. Steel pipe connected to copper plumbing.
- 3. Steel propeller shaft in bronze bearing.
- 4. Zinc coating on mild steel.
- 5. Lead—tin solder around copper wires.

Galvanic Corrosion – prevention/control

- ✓ Selection of alloys which are similar in electrochemical behavior and/or alloy content.
- ✓ Area ratio of more actively corroding material (anode) should be large relative to the more inert material (cathode).
- ✓ Use coatings to limit cathode area.
- ✓ Insulate dissimilar metals.
- ✓ Use of effective inhibitor.

2. Differential Aeration Corrosion (Concentration Cell Corrosion) (Waterline Corrosion)

When a metal is exposed to differential air or oxygen concentration



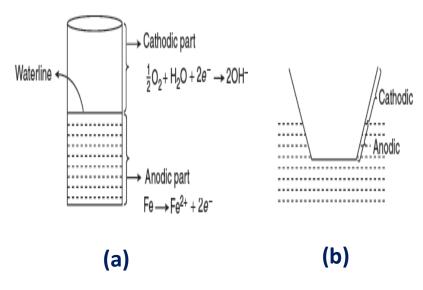
When a metal is partially dipped in an electrolyte,

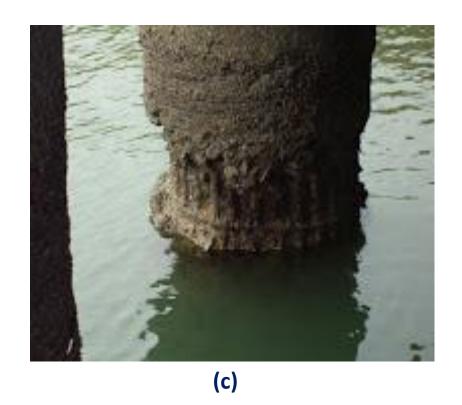
- the portion dipped in the electrolyte is poor in oxygen concentration and works as an anode which gets corroded
- the portion above the electrolyte acts as cathode

The examples of differential aeration corrosion include

- 1. Half-immersed iron plate in aqueous solution.
- 2. Steel pipe carrying any liquid exposed to atmosphere.
- 3. Ocean going ships.
- 4. Steel storage tanks.

Waterline Corrosion





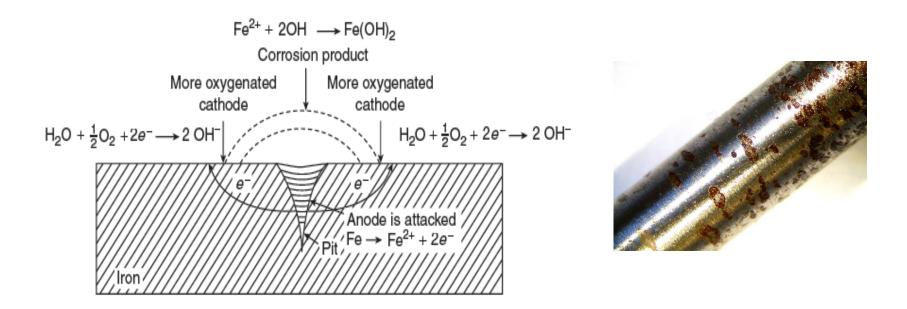
Waterline corrosion: (a) Water storage tank and (b) ocean going ship (c) Metallic pillar in water and outside

Differential Aeration Corrosion – prevention/control

- ✓ Apply a passive coating that prevents the contact between the electrolyte (e.g. water) and the electrode (e.g. metallic Fe)
- ✓ Use of suitable effective inhibitor

3. Pitting corrosion

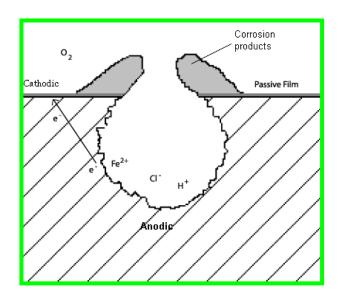
Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material.

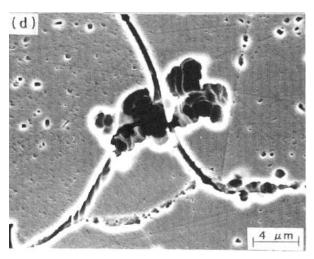


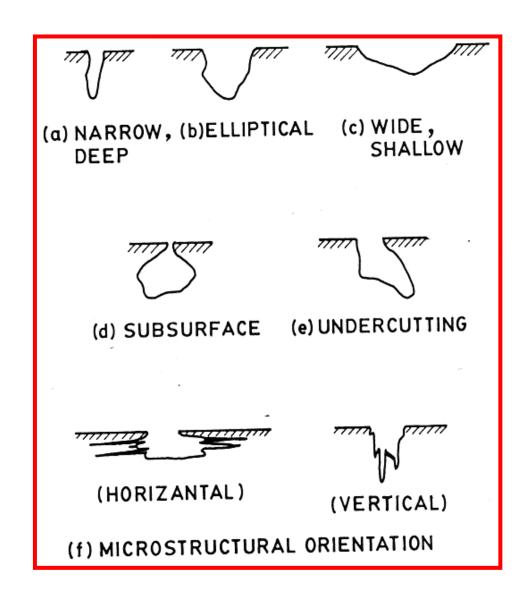
Due to crack on the surface of a metal,

- there is a formation of a local galvanic cell.
- The crack portion acts as anode and the rest of the metal surface acts as cathode.
- ❖ It is the anodic area which is corroded and the **formation of a pit** is observed.

Pitting corrosion







Pitting Corrosion – prevention/control

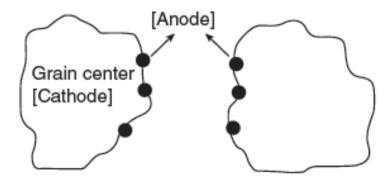
- ✓ Proper selection of materials with known resistance to the service environment
- ✓ Control pH, chloride concentration and temperature
- ✓ Cathodic protection and/or Anodic Protection
- ✓ Selection of alloy with higher alloy content (e.g. in stainless alloys-higher Cr, Mo and N) for increased resistance to pitting corrosion

4. Intergranular Corrosion:

- ➤ Generally observed in alloys, this corrosion involves an attack on the grain boundaries of a metal of alloys, where the formation of corrosion products takes place (like carbides in steel).
- Externally not visible and there is a sudden failure of material due to this corrosion

Example

- During the welding of stainless steel (an alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries which causes depletion of chromium composition in the adjacent regions.
- This become anode with respect to the region within the grains richer in chromium.



Cathode: Chromium –rich grain centers

Anode: Grain Boundary – Chromium depleted regions

Intra granular Corrosion – prevention/control

Rapid quenching after heat treatment of a metal is the remedy of inter-granular corrosion

Consider organic coating

✓ Paint, ceramic, chrome, etc. (Danger if it gets scratched)

Consider cathodic protection

- ✓ Such as zinc (or galvanized) plating on steel
- ✓ Mg sacrificial anode on steel boat exterior

5. Soil corrosion:

Underground pipes, cables, tank bottoms, etc., get corroded due to

- > moisture
- > pH of soil
- > ionic species like chlorides
- micro-organisms like bacteria

It is further enhanced by differential aeration of various parts of the soil



Soil Corrosion – prevention/control

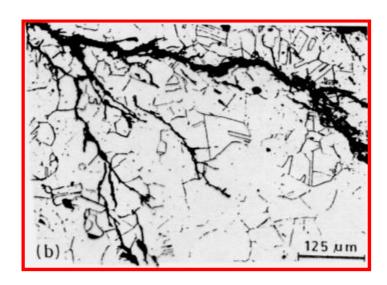
- ✓ Using organic and inorganic coatings
- ✓ Applying metallic coatings
- ✓ Alteration of soil
- ✓ Cathodic protection

6. Stress corrosion cracking:

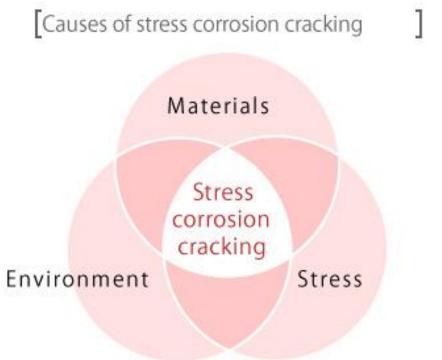
- In a metallic structure, if there is a portion under stress, it acts as anode and rest part of the structure acts as cathode
- This small anodic region undergoes corrosion

Example

 Caustic embrittlement is a type of stress corrosion occurring in boiler at high temperature and in alkaline medium



Stress Corrosion Cracking



Stress Corrosion Cracking – prevention/control

- ✓ Choosing a material that is not susceptible to

 Stress Corrosion Cracking in the service

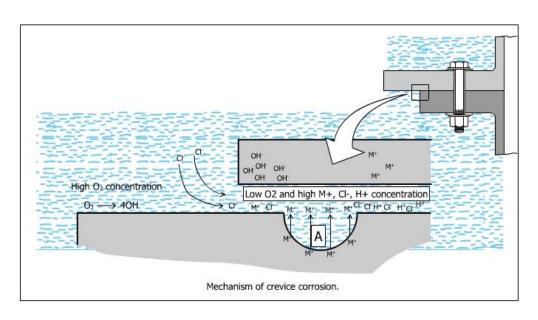
 environment
- ✓ Residual stresses can be relieved by annealing
- ✓ Neutralizing the environment whenever possible. For e.g. reducing chloride ion concentration

7. Crevice corrosion:

- Crevice corrosion occurs when two components are joined close together to form a crevice
- Corrosion occurs as the crevice accumulates water.

Gap → wide enough to liquid to enter, narrow enough to make it stagnant

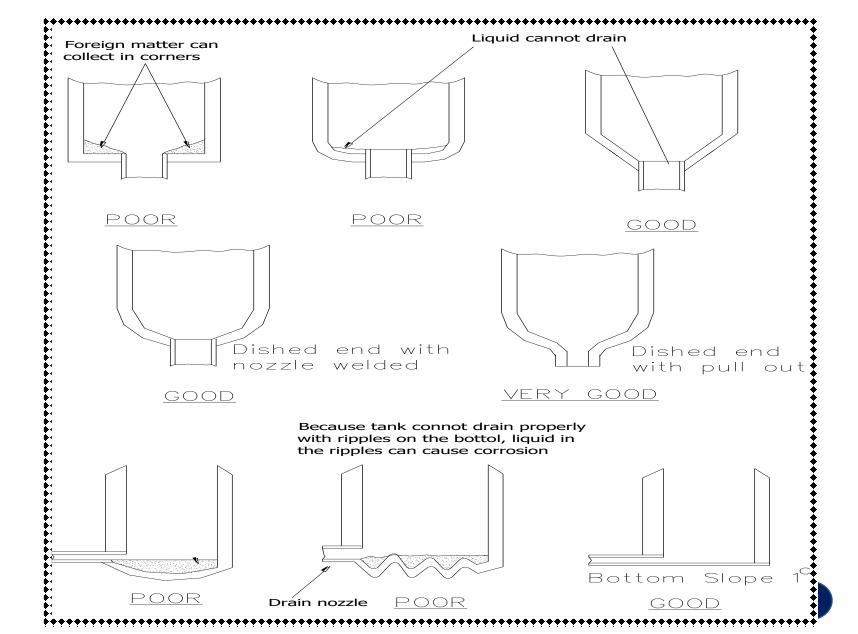
When this happens the base of the crevice becomes anodic to the upper region.





Crevice corrosion often occurs under bolts, rivet heads, etc.

Design against Corrosion



Crevice Corrosion -prevention/control

- Design vessels for complete drainage; avoid sharp comers and stagnant areas. Complete draining facilitates washing and cleaning and tends to prevent solids from settling on the bottom of the vessel.
- Inspect equipment and remove deposits frequently
- Use "solid," non-absorbent gaskets, such as Teflon, wherever possible.