

CORROSION

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Protection Against Corrosion (Coatings & Paints)

1) Metallic Coating (Anodic & Cathodic) (Application Methods)

2) Chemical Conversion Coating.

3) Paints, Varnishes, Enamels.

Metals are extracted from (oxide, sulfide, etc) over by giving some energy. Thus, pure extracted metals have less excited state and tend to lose this energy. When taken in use they come in contact with environ. gases, moisture to lose energy and decay. This is corrosion. It may be directly chemical or electrochemical.

Losses due to Corrosion

I Economic Loss : (Around 50 million dollars per annum worldwide)

(i) Direct → Replacement of Components → labor & material cost

> Cost of protective (anti-corrosion) compounds

(ii) Indirect
→ Unplanned equipment failures → shutdowns

> Contamination

> Loss of product due to leakages

> Loss in efficiency

II Safety Failure: Hazard in boiler, chemical, nuclear industries increase

III Conservation loss: > Loss of raw metals

> Loss of energy

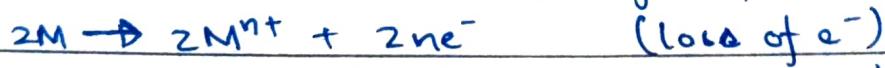
DRY / CHEMICAL CORROSION :

Through direct chemical attack of atm. gases

Oxidation Corrosion:

> Attacks alkali & alkaline earth metals at low temp.

> Attacks all metals (except Ag, Au, Pt) at high temp.



⇒ Mechanism:

> Oxidation firstly makes a metal oxide barrier at the surface to limit further oxidation

> Now for further oxidation either the metal diffuses outwards (towards surface) or oxygen diffuses inwards.

> The former process is rapid while the latter slower as metal ions are small and mobile.

* > Nature of surficial oxide plays imp. role.

(i) Stable layer

> Fine grained structured

> Adheres tightly to metal

> Impervious (restricts inward penetration of oxygen)

> e.g.: Al, Sn, Pb, Cu, etc.

(ii) Unstable layer:

> Oxide layer decomposes back to \rightarrow metal & oxygen

> Thus corrosion doesn't occur.

> e.g.: Ag, Au, Pt

(iii) Volatile layer:

> Oxide layer volatilizes and leaves metal surface

$\xrightarrow{\text{exposed}}$ for further corrosion

e.g.: Manganese oxide (MnO_3)

(iv) Porous layer:

> Contains cracks & pores

> Allows penetration thus complete corrosion occurs.

> e.g.: Alkali & Alkaline earth metals.

* Pilling - Bedworth Rule:

> An oxide is protective (Non porous) if

$$V_{\text{metal oxide}} \geq V_{\text{metal}} \quad (V = \text{volume})$$

e.g.: Al.

> An oxide is porous if

$$V_{\text{metal oxide}} < V_{\text{metal}} \quad (V = \text{volume})$$

e.g.: alkalis, alkaline earth metals.

Corrosion by Other gases (SO_2 , CO_2 , Cl_2 , H_2S , etc.)

- > Extent of corrosion depends on affinity b/w metal & gas.
- Whichever the degree of attack depends on surficial layers
- > $Cl_2 + Ag \rightarrow$ Protective film (decreasing corrosion)
- > $Cl_2 + Sn \rightarrow$ Volatile film

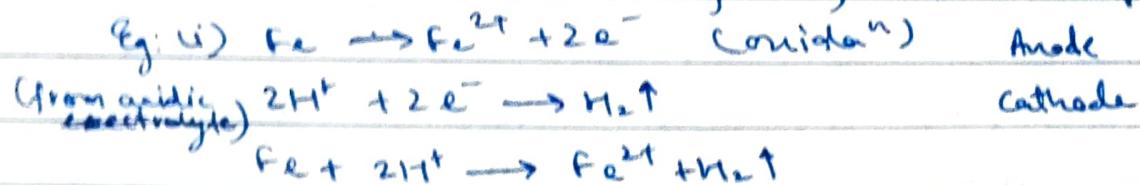
WET / ELECTROCHEMICAL CORROSION

- Occurs if (i) conducting liquid in contact with metal
- (ii) two dissimilar metals immersed/dipped in a soln.
- Separate oxidation & reduction.
 - Oxidation at anode (anodic metal destroyed)
 - Reduction at cathode (accepts OH^- , O_2^-)
- At anode metal ions react with cations to form corroded product

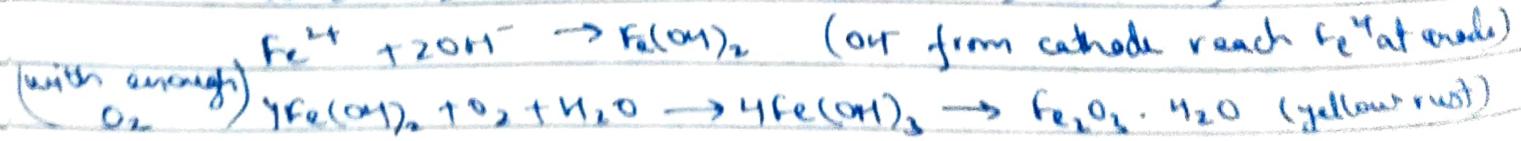
⇒ Mechanism:



Cathode: (i) evolution of H_2 , or (ii) absorption of O_2



eg(ii) In presence of O_2 iron makes an surfacial oxide film when cracks develop in this film, anodic surfaces are exposed while the well-metal is cathode.



#1 Galvanic Corrosion:

- Two electrically connected dissimilar metals in electrolyte
- This makes the less noble metal dissolve (higher in electrochemical series).
- More noble metal at cathode is protected

> e.g. In an Cu-Zn couple, Zn is higher in EC series (anode)



> e.g.: Steel pipe connected to Cu plumbing.

#2 Concentration Cell Corrosion:

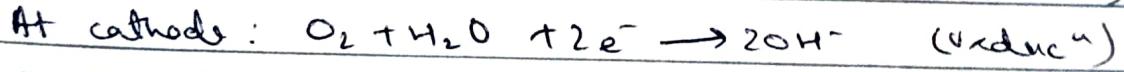
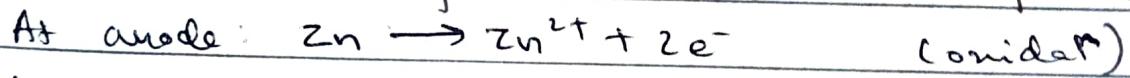
> One metal surface exposed to an electrolyte with varying concentration/aeration.

> Most common type: Differential aeration corrosion.

> Poor oxygenated parts \rightarrow anode

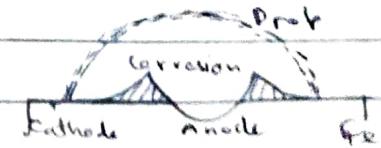
> This causes current flow called differential current.

> e.g. ①: Zn is partially immersed in NaCl solⁿ. The part above and close to waterline are aerated more to become cathodic. While parts deep in solⁿ with low O₂ access become anodic. The potential diff. causes current flow. Zn dissolves from anode



> e.g. ②: A drop of salt solⁿ of Fe surface parts under the drop have low O₂ access while those around the water line have high O₂ access.

* Corrosion can be accelerated in O₂ inaccessible places by the use of dirt, sand, wood etc. by blocking O₂.



Passivity

> When protective thin film makes the metal highly corrosion resistance unexpected from its EC series formation. (0.0004mm-thick layer)

- > This film is insoluble, non porous, self healing.
- > e.g.: Ti, Al, Cr, stainless steel alloys with Cr.
- * > In reducing environment however these films become active.
- > Passivity order: Ti > Al > Cr > Be > Mo > Mg > Fe > Zn > Pb > Cu

#3 Soil / Underground Corrosion:

- > Depends on soil's: acidity, degree of aeration, moisture/salt content, texture, microbes, conductivity.
- > Types:
 - (a) In Gravelly & Sandy Soils: (Porous & aerated)
 - Higher the moisture, greater the corrosion
 - (b) In Water-logged Soils: (Not aerated but high microbes)
 - Leads to micro-biological corrosion.
 - (c) In Acidic Soils: (Similar to hydrogen evolution wet corrosion)
 - Higher the presence of salt, and O₂, greater the corrosion.
 - (d) In Intermediate character soil: (localized corrosion)
 - Air pockets and differential aeration causes corrosion.

#4 Pitting Corrosion:

- > Usually after cracking of films anode is thoroughly attacked and the surroundings remain relatively un-attacked
- > Gives rise to small anodic pinholes and large remaining cathodic areas.
- > Presence of sand, dust, scale etc. also lead to pitting.
- > As the area underneath these impurities gets more inaccessible for O₂, rate of corrosion increases.

#5 Intergranular Corrosion:

- > Molten metal solidifies at randomly localized zone to form granular structures. Too
- > This corrosion occurs on these grain boundaries and not inside grains.
- > Common in alloys
- > e.g.: In stainless steel welding, chromium carbide is precipitated at grain boundaries. These boundaries have low Cr composition than interiors and behave anodic.

#6 Waterline Corrosion:

- > Due to differential aeration area just below the water meniscus gets corroded easily.
- > As surface above meniscus gets more or exposure it becomes cathodic and water being poor conductor allows ions from the area below meniscus (colder) move easily making it highly anodic & easily corrosive.
- > Water Acid-free water is resistant to this corrosion, but water with anionic impurities is highly prone.
- > Antifouling paints restrict this corrosion to some extent.

#7 Stress Corrosion / Cracking:

- > Combined effect of tensile stress & corrosion.
- > Usually seen in alloys that bear heavy working.
- > The strain results in localized zones with high potential.
- > This active zone is easily corroded by even mild conditions.

8 Microbiologically Influenced Corrosion (MIC):

- > Caused by microbes - mainly 12 different bacteria
- > These microbes develop O₂ rich or less O₂ ambiance depending on aerobic or anaerobic class.

> Some common types of such bacteria are :

(i) Sulphate Reducing Bacteria (SRB):

- Anaerobic corrosion of iron & steel
- Grow @ 25-30°C & 5-9 pH.
- Produce black iron sulphide & ferrous hydroxide.

(ii) Sulphur Bacteria :

- Aerobic corrosion of iron
- Oxidize sulphur (from their cells) to H₂SO₄
- Grow @ 0-1 pH.

(iii) Iron and Manganese microbes :

- Aerobic corrosion of Fe & Mn
- Digest Fe & Mn in presence of O₂ to make insoluble Fe & Mn hydrates as corrosion products
- Grow @ 5-40°C & 4-10 pH with small DO in water
- (iv) Film-forming microbes (bacteria, fungi, algae, diatoms)
- form film on Fe surface.
- Lead to local "biological concentration" cells leading to corrosion.

FACTORS AFFECTING CORROSION :

I# Nature of Metal:

(1) Position in Galvanic Series:

- The higher the anode (w.r.t cathode), greater the corrosion

(ii) Area of Anodic & Cathodic Parts:

→ Smaller the anodic area (w.r.t cathode), faster and greater is the corrosion due to high current density.

(iii) Purity of Metal:

→ Impurity of other metals \Rightarrow heterogeneity \Rightarrow small electrochemical cells \Rightarrow increased corrosion.

(iv) Physical State of Metal: (grain size, stress, crystal orientation)

→ Smaller the grain size, greater the solubility, greater corrosion.

→ Greater the area under stress, greater the corrosion.

(v) Nature of surface film:

* Ratio of volume of protective metal oxide film to the volume of metal is known as Specific Volume Ratio.

→ Greater the SVR, lesser the corrosion.

$$(\text{SVR: Ni}(1.6) < \text{Cr}(2.0) < \text{W}(3.6))$$

(vi) Solubility of Corrosion Products:

→ Greater the solubility, faster the corrosion

* Pb forms PbSO_4 which is in turn insoluble (corrosion product)

(vii) Volatility of Corrosion Products:

→ Greater the volatility, greater the corrosion (e.g. MnO_2)

(viii) Passive Character of Metal: (self-healing protective film)

→ Greater the passivity, lesser the corrosion

$$(\text{e.g.: Ti, Al, Cr, Mg, Ni, Co})$$

II# Nature of Corroding Environment:

(i) Temperature:

→ Greater the temp. faster the diffusion, faster the corrosion.

(ii) Humidity of air:

* Critical humidity: relative humidity above which rate of corrosion sharply increases.

→ Greater the humidity, faster the corrosion.

→ Oxide films can absorb water for wet corrosion.

→ Nature of source of moisture: rainwater due to its mechanical properties may wash away oxide films.

(iii) Presence of Impurities:

→ Greater the amount of corrosive gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 etc that increase acidity (in turn conductivity), faster the corrosion.

→ In marine atmosphere, chlorides lead to increased conductivity and faster corrosion.

(iv) Presence of suspended particles:

→ Chemically active suspended particles absorb moisture to increase corrosion. While,

→ chemically inactive suspended particles absorb sulphur gases to slowly increase corrosion.

(v) Conductance of medium (underground / submerged)

→ Clayey mineralized soil has conductance more than dry sandy soil. Thus, supports corrosion.

(vi) Formation of oxygen concentration cell:

→ Greater the supply of O_2 , greater is the cathodic tendency, greater the potential difference, greater corrosion.

CORROSION CONTROL:

1# Design And Material Selection:

- > If material can't be corrosion-proof, it should go through uniform (non-localized) corrosion.
- > Design should be such that contact of dissimilar metals should be avoided.
- > If contact is unavoidable, anodic part must be large as against cathodic part.
- > If contact is unavoidable, they should be as close in EC series as possible.
- > If contact is unavoidable, an insulated fitting may be used.
- > Anodic part must not be coated (break in coating leads to intense corrosion)
- > Prevent heterogeneities
- > Prevent services
- > Allow critical part cleaning. Avoid sharp corners
- > Should be supported on legs to allow air circulation
- > Uniform flow of corrosion liquid must be allowed.
- > Prevent localized stress.

2# Using Pure Metal:

- > Purification of Al, Mg etc. enhances oxide film formation.
- > However pure metal might increase cost & hinder mechanical properties like strength.

3# Using Alloys:

- > Alloying metals with noble metals like Pt & Au brings corrosion resistance

> Cr is alloyed with Fe in steel to get self healing film. (13%)

4# Cathodic Protection:

> If nature of medium, metal can't be changed, cathode can be protected by:

* (i) Sacrificial Anodic Protection:

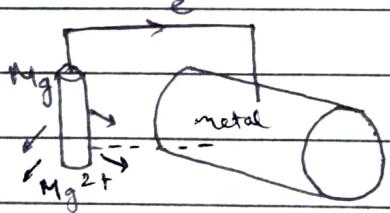
→ Metal is connected by wire to more anodic metal to divert concentration of corrosion. (sacrificial anode)

→ Mg, Zn, Al and their alloys are sacrificial anodes.

→ Mg has -ve potential and high current output.
Thus good for electrolytes like soils.

→ Zn is used in electrolytes like seawater

* Applications:

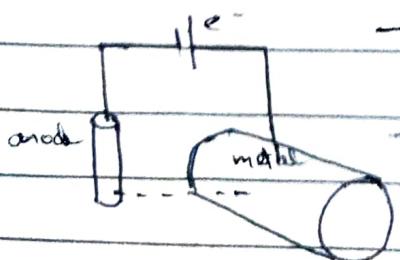


- (i) Protect buried pipelines from soil corrosion
- (ii) Protect cables & ship hulls from marine corrosion.
→ Cheap → Short-term

* (ii) Impressed Current Cathodic Protection:

→ Greater the current flow between cathode & anode faster the corrosion. Thus, external current in opposite direction nullifies this current to resist corrosion.

→ A dc current is applied to an insoluble anode (graphite, silica etc.) and connected to protectable metal.



→ Anode comprises coke breeze/gypsum for more coil contact.

→ Used in water-tube boilers, tanks, buried pipes, marine piers, laid-up ships, condensers etc.

→ Long-term.

PROTECTIVE COATINGS:

- Physical barrier b/w surface & environment
- Chemically inert under specific temp. & press.
- May also impart water-resistance, hardness, conductivity, aesthetics, oxidation-resistance, thermal insulation.
- Can be metallic (inorganic) or non-metallic (organic).

#1 Metallic Coatings:

- Zn, Sn, Ni, Cr, Al, Cu, etc coatings on iron and steel.
- Two Types:

(i) Anodic Coatings: Coatings which are anodic to the metal to be protected. Eg. Zn, Al, Cr on steel/Fe.

> Even in case of pores/ cracks, galvanic cell forms with coating metal as anode and metal as cathode. Thus, metal stays protected.

(ii) Cathodic Coatings: Coatings with noble metals than parent

- > They protect due to high individual corrosion resistance
- > Can't survive pores, cracks, punctures
- > Pores can lead to very intense corrosion.

#2 Organic Coatings:

These include Paints, Varnishes, Lacquers, enamels.

* Factors affecting protection values:

- > Chemical Inertness
- > Surface Adhesion
- > Water / Gas Impermeability
- > Application Method.

(i) Paints: → Binders + Solvent + Pigment + Additives.

→ Binders: Polymers (resins) which form consistent film

> It holds pigment particles together and is carried by the solvent in molecular or colloidal form (emulsions)

* Requisites of Good Paint

- Fluidity (enough to spread easily)
- Covering Power
- Adherent & Uniform film formation
- Should not crack on drying
- Corrosion resistant
- Stable & Decent color
- Glossy film.

→ Pigments: Solid constituent in paint

> Provides color / opacity and strength

> Reflects harmful UV light

> Resists wear & abrasion

> Improves moisture impermeability

> Increases weather resistance.

* Types of Pigment :

- Natural : Talc, clay, iron oxides
- Synthetic : TiO_2 , $BaSO_4$
- Reactive : Red Pb, ZnO (react with oils to form soaps)

* Commonly Used pigments: Yellow (chrome & zinc), Brown (iron clays), Green (Cr oxide), Red (red Pb), Black (graphite), Blue (ultramarine), White (ZnO, White Pb).

* Pigment Volume Concentration (P.V.C.) =

Volume of pigment in paint

Total volume of non-volatile constituents in paint