

CORROSION AND ITS CONTROL

Introduction and Mechanism of Chemical and Electrochemical Corrosion, Galvanic Corrosion, Concentration Cell Corrosion, Galvanic Series, Passivity

Soil Corrosion, Pitting Corrosion, Intergranular Corrosion, Waterline Corrosion, Stress Corrosion,

Factors influencing Corrosion,

Ways to protect against Corrosion.

Introduction of Protective Coatings,

Metallic Coatings (Introduction of Anodic and Cathodic Coatings, Methods of application of Metal Coatings, Objectives and theory of Electroplating), Chemical Conversion Coatings,

Paints, Varnishes and Enamels

CONCEPT

- Most metals (except noble metals) exist in nature in combined forms (oxides, sulphides, chlorides, carbonates, etc.).
- During their extraction processes, these are reduced to their metallic states from their ores by applying some amount of energy.
- Thus, pure metals can be regarded in excited state (a higher energy state) than their corresponding ores, and they have a natural tendency to revert back to combined state (or lower energy state).

- Hence, when metals are put into use, they are exposed to environment (such as dry gases, moisture, liquids, etc.), the exposed metal surfaces begin to decay (i.e. conversion into more stable metal compounds) more or less rapidly, when they come in contact with gaseous and/or liquid environment (or surroundings).
- In other words, destruction or deterioration of the metal starts at the surface.
- This type of metallic destruction may be due to direct chemical attack (by the environment) or electrochemical attack.

CORROSION

- The process of destruction or deterioration and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface.
- The most familiar example of corrosion is rusting of iron, when exposed to the atmospheric conditions. During this, a layer of reddish scale and powder of oxide (Fe_3O_4) is formed, and iron becomes weak.
- Another common example is formation of green film of basic carbonate on the surface of copper, when exposed to moist air containing carbon dioxide.

- The process of corrosion is slow and occurs only at surface of metal but the losses incurred, due to corrosion, are enormous.
- 50 billion US dollars per annum worldwide.

Economic Losses

a. Direct Losses – Replacement of corroded structures, equipment, components (both labour and materials cost);

- Application of protective coatings and paints;
- Using costly corrosion-resistant materials

b. Indirect losses – Unplanned shutdowns due to equipment failure leading to loss of production,

- Contamination of stored products,
- Loss of products due to leakage in pipelines and tanks,
- Loss in efficiency,
- Environmental damage
- **Safety** failures of pressure vessels, boilers, metallic containers for toxic chemicals, turbine blades, rotors, airplane components, automotive steering mechanisms, equipment of nuclear plants.
- **Conservation Losses**, Loss of raw material (metals), Loss of energy and water during processing of metals, Human energy

Dry or Chemical Corrosion

- It occurs through the direct chemical action of environment / atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surfaces in immediate proximity.

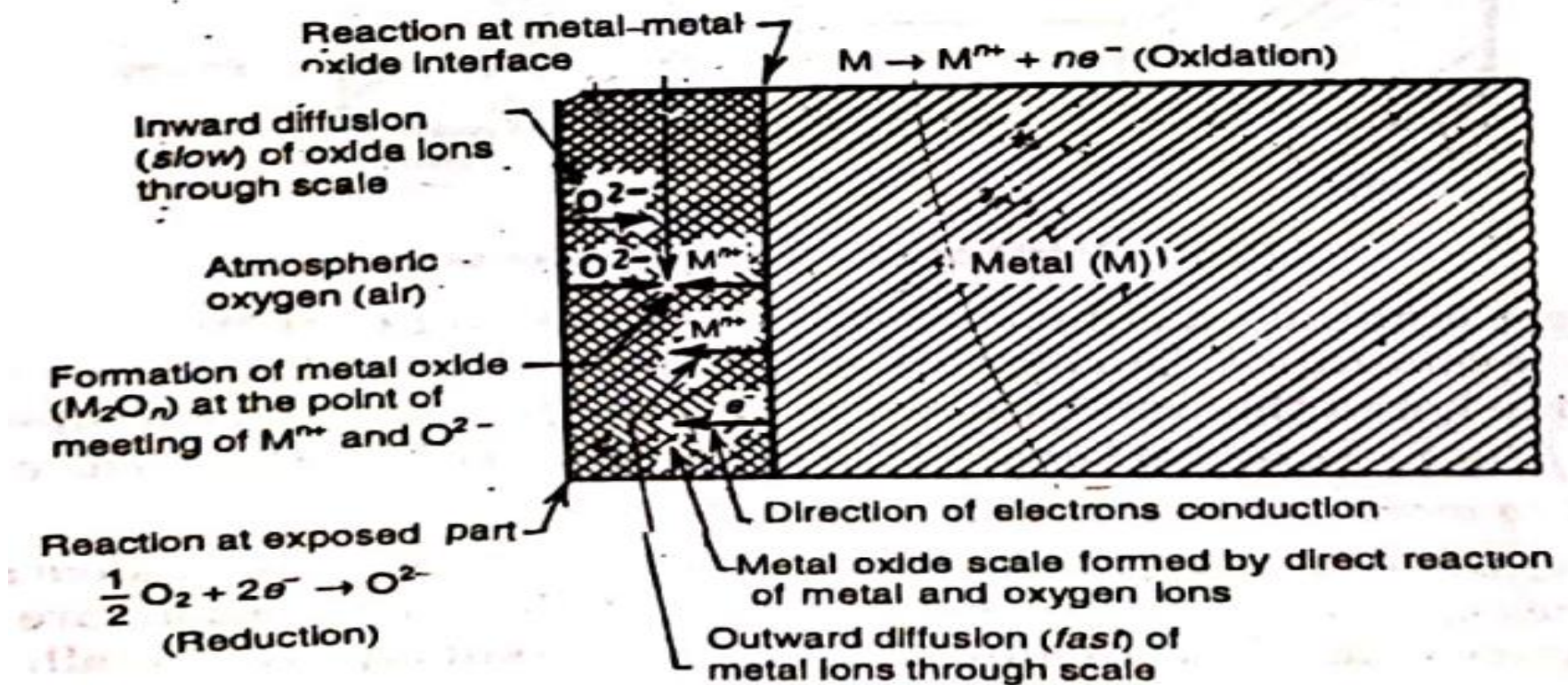
1. Oxidation Corrosion:

- It occurs due to direct action of oxygen at low or high temperatures on metals, usually, in the absence of moisture.
- At ordinary temperatures, metals, in general, are very slightly attacked. However, alkali metals (Li, Na, K, Rb, etc.) and alkaline-earth metals (Be, Ca, Sr, etc.) are even rapidly oxidized at low temperatures.
- At high temperatures, almost all metals (except Ag, Au and Pt) are oxidized.

The reactions in the oxidation corrosion are:



Mechanism



- Oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier that tends to restrict further oxidation.
- For oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal.
- Both transfers occur, but the outward diffusion of metal is, generally, much more rapid than the inward diffusion of oxygen, since the metal ion is appreciably smaller than the oxygen ion and thus more mobile.
- Nature of the oxide formed plays an important part in oxidation corrosion process.

Nature of the Oxide Formed

1. Stable layer

- Fine-grained in structure and can get adhered tightly to the parent metal surface.
- Hence, such a layer can be of impervious nature (i.e., which cuts-off penetration of attacking oxygen to the underlying metal).
- Such a film behaves as protective coating, thereby further oxidation corrosion is prevented.
- **Thus it is a smooth and compact structured layer, sticking firmly to metal, no further attack of oxygen, act as protective coating. e.g. Oxide films on Al, Sn, Pb, Cu, etc.**

- **Unstable Layer**
- The oxide layer formed decomposes back into metal and oxygen.
- Consequently, oxidation corrosion is not possible in such a case.
- Because of this Ag, Au, and Pt do not undergo oxidation corrosion.

Volatile Layer

- The oxide layer volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack.
- Thus rapid and continuous corrosion takes place, leading to excessive corrosion, e.g., molybdenum oxide (MoO_3)

Porous Layer: The oxide layer having pores or cracks.

- The atmospheric oxygen have access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.
- Examples are alkali and alkaline earth metals.

Pilling – Bedworth Rule

- An oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal from which it is formed.

$$V_{\text{Metal Oxide}} \geq V_{\text{Metal}}$$

- E.g. Aluminium, tightly-adhering non-porous layer formation
- If the volume of the oxide is less than the volume of the metal from which it is formed, the oxide layer is porous or cracked.

$$V_{\text{Metal Oxide}} < V_{\text{Metal}}$$

- E.g. alkali and alkaline earth metals, stressed and porous layer formation.

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

- The extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.
- The degree of attack depends on the formation of protective or non-protective films on the metal surface.
- (a) If the film formed is protective or non-porous (e.g. AgCl film, resulting from the attack of Cl_2 on silver), the intensity or extent of attack decreases, because the film formed protects the metal from further attack.
- (b) If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed.
- For example, dry Cl_2 gas attacks on tin (Sn) forming volatile SnCl_4 , which volatilizes immediately, thereby leaving fresh metal surface for further attack.

Wet or Electrochemical Corrosion

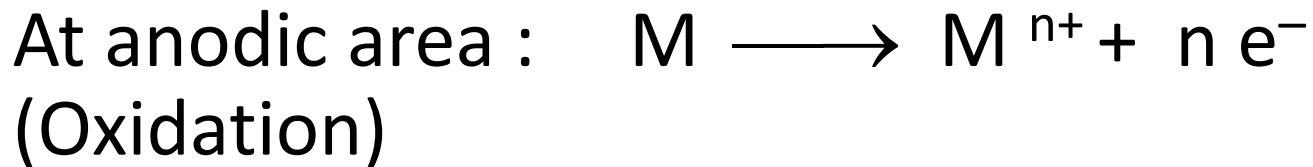
- This type of corrosion occurs when
 - (i) a conducting liquid is in contact with metal, or
 - (ii) two dissimilar metal or alloys are either immersed or dipped partially in a solution.
- Oxidation and reduction takes place at separate locations.
- This corrosion occurs, due to the existence of separate 'anodic' and 'cathodic' areas, between which current flows through conducting solution.

- At anodic area, oxidation reaction (i.e., liberation of free electrons) takes place, so anodic metal is destroyed by either dissolving or assuming combined state (such as oxide).
- At cathodic areas, reduction reaction (i.e., gain of electrons) takes place.
- Usually, cathode reactions do not affect the cathode, since most metals cannot be further reduced.

- So at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form ions like OH^- , O^{2-} .
- The metallic ions (at anodic part) and non-metallic ions (formed at cathodic part) diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.
- The electrons set free at the anode flow through the metal and are finally consumed in the cathodic reaction.

Mechanism

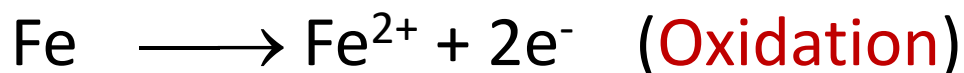
- It involves flow of electron-current between the anodic and cathodic areas.
- The anodic reaction involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons.



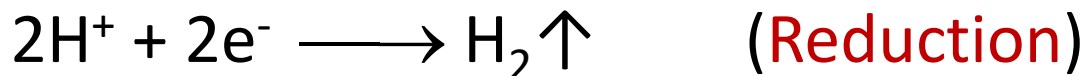
- The cathodic reaction consumes electrons either by evolution of hydrogen or absorption of oxygen, depending on the nature of the corrosive environment.

Evolution of Hydrogen

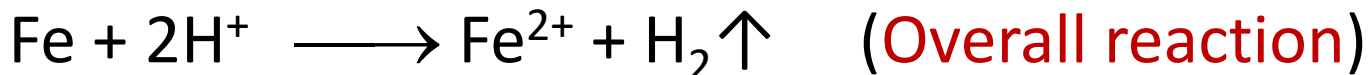
- Occurs mostly in acidic environment
- Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.



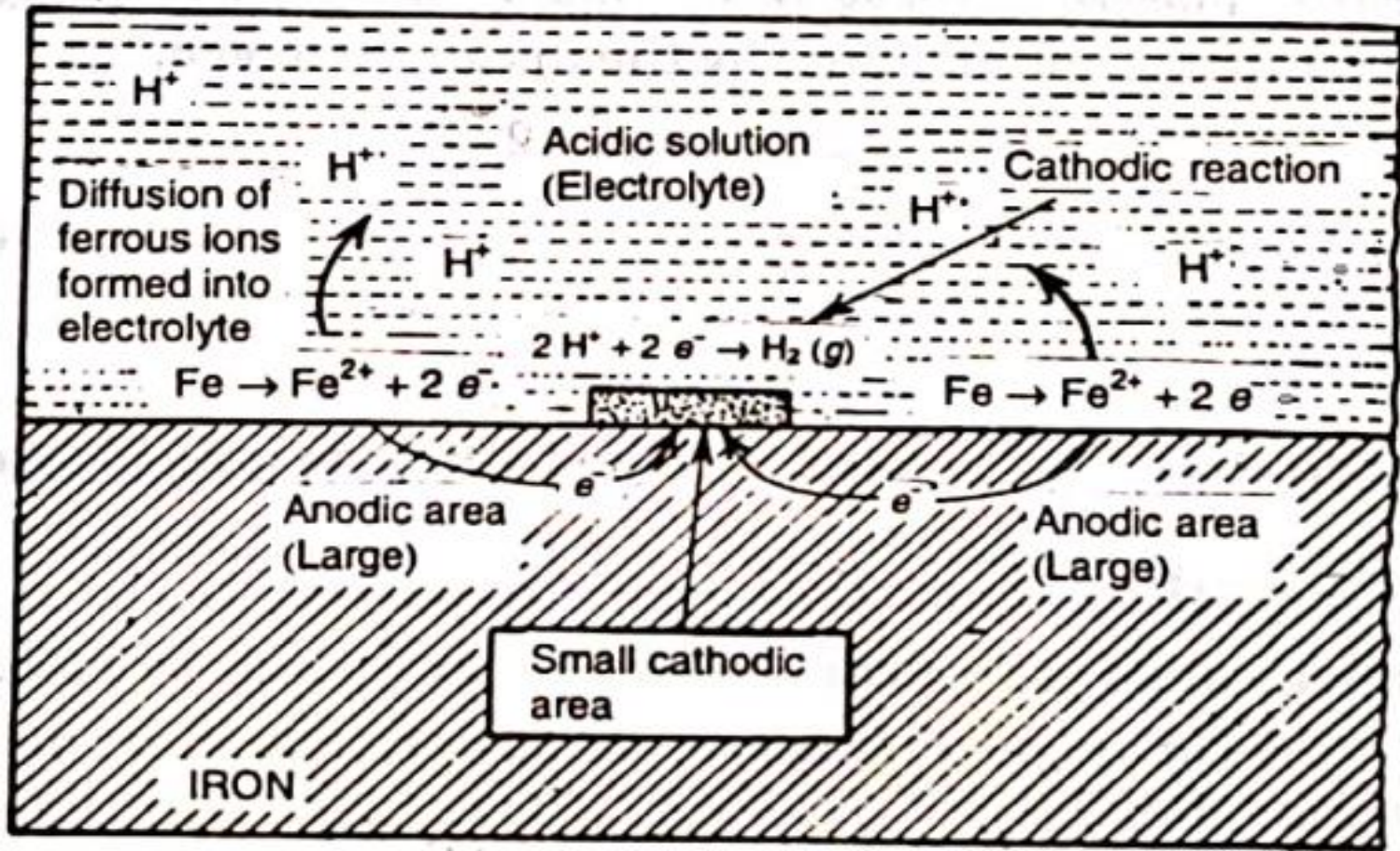
- These electrons flow through the metal, from anode to cathode, where H^+ ions are eliminated as hydrogen gas.



- Thus, this type of corrosion causes displacement of hydrogen ions from the acidic solution by metal ions.



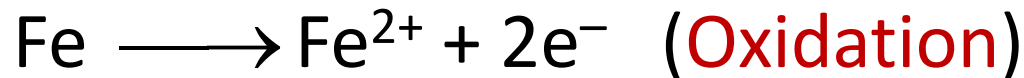
Mechanism of wet corrosion by hydrogen evolution



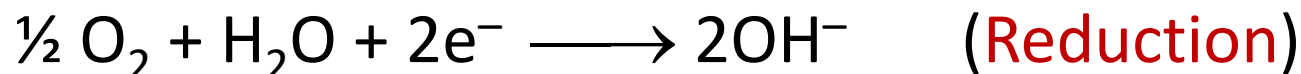
All metals above hydrogen in the electrochemical series have a tendency to dissolve in acidic solution with evolution of hydrogen.

Absorption of Oxygen

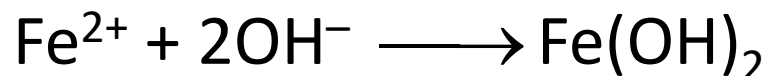
- Rusting of iron in neutral aqueous solution of electrolytes in the presence of oxygen is a common example of this type of corrosion.
- The surface of iron is, usually, coated with a thin film of iron oxide.
- However, if this iron oxide film develops some cracks, anodic areas (small) are created on the surface; while the well-metal parts act as cathodes (large).
- At anodic areas, iron dissolves as ferrous ions with liberation of electrons.



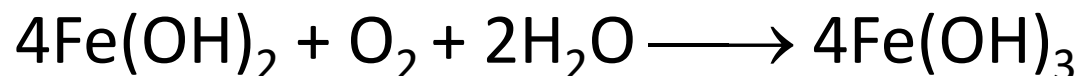
- The liberated electrons flows from anodic to cathodic areas, through iron metal, where electrons are intercepted by the dissolved oxygen as:



- The Fe^{2+} ions (at anode) and OH^- ions (at cathode) diffuse and when they meet, **ferrous hydroxide** is precipitated.

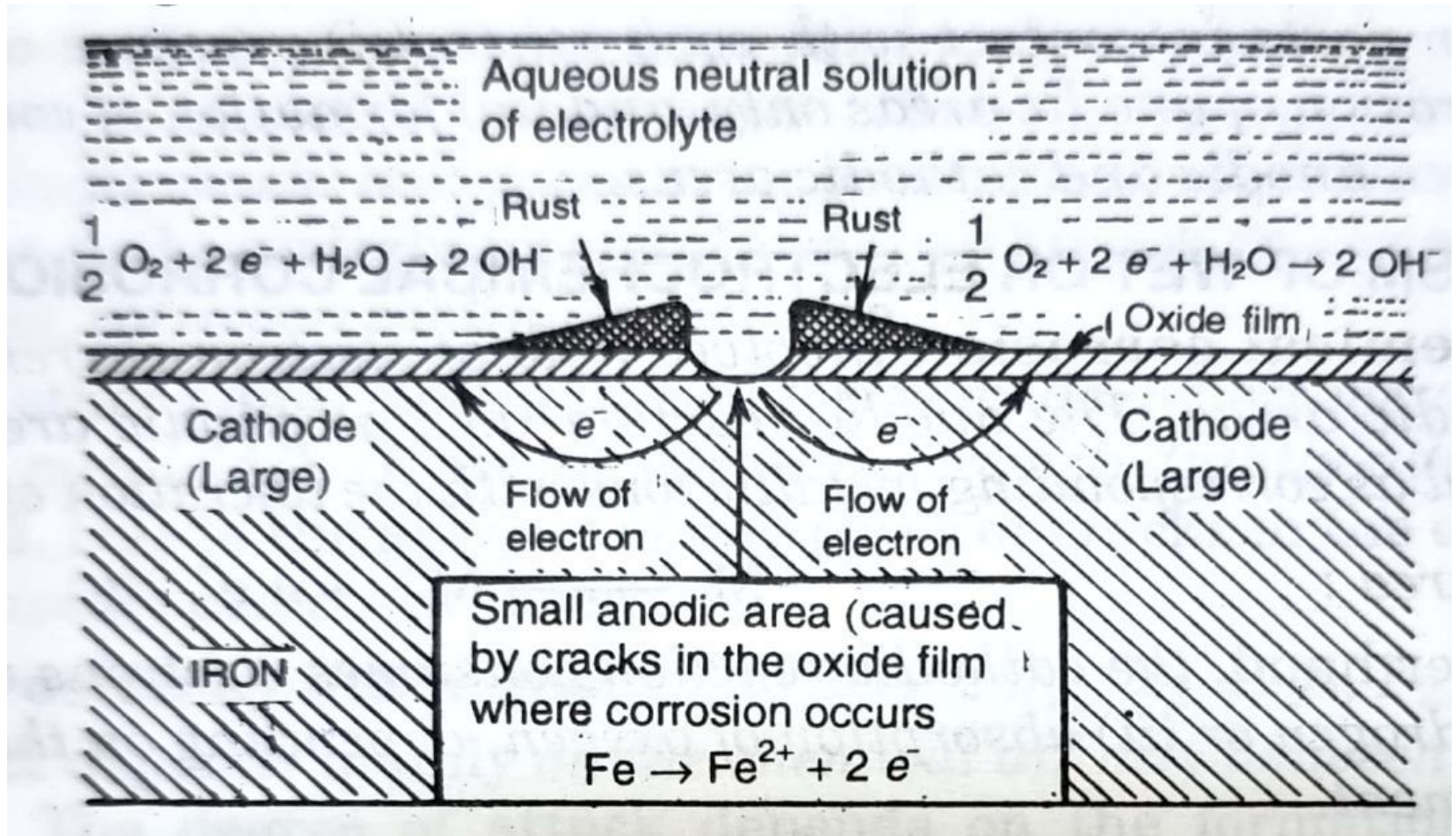


- If enough oxygen is present, ferrous hydroxide is easily oxidized to **ferric hydroxide**.



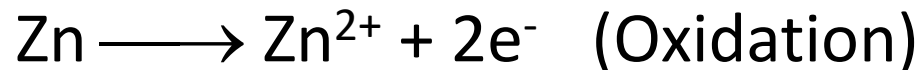
- This product, called yellow rust, actually corresponds to $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Mechanism of wet corrosion by oxygen absorption



Galvanic Corrosion

- When two dissimilar metals are electrically connected and exposed to an electrolyte, an electric potential exists.
- This potential difference will provide a stronger driving force for the dissolution of the less noble material.
- **The metal higher in electrochemical series undergoes corrosion.** This type of corrosion is called "**galvanic corrosion**".
- Higher potential/more noble/cathodic/protected end
- E.g. Zinc and copper, zinc higher in electrochemical series forms anode and corrodes.



- Examples: Steel pipe connected to copper plumbing, Steel screws in a brass marine hardware

- Electrochemical series of elements is the arrangement of elements according to increasing or decreasing electrode potentials.
- Lithium (Li) has got the highest electrode potential while the fluorine has got the lowest potential.
- Elements that have a greater tendency than hydrogen to lose electrons to their solution are taken as **electropositive** (placed above); those that gain electrons from their solution are below hydrogen in the series and are called **electronegative**.

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E° , volt
Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.05
K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2\text{e}^- \rightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.7628
Cr	$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2\text{e}^- \rightarrow \text{Sn}$	-0.14
H_2	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	+0.337
I_2	$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	+0.535
Ag	$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	+0.799
Hg	$\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg}$	+0.885
Br_2	$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	+1.08
Cl_2	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	+1.36
Au	$\text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}$	+1.50
F_2	$\text{F}_2 + 2\text{e}^- \rightarrow 2\text{F}^-$	+2.87

Concentration Cell Corrosion

- This type of corrosion is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentration or of varying aeration.
- The most common type of concentration cell corrosion is

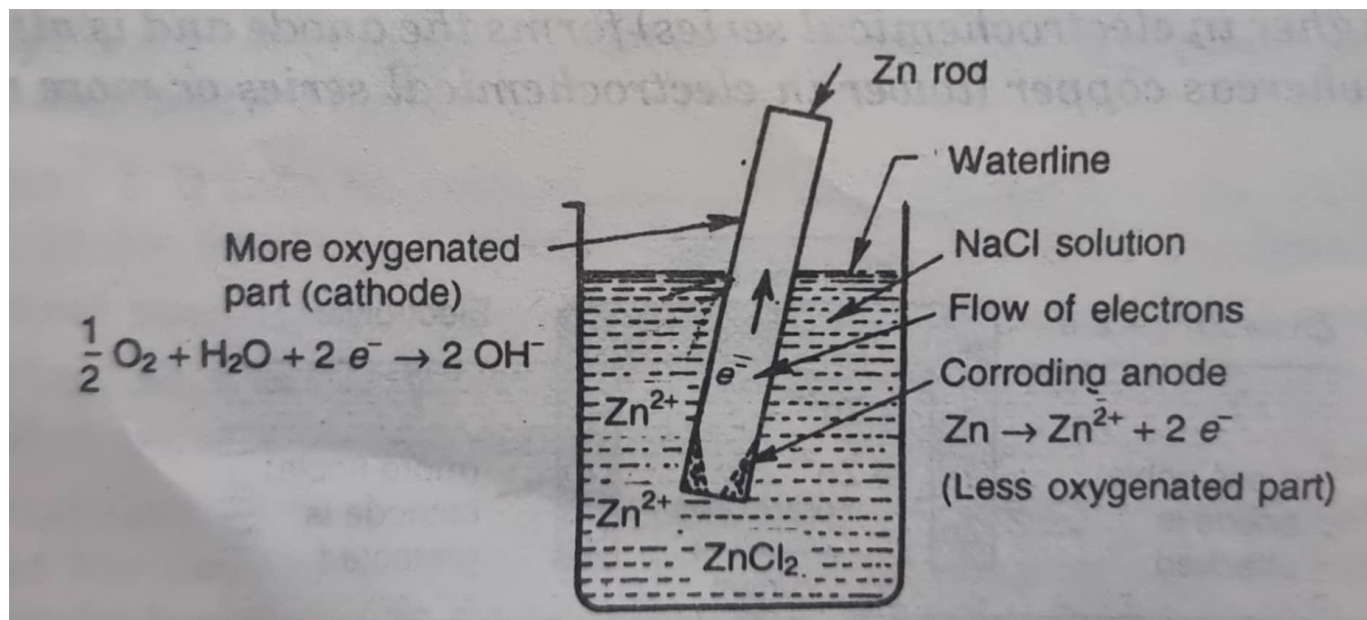
Differential aeration corrosion

- It occurs when one part of metal is exposed to a different air concentration from the other part.
- **Poor-oxygenated parts acts like anode** and causes a flow of current, called the differential current.

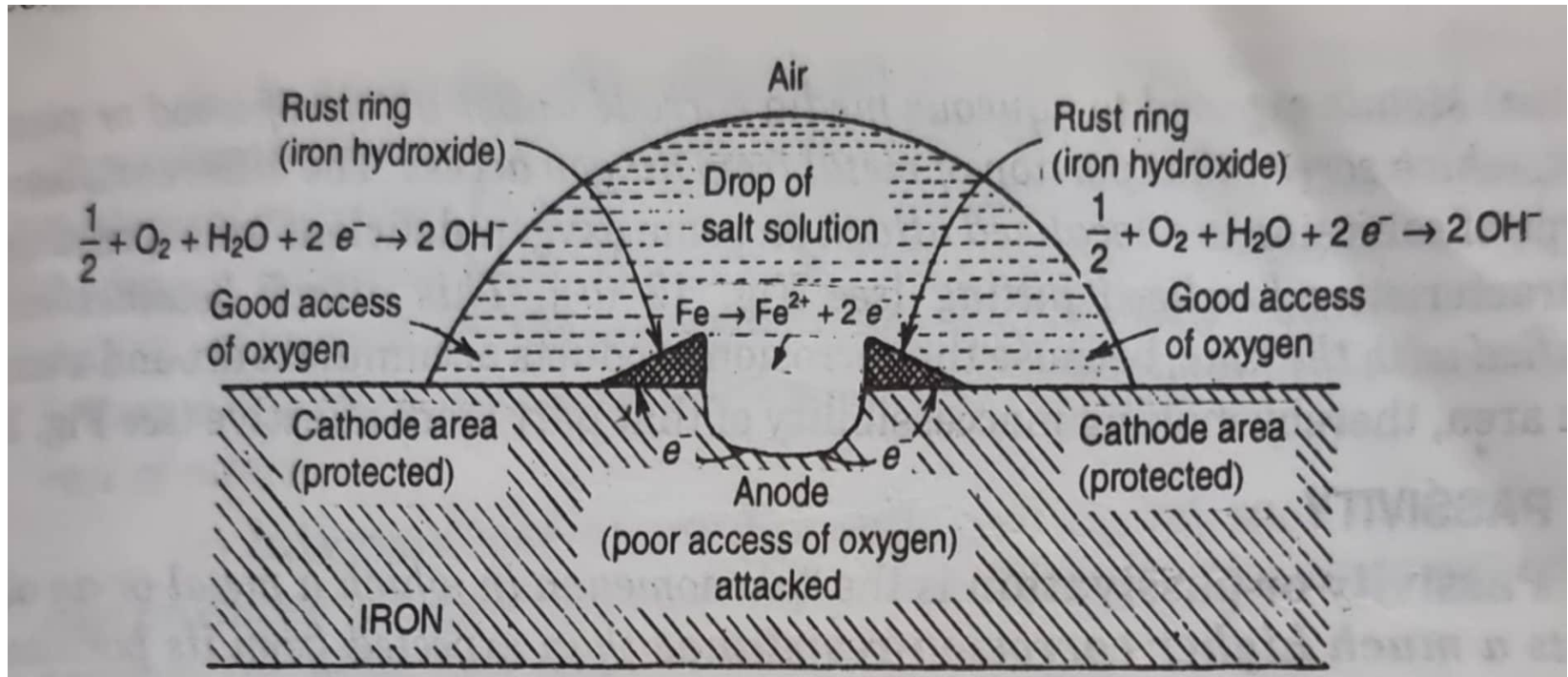
- Differential aeration accounts for the corrosion of metals, partially immersed in a solution, just below the waterline.
- For example, if a metal (say Zn) is partially immersed in a dilute solution of a neutral salt (say NaCl). The solution is not agitated properly.
- Then, the parts above and closely adjacent to the waterline are more strongly aerated (because of the easy access of oxygen) and hence, become cathodic.

- On the other hand, parts immersed to greater depth (which have less access of oxygen) show a smaller oxygen concentration and thus, become anodic.
- So, a difference of potential is created, which causes a flow of current between the two differentially aerated areas of the same metal.
- Zinc will dissolve at the anodic areas, and oxygen will take up electrons at the cathodic areas to form hydroxyl ions.

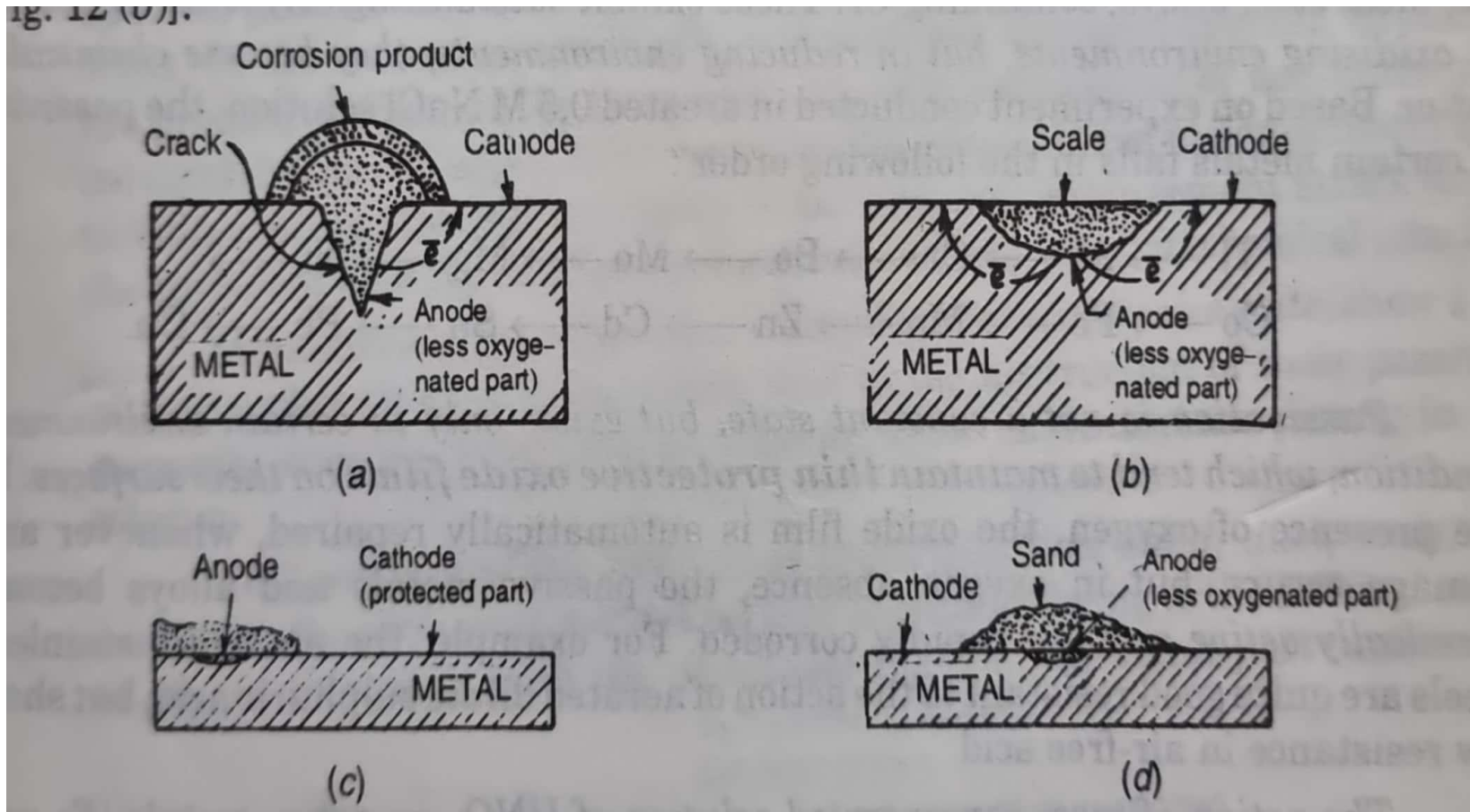
- At Anode $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ (Oxidation)
- At Cathode $\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$ (Reduction)
- The circuit is completed by migration of ions, through the electrolyte, and flow of electrons, through the metal, from anode to cathode.



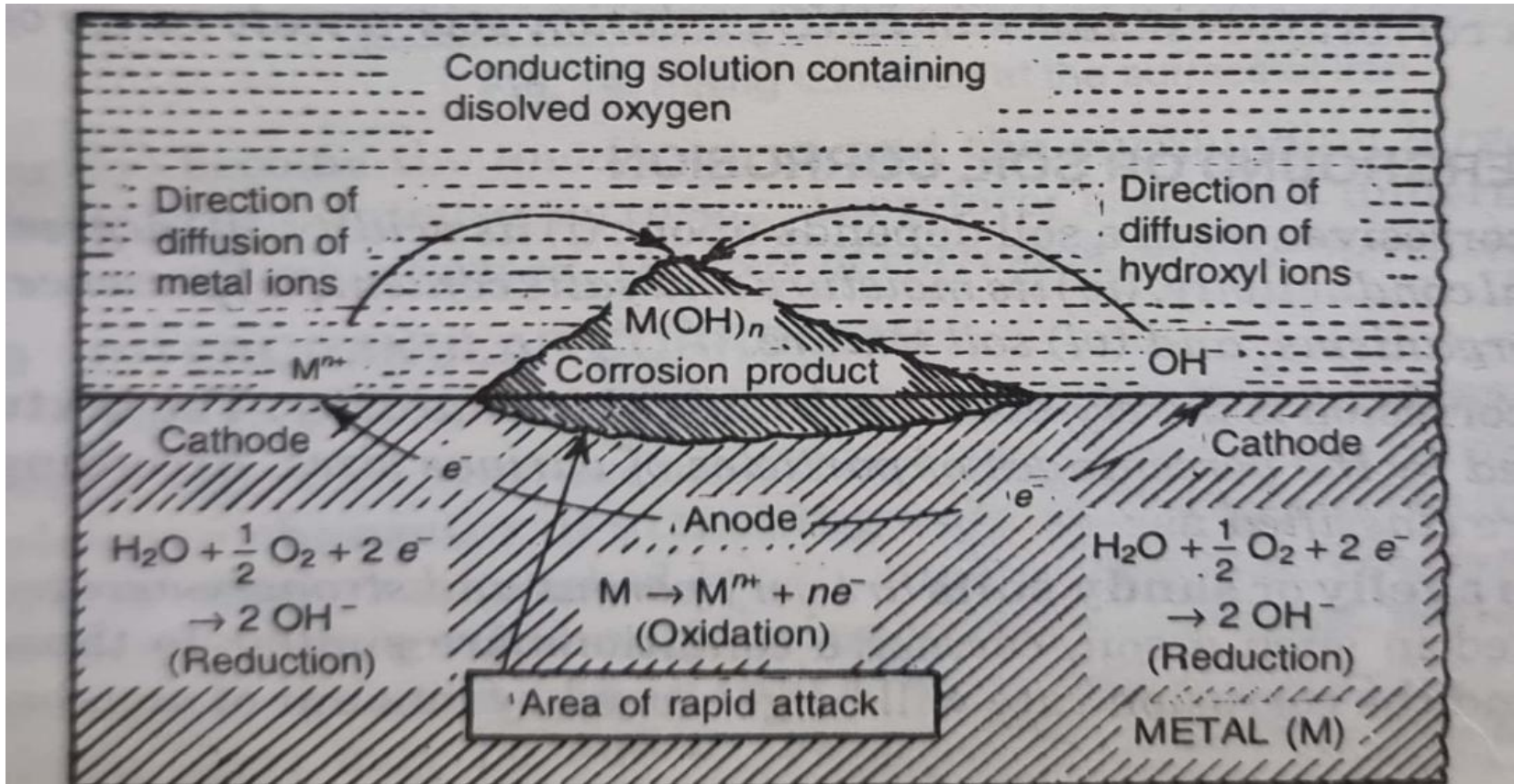
- Similarly, iron corrodes under drops of water (or salt solution).
- Areas covered by droplets, having no access of oxygen, become anodic with respect to the other areas, which, are freely exposed to air.



- Corrosion may be accelerated in inaccessible places, because these areas have less oxygen.



- Corrosion is accelerated under the accumulation of dirt, sand, other contamination, blocks of wood, beneath glass etc.



Passivity

- It is the phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series.
- Due to formation of a highly protective, thin film (about 0.0004 mm thick) on the surface of metal or an alloy, which makes it more noble.
- This film is insoluble, non-porous and self-healing in nature i.e. when broken, it will repair itself on re-exposure to oxidizing conditions.
- Examples : Ti, Al, Cr, and stainless steel alloys containing Cr.

- These exhibit outstanding corrosion resistance **in oxidizing environments**, but in reducing environments, they become chemically active.
- Based on experiment conducted in aerated 0.5 M NaCl solution, the passivity of certain metals falls in the following order :

$$\text{Ti} > \text{Al} > \text{Cr} > \text{Be} > \text{Mo} > \text{Mg} > \text{Ni} > \text{Co} > \text{Fe} > \text{Mn} > \text{Zn} > \text{Cd} > \text{Sn} > \text{Pb} > \text{Cu}$$

- Passivity is not a constant state, but exists only in certain environment condition, which tend to maintain thin protective oxide films on their surfaces.

Underground or Soil Corrosion

- Soil corrosion is purely electrochemical in character.
- The corrosiveness of a soil depends upon:
 - (i) its acidity,
 - (ii) degree of aeration,
 - (iii) electrical conductivity,
 - (iv) its moisture and salts content,
 - (v) presence of bacteria and micro - organisms
 - (vi) soil texture

Classification of Soil According to Particle Size

(a) Gravelly and Sandy Soils are very porous and strongly - aerated.

- If a metal pipe is buried in such a soil, corrosive conditions are similar to those under wet condition, and the corrosion rate will be governed by amount of moisture content in the soil.

(b) In Water - Logged Soils, the amount of free oxygen available is very small, but various bacteria and micro - organisms can grow, which may lead to micro- biological corrosion.

(c) In Acidic Soils, the mechanism of soil corrosion is similar to the hydrogen evolution type. The rate of such a corrosion depends on:

(i) the pH (or acidity)

(ii) the presence of salt

(iii) the presence of oxygen: It facilitates the evolution of hydrogen and, hence, accelerates the rate of attack.

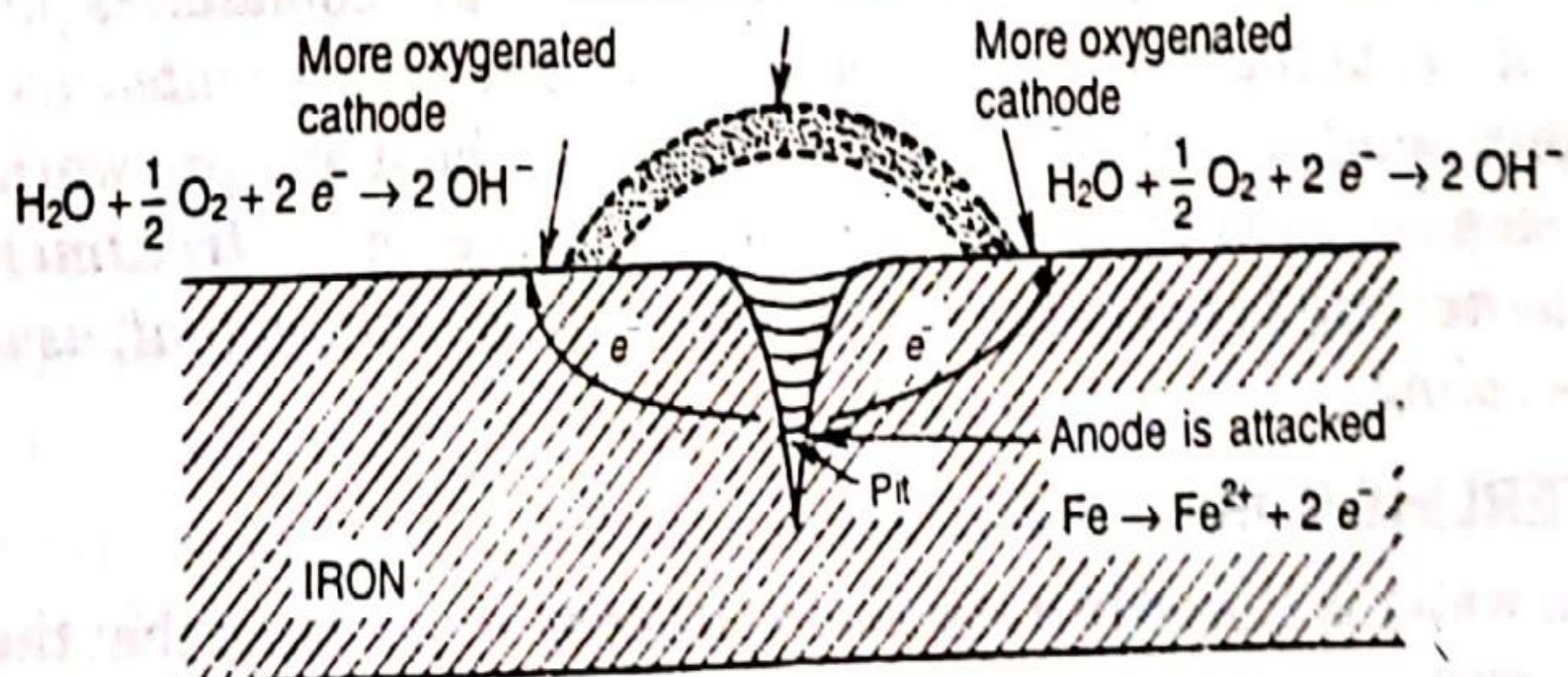
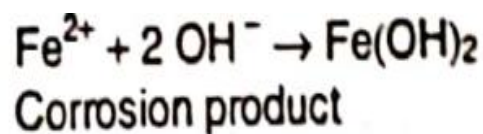
(d) Intermediate character soils (fine gravel, sand and salt containing) may produce a localized and intense corrosion.

- Buried pipelines or cables passing from one type of soil to another may get corroded due to differential aeration.
- Air pockets in the soil may also cause corrosion due to differential aeration.

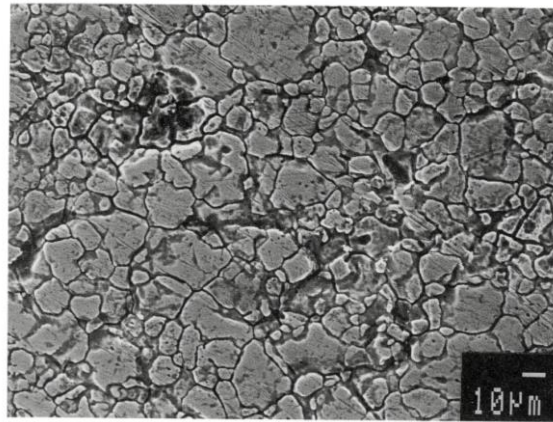
Pitting Corrosion

- Pitting corrosion is a localized accelerated attack, resulting in the formation of cavities around which the metal is relatively un-attacked.
- formation of pinholes, pits and cavities in the metal.
- Pitting is, usually, the result of the breakdown or cracking of the protective film on a metal at specific points.
- This gives rise to the formation of small anodic and large cathodic areas.

- The presence of the extraneous impurities, (like sand, dust, scale, etc.), on the surfaces of metals also lead to pitting.
- Owing to the differential amount of oxygen in contact with the metal, the small parts (underneath the impurity) become the anodic areas and the surrounding large parts become the cathodic areas.
- Intense corrosion, therefore, start just underneath the impurity. Once a small pit is formed, the rate of corrosion will be increased.



Intergranular Corrosion



- When a molten metal is cast, the solidification starts at many randomly distributed nuclei. Each of them grows in a regular atomic array to form grains.
- This type of corrosion occurs along grain boundaries and only where the material, especially sensitive to corrosive attack exists but leaving the grain interiors untouched or only slightly attacked.

- It is due to the fact that the grain boundaries contain material, which shows electrode potential, more anodic than that of the grain center in the particular corroding medium.
- It is generally encountered in alloys.
- For example, during the welding of stainless steel (an alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries, thereby, region just adjacent to grain boundaries becomes depleted in chromium composition and is more anodic with respect to the solid solution within the grain (which is richer in Cr).

Waterline Corrosion

- This type of corrosion results from differential aeration, due to which oxygen concentration cells are formed.
- When water is stagnant in a steel tank for long time, it is generally found that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus.
- The area above the waterline (highly oxygenated) acts as the cathodic with respect to the metal below the water level.
- As water is poor conductor, the ions just below the water level are more readily available for the reactions.
- Thus metal just below the water gets corroded.

- If the water is relatively free from acidity, little corrosion takes place.
- But if the liquid is in motion and contains chlorides, hydroxides, carbonates, phosphates, silicates, then intense attack at waterline may take place.
- The use of special antifouling paints restricts this to some extent.

Stress Corrosion/ stress cracking



- It is the combined effect of static tensile stresses and the corrosive environment on a metal.
- It is characterized by a highly localized attack.
- This type of corrosion is seen in fabricated articles of certain alloys (like high-zinc brasses and nickel brasses) due to the presence of stresses caused by heavy working like rolling, drawing etc.
- However, pure metals are relatively immune to stress corrosion.

- Stress corrosion involves in localized electrochemical corrosion, occurring along narrow paths, forming anodic areas with respect to the more cathodic areas at the metal surface.
- Presence of stress produces strains, which result in localized zones of higher electrode potential.
- These become so chemically active that they are attacked, even by a mild corrosive environment, resulting in the formation of a crack, which grows and propagates.

Microbiologically influenced Corrosion (MIC)

- Corrosion caused by the metabolic activity of various microorganisms is called "microbiological corrosion".
- There are about 12 different types of bacteria which affects mostly carbon steels, stainless steel, aluminium alloys and copper alloys.
- The microorganisms can develop in an environment with or without oxygen and are classed as aerobic or anaerobic.
- Most popular corrosions due to activity of microorganisms are:

(1) Sulfate reducing bacteria (SRB)

(like 'sporovobrio desulphuricus) are major groups involved in MIC. They are responsible for anaerobic corrosion of iron and steel.

- Optimum conditions for their growth are 25-30°C and pH from 5 to 9.
- The principal corrosion products are black iron sulfide and ferrous hydroxide. The corrosion is intense and localized.

(2) Sulfur bacteria (like thioracillus) are mostly aerobic, and oxidize sulfur (present in their cells) to yield sulfuric acid, which attacks the iron.

- They grow best under acid conditions of pH from 0 to 1.

(3) Iron and manganese micro-organisms are aerobic micro-organisms and live by taking into their cells iron and manganese ions, which they digest in presence of oxygen, forming insoluble hydrates of iron and manganese dioxide, which are then thrown out of their bodies.

- Iron bacteria grow in stagnant or running water at 5°C to 40°C and pH between 4 to 10 and with a small amount of free dissolved oxygen.

(4) **Film-forming microorganisms** (like bacteria, fungi, algae, and diatoms) can form microbiological film on an iron surface.

- Such films are capable of maintaining concentration gradients of dissolved salts, acids and gases on the iron surface, thereby leading to the formation of local biological concentration cells and consequent corrosion.

Factors Influencing Corrosion

A. Nature of the Metal:

- **(i) Position in Galvanic Series:** When two metals or alloys are in electrical contact, in presence of an electrolyte, the more active metal (or higher up in the series) suffers corrosion.
- The rate and severity of corrosion, depends upon the difference in their positions, and greater is the difference, the faster is the corrosion of the anodic metal/alloy.

- **(ii) Relative areas of the anodic and cathodic parts:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.
- Corrosion is more rapid, severe, and highly localized, if the anodic area is small (e.g., a small steel pipe fitted in a large copper tank).
- This is because the current density at a smaller anodic area is much greater, and the demand for electrons (by the large cathodic areas) can be met by smaller anodic areas only by rapid corrosion.

- **(iii) Purity of metal:** Impurities in a metal, generally, cause "heterogeneity", and form minute/tiny electrochemical cells (at the exposed parts), and the anodic parts get corroded.
- For example, zinc metal containing impurity (such as Pb or Fe) undergoes corrosion of zinc, due to the formation of local electrochemical cells.
- The rate and extent of corrosion increases with the increasing exposure and extent of the impurities.

- **(iv) Physical state of metal:** The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.).
- The smaller the grain-size of the metal or alloy, the greater will be its solubility and hence, greater will be its corrosion.
- Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

- **(v) Nature of surface film:** In aerated atmosphere, practically all metals get covered with a thin surface film of metal oxide.
- The ratio of the volumes of the metal oxide to the metal is known as a "specific volume ratio." Greater the specific volume ratio, lesser is the oxidation corrosion rate.
- The specific volume ratios of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. Consequently, the rate of oxidation of tungsten is least, even at elevated temperatures.

- **(vi) Solubility of corrosion products:** In electrochemical corrosion, if the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate.
- On the contrary, if the corrosion product is insoluble in the medium or it interacts with the medium to form another insoluble product (e.g., PbSO_4 formation in case of Pb in H_2SO_4 medium), then the corrosion product functions as physical barrier, thereby suppressing further corrosion.

- **(vii) Volatility of corrosion products:** If the corrosion product is volatile, it volatilizes as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack.
- This causes rapid and continuous corrosion, leading to excessive corrosion. For example, molybdenum oxide (MoO_3), the oxidation corrosion product of molybdenum, is volatile.

- **(viii) Passive character of metal:** Metal like Ti, Al, Cr, Mg, Ni, and Co are passive and they exhibit much higher corrosion-resistance than expected from their positions in galvanic series, due to the formation of highly protective, but very thin film (of oxide) on the metal or alloy surface.
- Moreover, the film is of such a "self-healing" nature, if broken, repairs itself, on re-exposure to oxidizing conditions. Thus, corrosion-resistance of stainless steel is due to passivating character of chromium present in it.

B. Nature of the corroding environment:

- **(i) Temperature:** With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.
- **(ii) Humidity of air:** It is the deciding factor in atmospheric corrosion.
- *Critical humidity: The relative humidity above which the atmospheric corrosion rate of metal increases sharply.*
- The value of critical humidity depends on the physical characteristics of the metal as well as nature of the corrosion products.

- Gases (CO_2 , O_2 , etc.) and vapors, present in atmosphere furnish water to the electrolyte to create electrochemical corrosion cell.
- Oxide films on a metal surface can also absorb moisture causing electrochemical corrosion.
- Nature of source of moisture: rainwater apart from supplying the necessary moisture for electrochemical attack, may also wash away oxide film from the metal surface.

- **(iii) Presence of impurities in atmosphere:**
Atmosphere, in the vicinity of industrial areas, contains corrosive gases like CO_2 , H_2S , SO_2 , and fumes of HCl , H_2SO_4 etc.
- It increases acidity (and its electrical conductivity) of the liquid, adjacent to the metal surfaces.
- results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces.
- Similarly, in the marine atmosphere, the presence of sodium and other chlorides (of seawater) lead to increase conductivity of the liquid layer in contact with the metal surface, thereby corrosion is speeded up.

- (iv) **Presence of suspended particles in atmosphere:** In case of atmospheric corrosion:
 - (a) if the suspended particles are chemically active in nature [like NaCl , $(\text{NH}_4)_2\text{SO}_4$] they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion
 - (b) if the suspended particles are chemically inactive in nature (e.g., charcoal), they absorb both sulfur gases, and moisture and slowly enhance corrosion rate.

- **(v) Conductance of the corroding medium:**
- Important in corrosion of underground or submerged structures.
- Conductance of dry sandy-soils is lower than those of clayey and mineralized soils.
- Consequently, stray currents (from power leakage) will cause more severe damage to the metallic structures, buried under clay and mineralized soils than those under dry sandy-soils.

- **(vi) Formation of oxygen concentration cell:**
With the increase in supply of oxygen to the moist-metal surface, the corrosion is promoted.
- Less oxygen concentration (e.g. oxide-coated part or loss-exposed part) parts becomes anodic; while the more oxygenated regions (or parts more exposed to oxygen) becomes cathodic, thereby leading to the formation of "oxygen-concentration cell" in which the anodic part suffers corrosion.

Corrosion Control (Protection Against Corrosion)

1. Design and material selection:

- The design of the material should be such that "corrosion, even if it occurs, is uniform and does not result in intense and localized corrosion".
- Important design principles are:
 - (i) Contact of dissimilar metals should be avoided in the presence of a corroding solution. If this principle is not followed, then corrosion is localized on the more active metal (in the immediate vicinity of contact); while the less active metal remains protected.

- (ii) When two dissimilar metals are to be in contact, the anodic material should have as large area as possible; whereas the cathodic metal should have as much smaller area as possible.
- (iii) If two dissimilar metals in contact have to be used, they should be as close as possible to each other in the electrochemical series.
- (iv) Whenever the direct joining of dissimilar metals is unavoidable, an insulating fitting may be applied in between them to avoid direct metal-metal electrical contact.

- (v) The anodic metal should not be painted or coated, when in contact with a dissimilar cathodic metal, because any break in coating would lead to rapid localized corrosion.
- (vi) Prevent the occurrence of heterogeneities, both in the metal and in the corrosive environment.
- Thus, a proper design should avoid the presence of crevices between adjacent parts of the structure, even in the case of the same metal, since crevices permit concentration differences.

- (vii) It is desirable that the design allows for adequate cleaning and flushing of the critical parts of the equipment. Sharp corners should be avoided.
- (viii) Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.
- (ix) Uniform flow of a corrosion liquid is desirable, since stagnant areas, highly turbulent flow and high velocities can cause accelerated corrosion.
- (x) A proper design should prevent areas of structure to stress (cold-worked part). Such an area could set up a galvanic couple with a non-stressed (not worked) areas of the metal.

- 2. Using pure metal: Impurities in a metal cause heterogeneity, which decreases corrosion-resistance of the metal.
- Thus, the corrosion-resistance of a given metal may be improved by increasing its purity.
- Purification of metals like Al, Mg, etc., provides a coherent and impervious protective oxide film on their surfaces, when exposed to environment.
- However, corrosion-resistance of a purified metal depends on the nature of corrosive environment.
- For example, the corrosion resistance of Al depends on its oxide film formation, which is highly protective only on the high purity metal.

- In many cases, it is not practical to produce a metal of high chemical purity, because:
 - (1) cost consideration in some cases, and
 - (2) very pure metal often possesses the disadvantages of inadequate mechanical properties like softness and low strength.
- Thus, the greater thickness of pure metal is required for a proper strength.

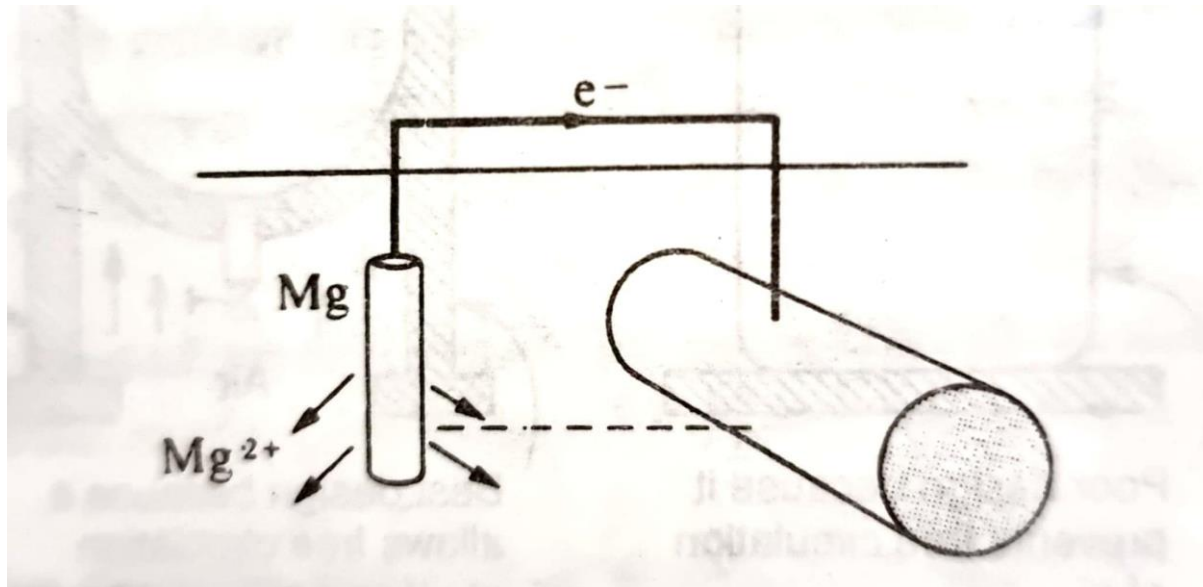
- **3. Using metal alloys:** Noble, but precious metals such as platinum and gold are corrosion-resistant.
- Alloying them with suitable elements best increases corrosion resistance of most metals, but for maximum corrosion resistance, alloy should be completely homogeneous.
- Chromium is the best suitable alloying metal for iron or steel. Its film is self-healing.
- Thus, steel containing up to 13% Cr are used in cutlery, surgical instruments, springs, etc.

4. Cathodic Protection

- In situations where it is impossible or impractical to alter the nature of the corrosion medium, corrosion control may be achieved by cathodic protection.
- There are two types of cathodic protection:
 1. By using galvanic or sacrificial anode
 2. By using impressed current

- **Sacrificial anodic protection method:** In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal.
- The more active metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so-employed is called "**sacrificial anode**".
- When corroded sacrificial anode block is consumed completely, a fresh one replaces it.
- Metals commonly employed, as sacrificial anodes are magnesium, zinc, aluminum and their alloys.

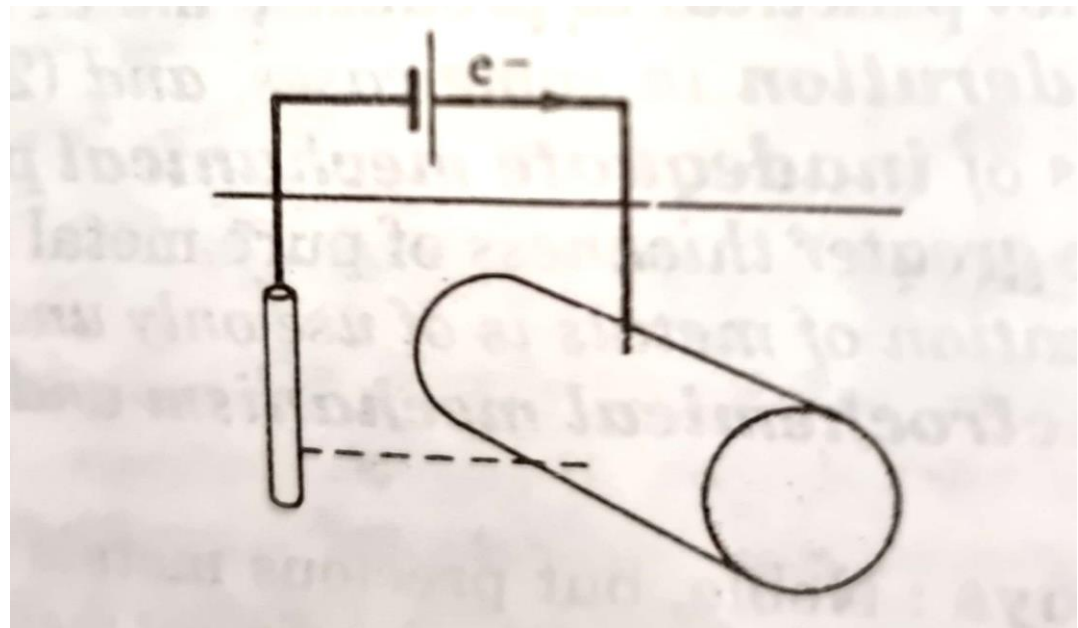
- Magnesium has the most negative potential and can provide highest current output. Thus it is widely used in high resistivity electrolytes such as soils.
- Zinc is generally used as sacrificial anode in good electrolytes such as seawater.



- **Important applications of sacrificial anodic method:**
 1. Protection from soil corrosion of underground cables and buried pipelines
 2. Protection from marine corrosion of cables, ship hulls etc.
- This is the most economical method particularly for short term protection because the capital investment is low.

- **Impressed current cathodic protection:**
- On a corroding metal surface, the higher the current the greater and faster will be the corrosion at the anode.
- The rate of corrosion can be controlled by imposing additional current on the metal, using an external circuit. In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

- Usually, the impressed current is derived from a direct current source (like battery or rectifier on a.c. line) with an insoluble anode (like graphite, high silica iron, scrap iron, stainless steel or platinum).
- Usually, a sufficient d.c. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium), and connected to the metallic structure to be protected.



- The anode is, usually, in a backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil.
- This type of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc.
- This kind of protection technique is, particularly, useful for large structure for long-term operations.

Protective Coatings

- Protective coatings makes continues physical barriers between the coated surface and its environment.
- Such coating barrier must be chemically inert to the environment under particular conditions of temperature and pressure.
- Along with corrosion protection and decoration, sometimes these coatings also impart wear-resistance, hardness, electrical properties, oxidation-resistance and thermal-insulating properties.
- The protective coatings may be metallic or inorganic, non-metallic or organic.

- **Metallic Coatings** – Iron and steel are the most commonly used construction metals due to their low cost, easy availability and ease of fabrication into desired structures.
- Iron and steel can be protected from corrosion by covering their surface with metallic coatings.
- The metallic coatings often used are of zinc, tin, nickel, chromium, aluminum, copper etc. There are two types of metallic coatings:

- **Anodic coatings:** Anodic coatings are produced from coating metals, which are anodic to the metal that is to be protected.
- For example, coating of Zn, Al and Cr on steel are anodic, because their electrode potential are lower than that of the base metal, iron.
- If any pores, breaks or discontinuities occur in such an anodic coating, a galvanic cell is formed between the coating metal and the exposed part of the base metal.
- E.g., in case of galvanised steel, zinc, the coating metal (being anodic) is attacked; leaving the underlying cathodic material (iron) unattacked. Zinc dissolves anodically; whereas the iron is protected.

- **Cathodic coatings:** These coatings are obtained by coating a more noble metal than the base metal.
- They protect the base metal, because they have higher corrosion resistance than the base metal.
- Effective protection is possible only when they are completely continuous and free from breaks, pores and discontinuities.
- If such coatings are punctured, much more corrosion damage can be done to the base metal than to metal without.
- This is due to the fact that exposed metal acts as an anode and coating becomes the cathode. Coating of tin on iron is an example.

- **Organic coatings –**

- Organic coatings are inert organic-barriers (like paints, varnishes, lacquers and enamels) applied on metallic surfaces and other construction materials for both corrosion protection and decoration.

The protective value of such a coating depends on:

- chemical inertness to the corrosive environment
- good surface adhesion
- impermeability to water and gases
- proper application method

- **Paints:** Wood, metal, cement and bricks are well known constructional materials for our homes, offices and industries. Over a period of time they get scratched.
- Paints form a protective layer over these surfaces, and keep them looking as good as new.

Chemically paint is a mixture of four ingredients:

Binders + Solvent + Pigment + Additives

- **Binder** is the main ingredient of paints.
- Binders are polymers (resins) forming a continuous film on the substrate surface.
- Binders are responsible for good adhesion of the coating to the substrate.
- The binder holds the **pigment** particles distributed throughout the coating.
- The binder is dispersed in a carrier, i.e. water or organic **solvent** either in molecular form (true solution) or as colloidal dispersions (emulsions)

- **Requisites of a good paint**
- It should be fluid enough to spread easily over the protected surface.
- It should have a high covering power.
- It should form a tough, adherent, uniform and impervious film.
- The film should not crack on drying.
- It should be corrosion resistant.
- It should give a stable and decent color to the surface.
- It should give a glossy film.
- It should adhere well on the surface.

- **Pigments**: essential solid constituent of a paint.

Functions :

- To provide desired color, opacity and strength to the paint
- To give aesthetical appeal to the paint
- To give protection to the paint film by reflecting harmful ultraviolet light
- To provide resistance to paint film against abrasion/wear
- To improve the impermeability of paint film to moisture
- To increase the weather resistance

Thus a pigment should be chemically inert, non-toxic, freely mixable with oil, opaque, cheap and easily available.

Types of pigments:

- Natural pigments: talc, clay, iron ores
- Synthetic pigments: titanium dioxide, barium sulfate
- Reactive pigments: red lead, ZnO (which react with drying oils to form soaps)

Most commonly used pigments:

- Yellow pigments: chrome yellow, zinc yellow
- Brown pigments: clays having iron
- Green pigments: chromium oxide
- Red pigments: red lead, cadmium lead
- Black pigments: carbon black, graphite
- Blue pigments: ultramarine, prussian blue
- White pigments: white lead, ZnO

- To meet all these requirements, various constituents of paint should be mixed in required proportions.
- **pigment volume concentration (P.V.C.)**
- **P.V.C.** is defined as the volumetric concentration of the pigments expressed as percentage of the total volume of the non-volatile constituents in the paint.
- $$\text{P.V.C.} = \frac{\text{Volume of pigment in paint}}{\text{Total volume of non-volatile constituents in the paint}}$$
- As the non-volatile constituents in paint is the sum of the volumes of pigment and non-volatile liquid (**called vehicle, which is liquid portion of a paint aside from its volatile thinner and water**) therefore
- $$\text{P.V.C.} = \frac{\text{Volume of pigment in paint}}{\text{Volume of (pigment+non-volatile vehicle) constituents of the paint}}$$

- **Vehicle or drying oil**: It is a film-forming constituent of the paint. The liquid portion of the paint in which the pigment is dispersed is called a vehicle.

The important functions of vehicle are:

- They hold the pigment on the metal surface
- They form the protective film
- They impart water-repellency, durability and toughness to the film
- They give better adhesion to the metal surface
- These are glyceryl esters of high molecular-weight fatty acids present in animal and vegetable oils.
- The mostly used ones are linseed oil, soyabean oil and dehydrated castor oil.

These are mainly of three types:

- ***Drying oil*** which dry quickly as they contain high percentage of conjugated fatty acid esters e.g. linseed oil, dehydrated castor oil
- ***Semi-drying oil*** which dry slowly in air and are not used alone in paint. They are used as blending agent e.g. rosin oil, fish oil
- ***Non-drying oil*** which do not dry at all e.g. mustard oil, sunflower oil

Reaction mechanism:

- The oil film, after it has been applied on the protected surface, absorbs oxygen at the double bonds, forming peroxides, diperoxides and hydroperoxides.
- These then isomerize, polymerise and condense to form a characteristic tough, elastic, coherent, hard, insoluble, infusible, highly cross-linked structured macromolecular film.

- **Thinners**: The important functions of the thinners are:
- They reduce the viscosity of the paint to suitable consistency so that they can be easily applied.
- They dissolve vehicle and additives.
- They evaporate rapidly and help in drying of the paint
- They increase the elasticity of the paint film
- Commonly used thinners are turpentine, mineral spirits, benzene, naphtha, kerosene etc.

- **Driers**: The main function of drier is to improve the drying quality of the oil-film.
- They accelerate the drying through oxidation, polymerization and condensation.
- The most commonly used dryers are linoleates, borates, naphthalenes, resinates and tungstates of heavy metals like Pb, Zn, Co and Mn.
- **Fillers or extenders**: These are low refractive indices materials, generally of white color.

The important functions are:

- They reduce the cost of the paint
- They serve to fill the voids in the film
- They improve the durability of the film by reducing the cracking of the paints after drying
- They acts as carrier for the pigment color
- Important extenders are BaSO_4 , talc, asbestos, ground silica, gypsum, ground mica, slate powder, CaCO_3 , calcium sulfate etc.
- **Plasticizers**: They are added to give elasticity to the paint film and to prevent cracking. Commonly used plasticizers are tricresyl phosphate, triphenyl phosphate, tributyl phthalate.
- **Antiskinning agents**: They prevent gelling and skinning of the paint film. Mostly used are polyhydroxy phenols.

- **Varnish**
- Varnish is a colloidal solution of natural or synthetic resin in oil or thinner or both.

A good varnish should possess the following characteristics:

- It should produce a glossy and shining surface.
- It should produce a protective film.
- It should be soft and adapt itself to contraction and expansion due to temperature changes.
- It should produce an elastic film.
- It should yield film whose color does not fade.

- There are two main types of varnishes:
- **Oil varnish:** It is a homogeneous solution of one or more natural or synthetic resins in a drying oil and a volatile solvent.
- It takes around 24 hours for drying.
- The film thus produced is hard, lustrous and quite durable. They are used for exterior as well as interior works.
- **Spirit varnish:** It is a homogeneous solution of one or more natural or synthetic resins in a completely volatile solvent.
- It dries quite rapidly, but leaves behind a film, which is brittle and so has a tendency to peel off or crack.
- Such varnishes are used for polishing wooden furniture.

- **Constituents of varnish:**
- **Resin:** Natural resins like rosin, copal, shellac and synthetic resins like phenol-aldehyde, urea-formaldehyde, terpene polymers. Resins provide hardening, resistance to weathering, durability, resistance to chemical action and water-proofness.
- **Drying oils:** linseed oil, dehydrated oil
- **Thinners:** turpentine, petroleum spirits, ethyl alcohols
- **Driers:** Pb, Co, Mn linoleates, naphthenates
- **Antiskinning agents:** tert-amyl phenol

- **Lacquer**
- A lacquer is a colloidal dispersion of solution of a cellulose derivative, resin and plasticizer in solvent and diluents.
- They dry in air-principally by evaporation of solvents, yielding a transparent, hard and water-proof film.

These are used for

- a. interior decoration like paintings of wood work and furniture,
- b. giving finishing coat to automobile bodies