Chapter 4

Forms of corrosion
Uniform corrosion

- In such type of corrosion there is a uniform decrease in the volume of the metal due to direct contact with the surrounding environment.

**Examples**
- Dissolution of Zn, Al metal in acids and Pb metal in base.
Atmospheric corrosion take place due to direct contact between metal and atmosphere

- Types of atmosphere:
  - Gas type: contain mainly oxygen gas (23% W / W) and water vapor.
  - Liquid type: contain mainly water and dissolved oxygen.
Atmospheric Corrosion of Copper
Iron rust

- Atmospheric corrosion involve formation of metal oxide layer when metal in direct contact with its surrounding environment.

- Example:

- Formation of iron rust due to contact with air

\[
\text{Fe} + \text{air, } \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 \rightarrow \text{Fe}_2\text{O}_3
\]

\[
\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \text{ is Iron rust (reddish brown ppt.)}
\]
# Oxide layers

<table>
<thead>
<tr>
<th>Protective</th>
<th>Non Protective</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non active</td>
<td>active</td>
</tr>
<tr>
<td>Non porous</td>
<td>porous</td>
</tr>
<tr>
<td>Ex: Zn, Al, Ni</td>
<td>Ex: iron rust</td>
</tr>
</tbody>
</table>
Rate of atmospheric corrosion depends on

- Nature of metal or alloy.
- Nature of oxide layer.
Factors affecting atmospheric corrosion:

- Type of metal or alloy.
- Type of atmosphere (dust, humidity, pollutant. Water vapor, gases,…)
- Temperature (as $T$ increase as rate increase)
- Time: The extent of corrosion increases with increased time
Surface Condition:

- more roughness, more corrosion
- The presence of foreign matter influence the speed of corrosion
Galvanic corrosion

Take place due to the contact between bimetallic couple exposed to the same environment due to the potential difference.

**Mechanism of galvanic corrosion:**
- For two different metals $M_1$ and $M_2$ when exposed to the same corrosive environment, if $M_1$ is more active than $M_2$
- **Anodic reaction:**
  \[ M \rightarrow M^{n+} + n\text{e}^- \quad (n=1, 2, 3, \ldots) \]
  Anodic metal will be corroded.

- **Cathodic reaction:**
  For strong acidic medium (pH<4)
  \[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]
  For neutral or basic medium (pH= 4-10)
  \[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \]
Application on galvanic corrosion

- Metal plating

To protect steel tanks (or sheet) we can use Zn, Al, Cu or Pb where zinc and aluminum metal is more active than steel so, they will acts as anode and they will be corroded instead of steel, but copper and lead are less active than steel so, they acts as Cathodic metal and the corroded metal will be the steel tanks.
I.e. to protect metal using metallic coating we must use the more active metal.

<table>
<thead>
<tr>
<th>Zn plating (corroded)</th>
<th>Cu plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel tank</td>
<td>Steel tank (corroded)</td>
</tr>
</tbody>
</table>
Welding and rivet process

<table>
<thead>
<tr>
<th>More active metal</th>
<th>The same metal</th>
<th>Less active metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Zn, Mg, Al…)</td>
<td>(steel)</td>
<td>(Cu, Pb, Au…)</td>
</tr>
<tr>
<td>welding material</td>
<td></td>
<td>welded material</td>
</tr>
<tr>
<td>corroded</td>
<td></td>
<td>Corroded</td>
</tr>
</tbody>
</table>

During the steel welding we may use
If use more active metal the welding material will be corroded, but if we use the less active the welded material will be corroded, so the best solution is to use the same metal.
Steel Welding
Steel rivet
Factors affecting galvanic corrosion

Potential Difference (P.D.)

As the P.D increases the galvanic corrosion increase
The rate of corrosion of (Zn/Fe) galvanic cell is slower than corrosion of (Zn/Cu) galvanic cell.

Distance

As distance increase as corrosion rate decrease.
Area

As the Area (C/A)ratio increases the galvanic corrosion increase.

As the Area (C/A)ratio decreases the galvanic corrosion decrease.
Differential Aeration Cell

This type of corrosion takes place due to the differential in oxygen concentration on the same metal or alloy.
Porous barrier allow the transfer of ions only through it, so oxygen gas will not penetrate the porous membrane.

Metal (poor $O_2$) // electrolyte // Metal (rich $O_2$)

Anode (+)          Cathode (-)

Corroded Area
Corrosion of ship hull
Corrosion of water tanks

Rich oxygen

Corroded area

Poor oxygen
5. Pitting Corrosion

- In this type, corrosion is concentrated at some places and is less in others, thus pits are formed.
- It’s a form of localized corrosion attack in which small pits or holes form.
Overall and pitting corrosion

Homogenous Corrosion

Concentrated Corrosion

Overall Corrosion

Pitting Corrosion
Thickness is reduced locally, majority of surface remains unattacked.

Pitting Corrosion
Reasons of Pitting Corrosion

- The Non-homogeneity of metal surface
  Due to the presence of impurities at the metal surface.

Example: such as manganese oxide (MgO) or ferrous sulfide (FeS) on steel alloy.
Reasons of Pitting Corrosion

- The Non-homogeneity of external environment
  Due to the presence of different areas in concentration or presence of concentrated acids.
- Example: dew point on steel surface make two different areas in oxygen concentration, acidic rain on steel surface tends to pitting corrosion
Reasons of Pitting Corrosion

- Corrosion products may be insoluble due to formation of insoluble corrosion products like ferrous sulfide (FeS) which formed by combination between corrosion products (ferrous ion) and sulfide ion from air on steel surface tends pitting corrosion (petroleum production area).
Reasons of Pitting Corrosion

- Oxide Layer in not uniformly perfect
  Due to the oxide layer may be broken in a small area
- Example: Effect of chloride ions on stainless steel alloy exposed to salt water tends to pitting corrosion of chromium content reduced less than 12%.
  This appear with stainless steel pumps used with salt water, after shut down the pump for few days, pitting corrosion greatly developed.
Factors affecting pitting corrosion

- Velocity

  as velocity of fluid increase, electrolyte solution become homogeneous, and hence pitting corrosion decrease and over all corrosion rate increase.

  as velocity of fluid decrease, electrolyte solution become non homogeneous, and hence pitting corrosion increase.
Factors affecting pitting corrosion

- Acidity (PH-value)
  
  as PH decrease, medium become more acidic which help in removal of impurities, corrosion products, dew and oxide layer, Hence pitting corrosion decrease and overall corrosion rate increase.

  as PH increase, acidity decrease and pitting corrosion will increase.
6. Stress corrosion cracking (S.C.C)

- This type of corrosion takes place due to presence of stress on the metal surface and specific corrosive environment.

- Stress = force / cross sectional area

- Any metal undergo stress corrosion cracking it must be under stress and in specific corrosive environment.
Examples

- Stressed steel + nitrate or hydroxide ion tends to S.C.C
- Stressed copper and its alloy + ammonia tends to S.C.C
- Stressed stainless steel + chloride ion tends to S.C.C
The diagram illustrates the conditions for Stress Corrosion Cracking (SCC) to occur. SCC occurs when all three conditions are met: a susceptible material, a corrosive environment, and tensile stress equal to or exceeding the threshold. The intersection of these three conditions is highlighted in the center of the diagram.
Mechanism of stress corrosion cracking:

- S.C.C starts as pitting corrosion.
- **At the tip:**
  - Very concentrated stress.
  - Very concentrated corrosion.
Factors affecting S.C.C:

- Specific environment
- Stress magnitude and direction.
- Structure and metal composition.
7. Inter granular corrosion (I.G.C)

- This type of corrosion occurs due to inter crystalline penetration of corroding medium and tends to loss of coherence force between grains.
- I.G.C is localized corrosion and it's dependent upon the metallic structure.

Example:
- Metal under microscope.
Examples

- Stressed grain boundary/ electrolyte/stressed grain.
- **steel alloy.**
  Stressed Steel grain / electrolyte / stressed carbon.
- **weld decay of stainless steel**
  The percent of chromium in stainless steel must be equal or higher than 12%, if this percent decrease the weld decay of stainless steel will take place.
Explanation

After finishing the welding the temperature will start to go down which take very long time for cooling till temperature reach (550 – 600 °C), at this temperature carbon will immigrate to grain boundaries forming chromium carbide (Cr$_{20}$C$_{14}$).
Chromium depleted zone formed near to grain boundaries.
Prevention of weld decay in st.st:

- Quenching: by sudden cooling directly after weld to fix the carbon at grain.
  Disadvantages (used with small structure only)
- By using low carbon stainless steel
  Disadvantages (not perfect mechanical properties)
- Stainless steel stabilizer: by addition of metal like titanium (Ti) to form (TiC) with carbon and fix carbon in grain.
  Disadvantages (high cost, %Ti = 0.1% in st.st).
8. Erosion corrosion

- It is a combination between corrosion and mechanical wear on the metal surface.
- Erosion takes place due to mechanical wear on metal surface.
- Corrosion takes place due to chemical or electrochemical reactions.
Erosion corrosion depends on

- **Metal surface (hardness of surface)**

<table>
<thead>
<tr>
<th>Soft metal</th>
<th>Hard metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, Cu, Ag</td>
<td>Cr, high carbon steel</td>
</tr>
</tbody>
</table>

Soft metals are more sensitive to erosion corrosion.

- **Environmental condition.**
Factors affecting erosion corrosion

- **High degree of turbulent:**
  Turbulent is formed due to high velocity of velocity of fluid and sudden change in direction of the fluid.

  As turbulent increase as mechanical wear increase and hence the erosion will increase.

  In order to decrease the turbulence effect, the thickness of tube or pipe in the turbulence area must be increased.
Factors affecting erosion corrosion

- **Presence of solid or suspended materials:**
  As suspended or solid material increase as the mechanical wear increase and hence erosion increase