# Engineering Chemistry
CHY1701

Dr. Krishnendu Biswas, SAS, #2, I Floor Annex
#1245, krishnendu.biswas@vit.ac.in

Module 3

Dry and wet corrosion - detrimental effects to buildings, machines, devices & decorative art forms, emphasizing Differential aeration, Pitting, Galvanic and Stress corrosion cracking; Factors that enhance corrosion and choice of parameters to mitigate corrosion.

The secret of effective engineering lies in controlling rather than preventing corrosion, because its is impossible to eliminate corrosion
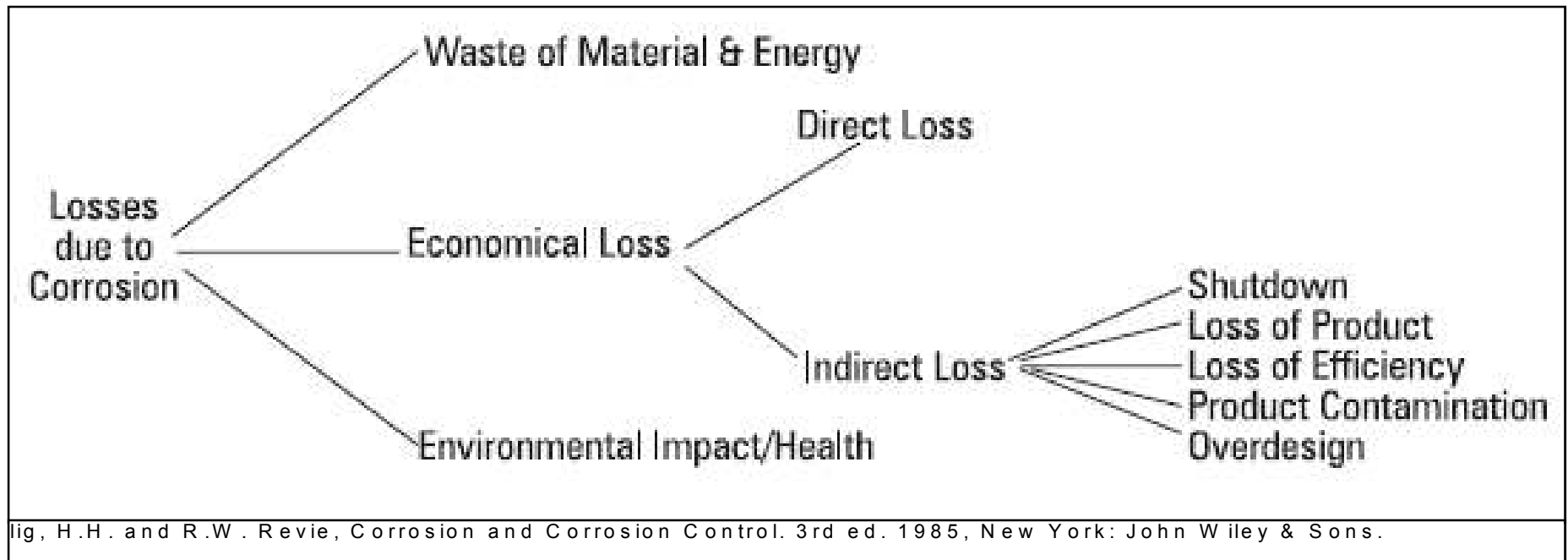*-- Michael Henthorne*

Corrosion
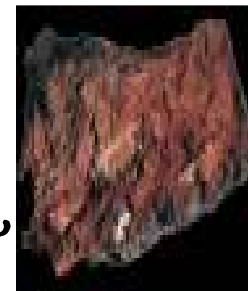
❑ Natural Abundance of Metals – In the form of oxides, carbonates, chlorides, silicates etc. (Ores)

❑ Extraction process – Combined forms are reduced to their metallic states from their ores – need energy hence metallic states can be considered excited states – unstable – natural tendency to revert back to lower energy (combined) state

❑ When the metals put into use – exposed to environment (dry gases, moisture, liquids) – exposed metal surfaces begin to decay – conversion into more stable metal compounds – destruction or deterioration starts at the surface

❑ Corrosion – Any process of destruction and consequent loss of solid metallic material, through an unwanted chemical or electrochemical attack by its environment
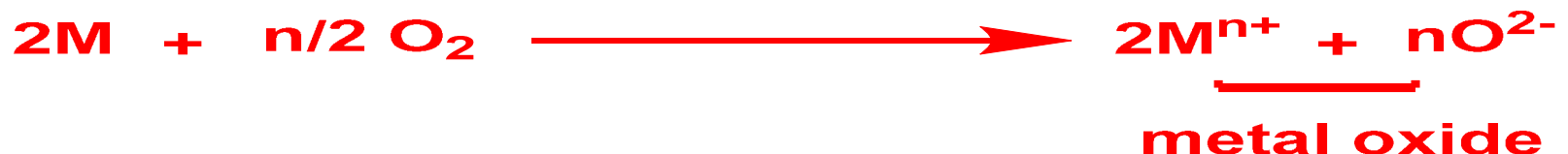
Metal $\underset{\text{Extraction of Metals}}{\overset{\text{Corrosion (Oxidation)}}{\rightleftharpoons}}$ **metallic compounds + Energy**

Effects

- Corrosion – slow process, it become severe over the time.
- It reduces material's strength, safety, aesthetic look, performance and eventually lead to enormous destruction of machines, equipments and economic loss.
- Loss due to corrosion is estimated to be $ 2–2.5 billion per year all over the world.
- SERIOUS problem — to avoid it the reason must be understood.

Waste of Material & Energy

Direct Loss

Losses due to Corrosion

Economical Loss

Shutdown
Loss of Product
Loss of Efficiency
Product Contamination
Overdesign

Indirect Loss

Environmental Impact/Health

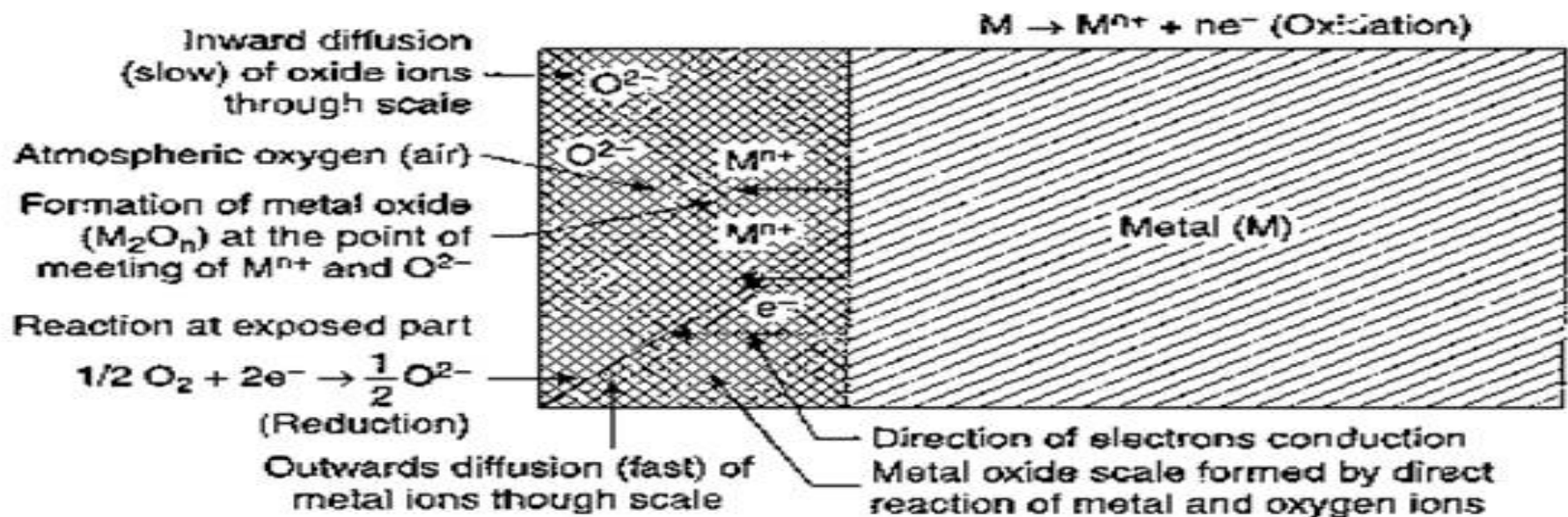lig, H.H. and R.W. Revie, Corrosion and Corrosion Control. 3rd ed. 1985, New York: John Wiley & Sons.

Corrosion - types

- Dry or Chemical Corrosion and Wet or Electrochemical Corrosion
- <u>Dry or Chemical Corrosion</u> – Occurs through direct chemical action of environment

    1. Oxidation Corrosion

    2. Corrosion by other gases

    3. Liquid Metal Corrosion

- Oxidation Corrosion – Oxygen present in the atmosphere attacks the metal surface – formation of oxide layers/scale

$$2M \longrightarrow 2M^{n+} + 2ne^-$$

$$n/2 \; O_2 + 2ne^- \longrightarrow nO^{2-}$$

$$2M + n/2 \; O_2 \longrightarrow \underline{2M^{n+} + nO^{2-}}$$

metal oxide

- ❑ Corrosion of metal due to exposure to oxygen at low or high temperature in the absence of moisture.
- ❑ At ambient temperature usually corrosion of metals are slow. But alkali (Li, Na, K, etc.) and alkaline (Be, Ca, Sr, etc.) earth metals reactive.
- ❑ At higher temperature almost all metals except noble metals are oxidized.
- ❑ Mechanism – Oxidation of metal – metal oxide – further oxidation occurs either through diffusion of metal towards metal oxide or diffusion of oxygen to metal surface – both occurs, former more prevalent.

Inward diffusion (slow) of oxide ions through scale

Atmospheric oxygen (air)

Formation of metal oxide (M_2O_n) at the point of meeting of M^{n+} and O^{2-}

Reaction at exposed part

$$1/2 \, O_2 + 2e^- \rightarrow \frac{1}{2} O^{2-}$$
(Reduction)

Outwards diffusion (fast) of metal ions though scale

O^{2-}

O^{2-} M^{n+}

M^{n+}

e^-

$M \rightarrow M^{n+} + ne^-$ (Oxidation)

Metal (M)

Direction of electrons conduction

Metal oxide scale formed by direct reaction of metal and oxygen ions

- ❑ Nature of the Oxide – When oxidation starts, a thin layer of oxide film will be formed on the surface and the nature of the film decides the further action i.e. porous film or non-porous film
- ❑ The oxide films are classified as

1. Stable oxide layer – A fine-grain of oxide which forms a compact surface adhered tightly to the parent metal surface. Eg. Oxides of Al, Sn, Cu, etc. Impervious in nature (cuts of the penetration of O_2) behaving like a protective coating

2. Unstable oxide layer – Oxides of noble metals such as platinum, silver, Gold etc.

$$Metallic\ Oxide \rightleftharpoons Metal + Oxygen$$
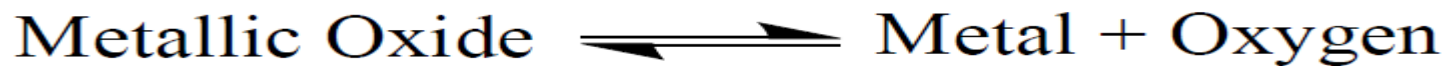
3. Volatile layer – Oxide layers volatilize as soon as they are formed – Leads to excessive corrosion Eg. Molybdenum oxide (MoO_3)

4. Porous Oxide layer – Oxide layers with minute pores/cracks – oxygen can access to surface of metal – continues till the entire metal is completely converted into its oxide

Pilling-Bedworth rule

$R = V_{scale}/V_{metal} = Md/nmD$

Where M - mass of metal oxide
m - atomic weight
d - density of the metal
D - density of the scale
n- number of metal atoms in a formula of the scale

- 1)R<1: If the volume of the metallic oxide is less than the volume of the metal surface the oxide layer is porous, non-protective. Eg. Alkali and alkaline earth metals – Li, Na, K, Mg
- 2) 2<R>1: – The metal surface is compact, non-porous protective. Eg. Cu, In, Al, Ni, Cr forms oxides whose volume is greater than the volume of the metal.
- 3)R>2 – non-protective as the oxide layer falls off Eg. Fe

Corrosion by other gases

- SO_2, CO_2, Cl_2, H_2S etc – induce corrosion action on metals
- Extent of corrosive effect depends on the chemical affinity between the metal and the gas – formation of protective or non-protective films on the metal surface.
- If the film is non-porous or protective, the intensity of attack decreases. Eg. Attack of Cl_2 on Ag – AgCl protective
- If the film is porous or non-protective, the surface of the whole metal is gradually destroyed. Eg. Dry Cl_2 gas attack on Sn – formation of volatile $SnCl_4$ – fresh surface is exposed for further attack
- <u>Corrosion by hydrogen</u>

  (a) HYDROGEN EMBRITTLEMENT:

 Contact of metal with H_2S results in the generation of atomic hydrogen

$$E.g. \quad Fe + H_2S \rightarrow FeS + 2H$$
$$H + H \rightarrow H_2 \uparrow$$
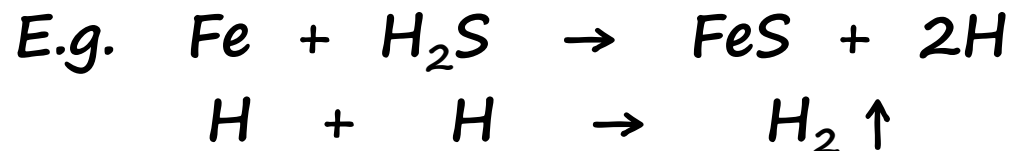
- Hydrogen in atomic state diffuses into the metal matrix and collects in the voids present in the metal forming H_2 gas.
- A very high pressure is developed, which results in cracks and blisters on metal- hydrogen embrittlement.

(b) Decarburisation

- At higher temperature atomic hydrogen is formed by the thermal dissociation of molecular hydrogen.

$$H_2 \rightarrow 2H$$

- When steel is exposed to this environment, the atomic hydrogen readily combines with carbon of steel and produces methane gas.

$$C + 4H \rightarrow CH_4\uparrow$$
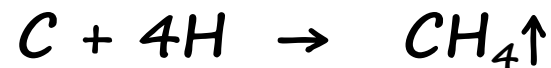
- Collection of these gases in the voids develop very high pressure, which causes cracking. Thus the process of decrease in carbon content in steel is termed as "Decarburisation" of steel.

Liquid Metal Corrosion

❑ Chemical action of flowing liquid metal at high temperatures on solid metal or alloy

    i) Dissolution of solid metal by liquid metal

    ii) Internal penetration of the liquid metal in to the solid metal

    Modes of corrosion cause weakening of the solid metal

❑ Eg. Liquid metal mercury dissolves most metals by forming amalgams

Wet or Electrochemical Corrosion

❑ When a conducting liquid is in contact with the metal

❑ When two dissimilar metals or alloys either immersed or partially dipped in a solution

❑ Existence of separate "anodic" and "cathodic" areas/parts, between which current flows through the conducting solution

❑ At Anode – loss of electrons

$$M \rightarrow M^{n+} + ne^-$$

❑ At Cathode

Reduction reaction- Gain of electrons

❑ Corrosion always occurs at anode

Mechanism

❑ It involves flow of electron/current between the anodic and cathodic area

❑ The anodic reaction involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons

❑ The cathodic reaction consumes electrons with either by

a) Evolution of hydrogen

b) Absorption of oxygen

– Depends on the nature of the corrosive environment

❑ Evolution of hydrogen type corrosion – Occurs in acidic environment. Eg. Dissolution of iron as ferrous ions with the liberation of electrons

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

❑ Electrons flow through the metal from anode to cathode, where H^+ ions are available and eliminated as hydrogen gas

$$2H^+ + 2e^- \rightarrow H_2\uparrow$$

$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2\uparrow$$
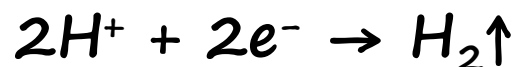
Absorption of oxygen

❑ Rusting of iron in neutral aqueous solution of electrolytes in the presence of oxygen

At anodic area: $Fe \rightarrow Fe^{2+} + 2e^-$

At cathodic area: $\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow$

❑ Enough Oxygen: $(2Fe_2O_3 . 6H_2O)$

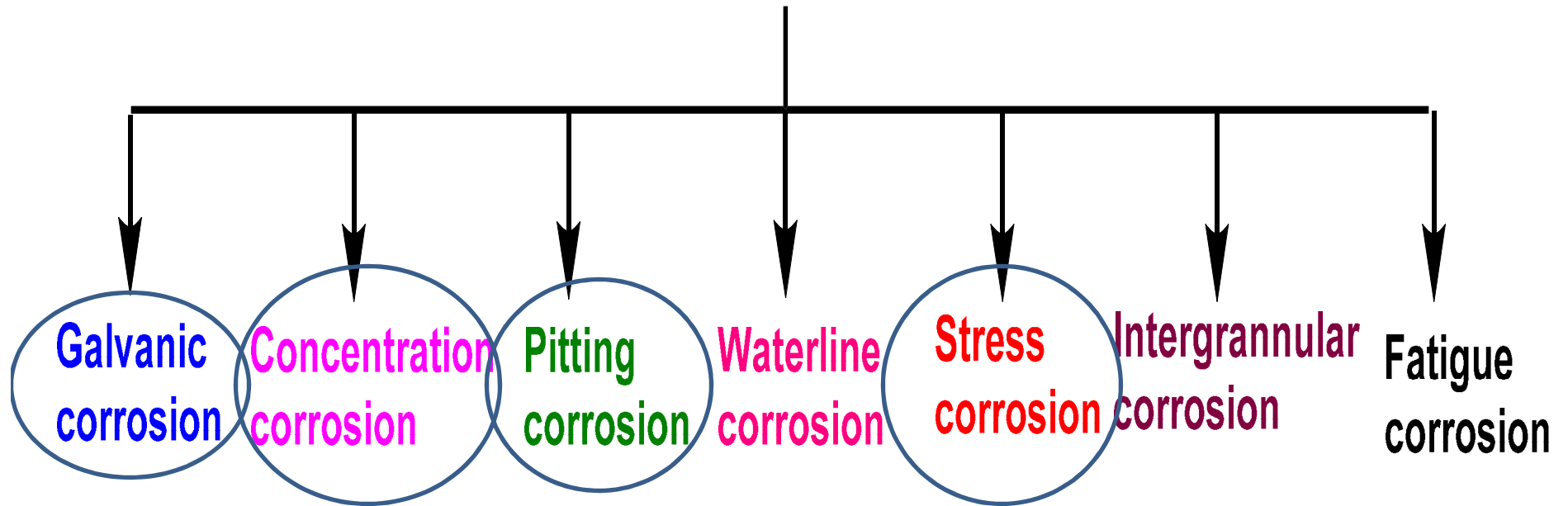$4\ Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\ Fe(OH)_3$ [yellow rust]

❑ Corrosion product forms at cathode – Smaller Fe^{2+} diffuse more rapidly than OH^- Corrosion occurs at the anode. Rust is deposited at or near cathode

❑ Oxygen is limited: Fe_3O_4 (Black anhydrous magnetite)

$Fe^{2+}Fe_2^{3+}O_4$

Water

OH⁻   OH⁻

Anodic Area
Where Metal Dissolves   Fe++   Fe++   Fe++   OH⁻   OH⁻   O₂   O₂

Iron – or Steel Pipe Wall

Corrosion   Fe(OH)₂   Cathodic Area – of Dissolved Oxygen Reduction
Iron Tuberculation

Forms of wet corrosion
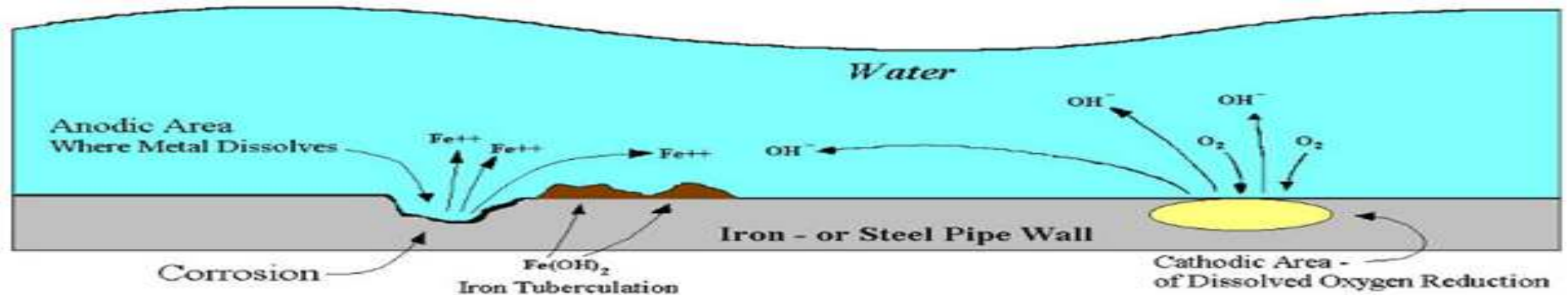
Galvanic corrosion **Concentration corrosion** **Pitting corrosion** **Waterline corrosion** **Stress corrosion** **Intergrannular corrosion** **Fatigue corrosion**

Differences between dry and wet corrosion

Dry corrosion	Wet or electrochemical corrosion
• Corrosion occurs in the absence of moisture.	• Corrosion occurs in presence of conducting medium.
• It involves direct attack of chemicals on the metal surface.	• It involves formation of electrochemical cells.
• The process is slow.	• It is a rapid process.
• Corrosion products are produced at the site of corrosion.	• Corrosion occurs at anode but rust is deposited at cathode.
• The process of corrosion is uniform.	• It depends on the size of the anodic part of metal.

Electrochemical series

➢ Electrode Potential (EP) – The tendency of an electrode to lose or gain electron when it is in contact with solution of its own ion.

➢ Standard Electrode Potential (SEP) – potential of electrode at a given temperature, depends upon the concentration of ions in the surrounding solution. If the concentration of the ions is unity and the temperature is 25 ° C, the potential of the electrode is termed as SEP.

➢ Arrangement of SEP value of electrodes either in increasing or decreasing order is called electrochemical series.

➢ Reduction potential – tendency of an electrode to gain e^- i.e tendency to get reduced is called reduction potential.

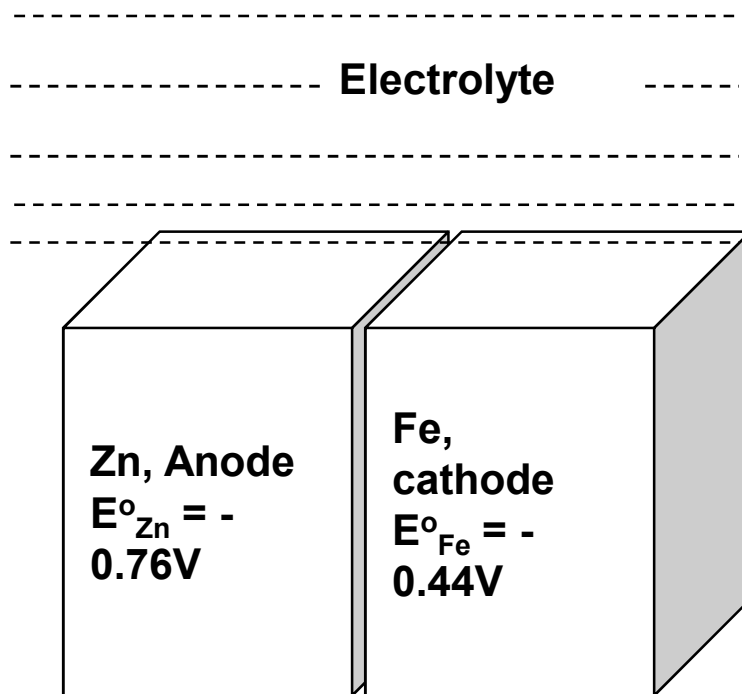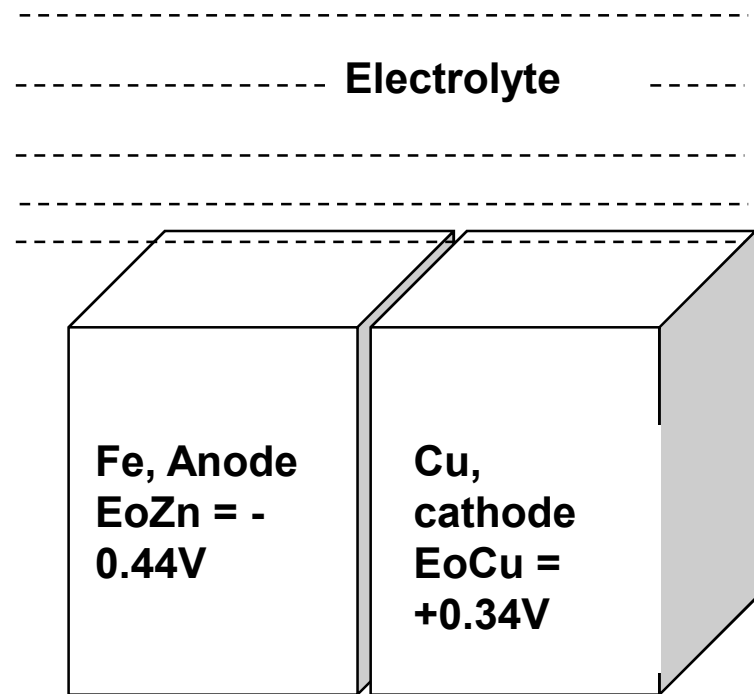| Electrode		Electrode reaction	E^0/V
Au	Gold	$Au^{3+} + 3e^- \rightleftharpoons Au$	+1.43
Ag	Silver	$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
Cu	Copper	$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
H	Hydrogen	$H^+ + e^- \rightleftharpoons H$	0
Pb	Lead	$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
Sn	Tin	$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
Ni	Nickel	$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
Cd	Cadmium	$Cd^{2+} + 2e^- \rightleftharpoons Cd$	−0.40
Fe	Iron	$Fe^{2+} + 2e^- \rightleftharpoons Fe$	−0.44
Zn	Zinc	$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76
Ti	Titanium	$Ti^{2+} + 2e^- \rightleftharpoons Ti$	−1.63
Al	Aluminium	$Al^{3+} + 3e^- \rightleftharpoons Al$	−1.66
Mg	Magnesium	$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.37
Na	Sodium	$Na^+ + e^- \rightleftharpoons Na$	−2.71
K	Potassium	$K^+ + e^- \rightleftharpoons K$	−2.93
Li	Lithium	$Li^+ + e^- \rightleftharpoons Li$	−3.05

Galvanic or Bimetallic Corrosion

- When two dissimilar metals (example: zinc and copper) are electrically connected and exposed to an electrolyte
- The metal higher in electrochemical series undergoes corrosion
- This type of corrosion is called galvanic corrosion
- Zinc – higher in electrochemical series forms the anode and is attacked and gets dissolved
- Copper – lower in electrochemical series acts as cathode
- $Zn \rightarrow Zn^{2+} + 2e^-$

Metal	Potential in volts	
$Li^+ + 1e^- = Li$	-3.05	
$K^+ + 1e^- = K$	-2.93	
$Ca^{2+} + 2e^- = Ca$	-2.90	
$Na^+ + 1e^- = Na$	-2.71	
$Mg^{2+} + 2e^- = Mg$	-2.37	
$Al^{3+} + 3e^- = Al$	-1.66	Anodic
$Zn^{2+} + 2e^- = Zn$	-0.76	
$Cr^{3+} + 3e^- = Cr$	-0.74	
$Fe^{2+} + 2e^- = Fe$	-0.44	
$Ni^{2+} + 2e^- = Ni$	-0.23	
$Sn^{2+} + 2e^- = Sn$	-0.14	
$Pb^{2+} + 2e^- = Pb$	-0.13	
$H^+ + 1e^- = 1/2 H_2$	0.00	
$Cu^{2+} + 2e^- = Cu$	+0.34	
$Ag^+ + 1e^- = Ag$	+0.80	
$Pt^{4+} + 4e^- = Pt$	+0.86	Cathodic
$Au^+ + 1e^- = Au$	+1.69	
$½ F_2 + 1e^- = F^-$	+2.87	

Zn undergoes corrosion

Electrolyte

Zn, Anode
E^o_{Zn} = -0.76V

Fe, cathode
E^o_{Fe} = -0.44V

Fe undergoes corrosion

Electrolyte

Fe, Anode
EoZn = -0.44V

Cu, cathode
EoCu = +0.34V

- ❑ Also called 'dissimilar metal corrosion'.
- ❑ Takes place when two metals are in physical contact with each other and are immersed in a conducting fluid.
- ❑ Corrosion damage induced when two dissimilar materials are coupled in a corrosive electrolyte.
- ❑ Examples: Plate and screw of different electrical potentials due to differences in processing, Copper and steel tubing are joined in a domestic water heater, the steel will corrode in the vicinity of the junction

The following fundamental requirements have to be met for galvanic corrosion:

- ❑ Dissimilar metals (or other conductors, such as graphite).
- ❑ Electrical contact between the dissimilar conducting materials (can be direct contact or a secondary connection such as a common grounding path).
- ❑ Electrolyte (the corrosive medium) in contact with the dissimilar conducting materials.
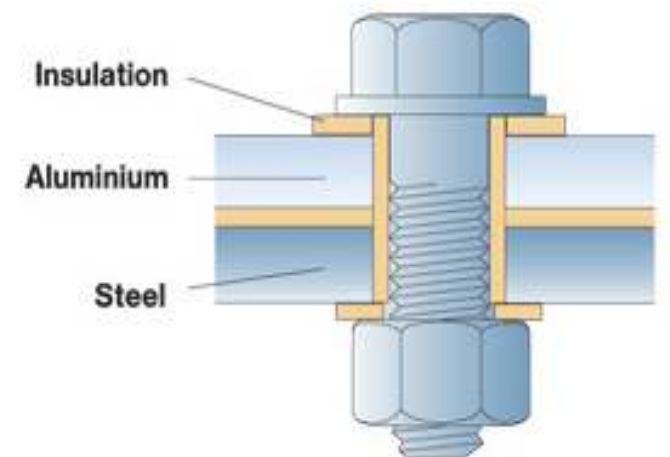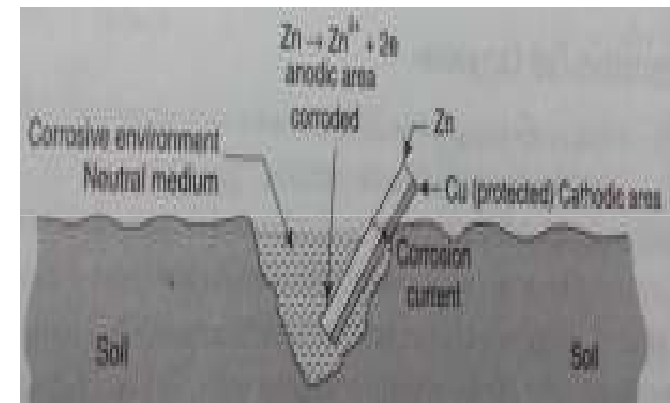
- Bolt and nut made of the same metal is preferred – to avoid galvanic corrosion due to homogeneous metals
- Galvanic type corrosion observed when Steel pipe connected to copper
- Zn coating on mild steel
- Tin coating on Cu vessel
- Pb–Sb soldering around Cu wire

Factors influencing galvanic corrosion
- Potential difference between electrodes
- Concentration of electrolyte
- Area of cathode vs. anode
- Formation of oxide film over metal
- Contact resistance between two electrodes

Prevention
- Avoid unfavorable area effect
- Selection of metals & alloys
- Using inhibitors
- Applying cathodic protection
- Insulating dissimilar metals

$Zn \rightarrow Zn^{++} + 2e$ anodic area corroded — Zn

Corrosive environment Neutral medium → Cu (protected) Cathodic area

Soil   Corrosion current   Soil

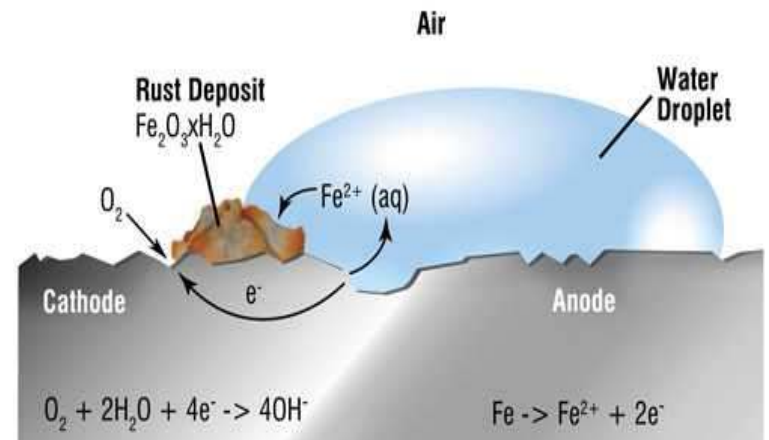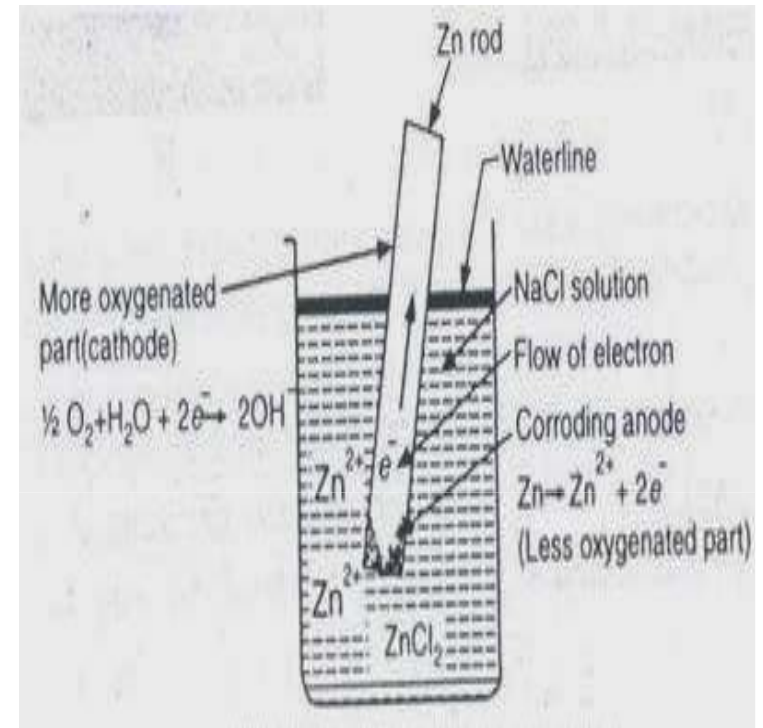Insulation

Aluminium

Steel

Concentration cell corrosion

➤ Two electrodes of same metal dipped in same electrolyte of different concentration. Eg. Zn in $ZnSO_4$ (c1 and c2)

➤ Electrochemical cell formed – one of the Zn act as anode (corrosion occurs) and the other Zn part act as cathode (deposition occurs).

➤ Potential difference exist which drives the e^- flow

➤ Difference in environment surrounding the metal – concentration cell.

Types of concentration–cell corrosion

Concentration-Cell Corrosion

Metal-ion concentration cell

Differential aeration
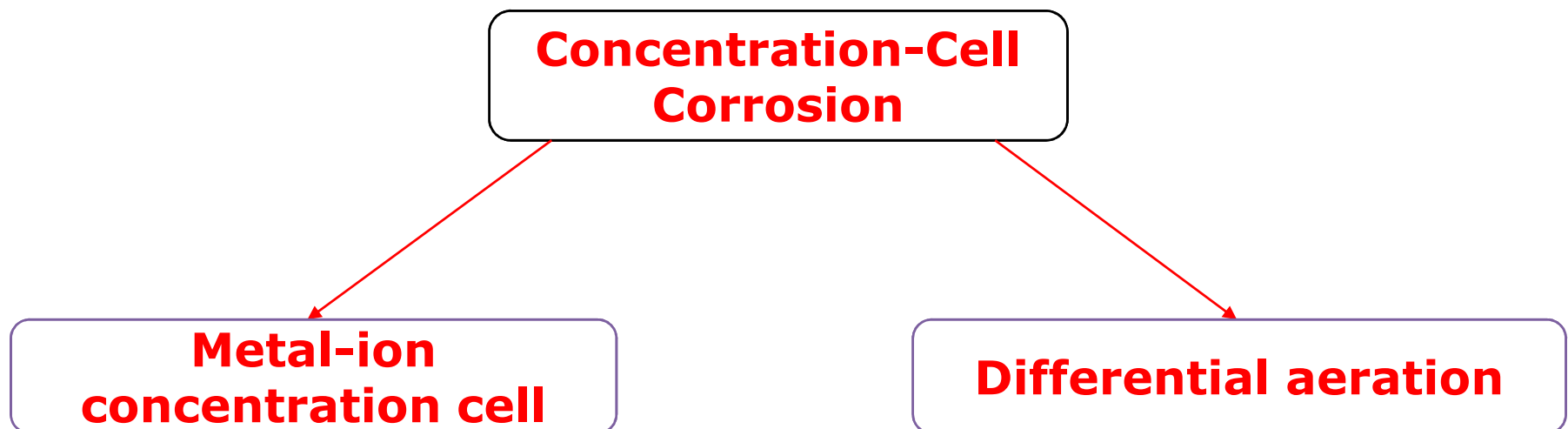
Differential aeration corrosion

➢ One part of metal is well aerated than other part – difference in potential – electrochemical cell created.

➢ Differential aeration accounts for corrosion of metals partially immersed in a solution, just below waterline.

➢ "Poor–oxygenated area – anode" – corrode

➢ The circuit is completed by migration of ions through the electrolyte and flow of electrons through the metal from anode to cathode.

➢ Corrosion of iron under drops of water (or salt solution) – differential aeration corrosion.

➢ Oxygen concentration cell increases corrosion, but it occurs where the oxygen concentration is lower.

Zn rod

Waterline

More oxygenated part(cathode)

NaCl solution

Flow of electron

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Corroding anode

Zn^{2+} e^-

$Zn \rightarrow Zn^{2+} + 2e^-$

(Less oxygenated part)

Zn^{2+}

$ZnCl_2$

Air

Rust Deposit
$Fe_2O_3xH_2O$

Water Droplet

O_2

Fe^{2+} (aq)

Cathode

e^-

Anode

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

$Fe \rightarrow Fe^{2+} + 2e^-$
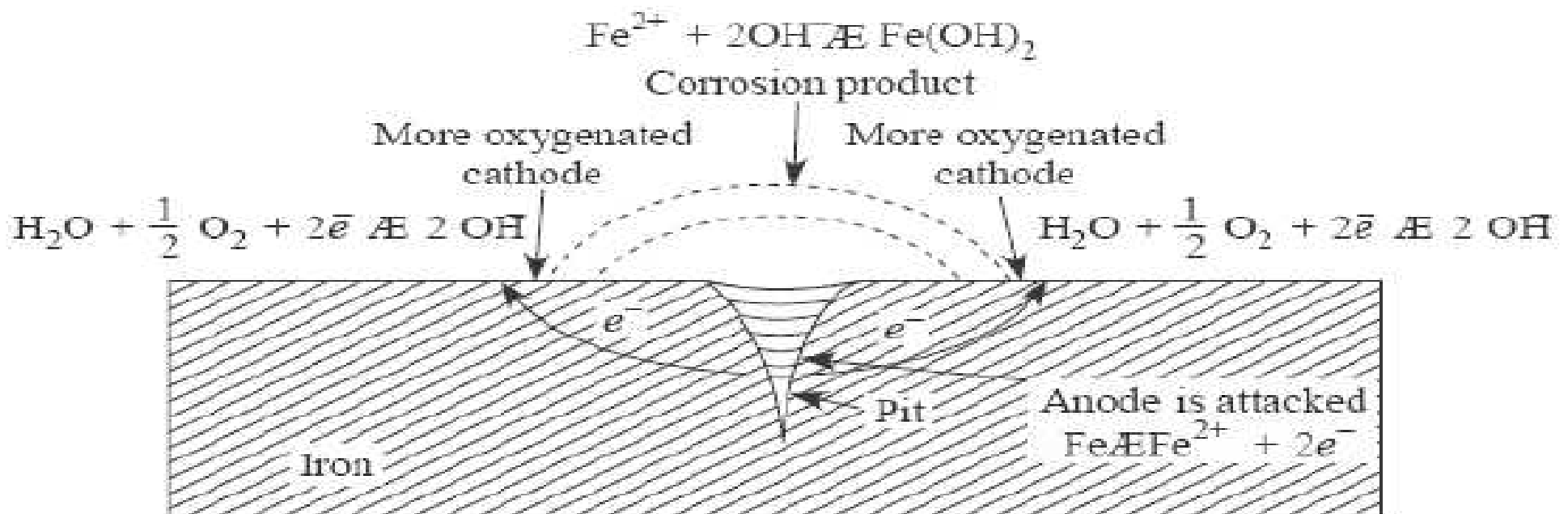
Differential aeration corrosion - facts

➢ Corrosion is accelerated in apparently inaccessible places because the oxygen deficient areas serve as anodes – cracks or crevices serve as foci for corrosion

➢ Corrosion is accelerated under accumulation of dirt sand, scale or other contamination – restricts the access of oxygen and establishes an anode to promote greater accumulation – Localized corrosion and non-uniform corrosion

➢ Metals exposed to aqueous media corrode under blocks of wood or piece of glass which screen that portion of metal from oxygen access – More intensified with the time

- 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.
- It is due to the formation of a highly protective thin layer being formed on the surface of that metal.
- Non-porous, insoluble and resistant to corrosive atmosphere – Self healing nature – broken – repair itself
- Passivity is not a constant state, but exists only in certain environment conditions which tend to maintain thin protective oxide films on their surface.
- Presence of oxygen – oxide film automatically repair
- In the absence of oxygen – chemical active – rapidly corroded
- Examples of passive metals and alloys are Ti, Al, Cr and some alloys of steels containing these metal systems.
- Alloy : More corrosion resistant than metal – thin film (0.0004 mm thick) : Resistance
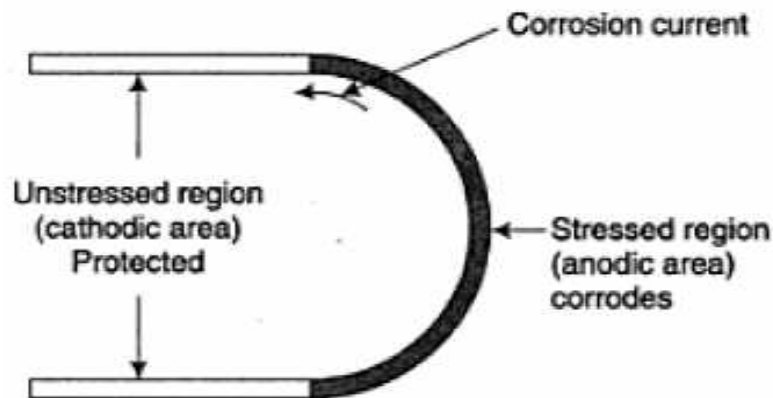
Pitting corrosion

➤ Pitting corrosion is a localized form of corrosive attack that produces holes or small pits in a metal.

➤ The bulk of the surface remains unattacked.

➤ Pitting is often found in situations where resistance against general corrosion is conferred by passive surface films.

➤ Localized pitting attack is found where these passive films have broken down.

➤ Pitting can be one of the most dangerous forms of corrosion because it is difficult to anticipate and prevent, relatively difficult to detect, occurs very rapidly, and penetrates a metal without causing it to lose a significant amount of weight.

- Pitting corrosion occurs – inaccessible places (cracks, dirt, dust and scale accumulated areas,) – O_2 deficient areas serves as anode – creates small pits, pinholes and cavities.
- Pitting also results from break down of protective film on a metal – due to a) surface roughness b) scratches or cut edges c) non-uniform stress d) sliding under load e) chemical attack
- Small anodic and large cathodic area created.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

Corrosion product

More oxygenated cathode

More oxygenated cathode

$$H_2O + \frac{1}{2}O_2 + 2\bar{e} \rightarrow 2OH^-$$

$$H_2O + \frac{1}{2}O_2 + 2\bar{e} \rightarrow 2OH^-$$

e^-

e^-

Pit

Anode is attacked
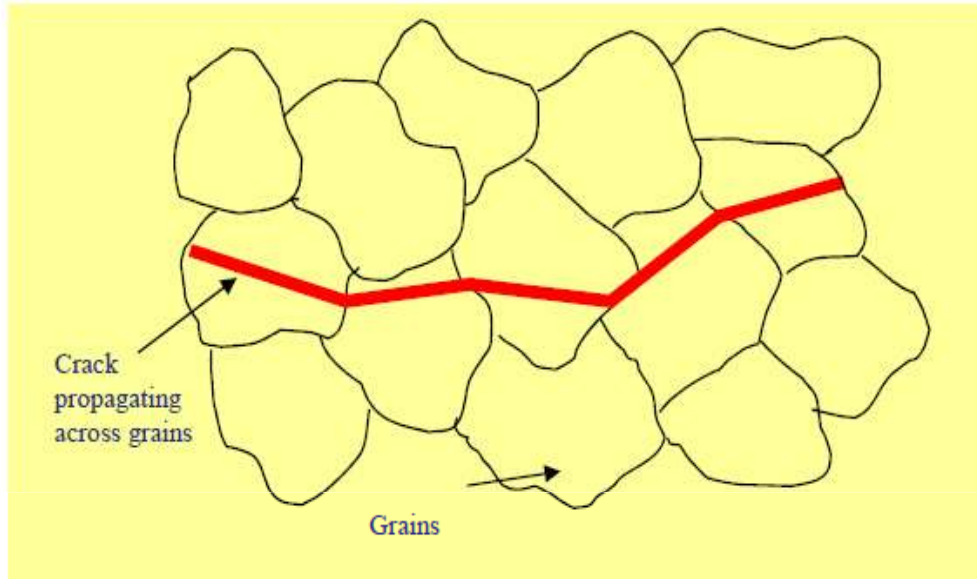$$Fe \rightarrow Fe^{2+} + 2e^-$$
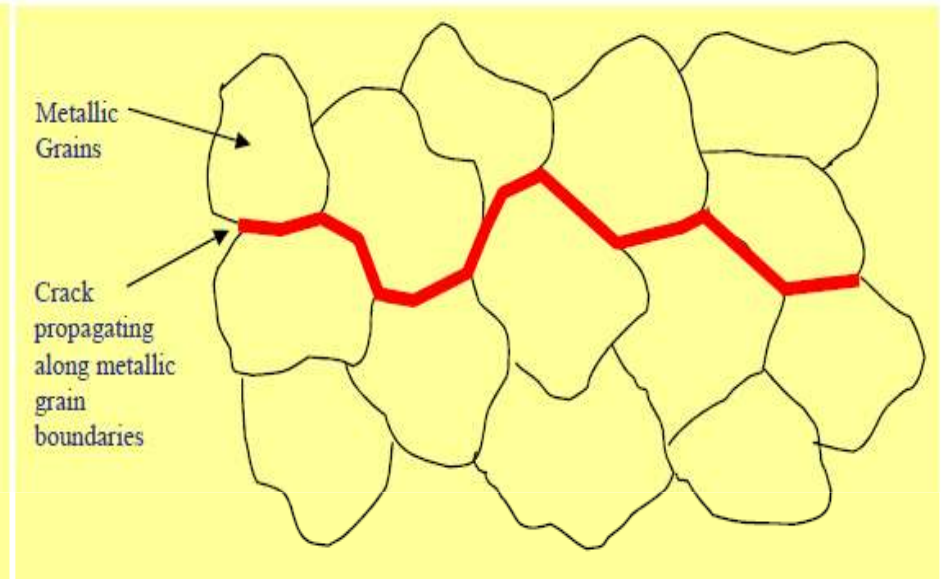
Iron

Stress Corrosion Cracking (SCC)

➢ In a metallic structure, if there is a portion under stress, it will act as anode and rest part of the structure will act as cathode.

➢ Spontaneous corrosion induced cracking of a material under static (or residual) tensile stress.

➢ It is now a galvanic system and hence anodic part which is small in area will corrode more.

➢ Cracks grow along grain boundaries as a result of residual or applied stress or trapped gas or solid corrosion products

➢ Stress corrosions are observed in the different systems– Two classic examples of SCC

    ➢ Caustic embrittlement

    ➢ Season cracking – Only specific environment cause failure

Corrosion current

Unstressed region (cathodic area) Protected

Stressed region (anodic area) corrodes

Stress corrosion cracking

Crack propagation

Transgranular

Intergranular

Caustic embrittlement

- A type of stress corrosion occurring in steel tank (Boiler) at high temperature and in alkaline medium.
- Boiler water has Na_2CO_3; it will be hydrolyzed at high temperature to give NaOH.
- It flows into hair cracks and crevices. There it reacts with iron and forms Na_2FeO_2 (sodium Ferroate) which decomposes to give Fe_3O_4 (ferro ferric oxide – $FeO.Fe_2O_3$) and NaOH.

$$3Na_2FeO_2 + 3H_2O \longrightarrow Fe_3O_4 + H_2 + 6NaOH$$

- NaOH thus formed further reacts with iron to cause corrosion. It is called caustic embrittlement.
- Remedy – Addition of Na_2SO_4 to boiler water in addition to tannin and lignin to boiler water prevents caustic cracking.
- By neutralization of excess of alkali with dilute acid (or) control of pH value caustic embrittlement can be controlled.

Season cracking

- It is applied to stress corrosion of copper alloys.
- Pure copper metal is less sensitive to stress corrosion.
- However, presence of alloying impurities like P, Zn, Al, etc. results in marked sensitivity for corrosion.
- Some of the alloys like brass are made of zinc and copper.
- In the presence of ammonia or amines, induces season cracking in zinc and copper
- These metals form complexes $[Cu(NH_3)_4]^{++}$
- $[Zn(NH_3)_4]^{++}$ which appear as corrosion products.
- Remedy – By applying protective coatings, Using corrosion inhibitors, stress relief heat treatments
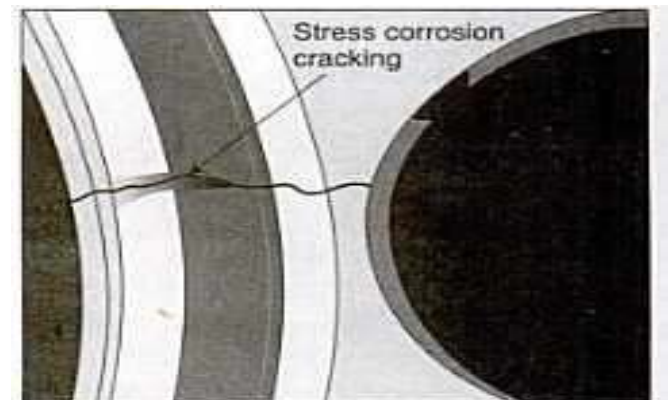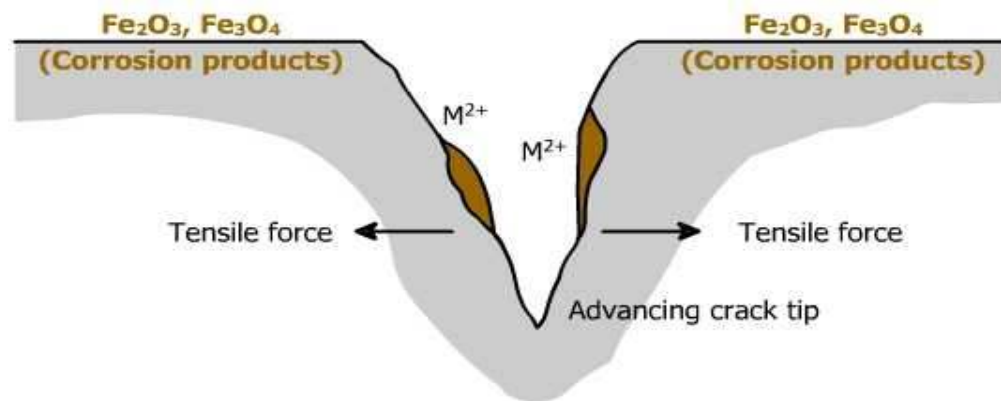
Difference between chemical and electrochemical corrosion

Sl. No.	Chemical Corrosion	Electrochemical Corrosion
1.	It occurs in dry condition.	It occurs in the presence of moisture or electrolyte.
2.	It is due to the direct chemical attack of the metal by the environment.	It is due to the formation of a large number of anodic and cathodic areas.
3.	Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
4.	Corrosion products accumulate at the place of corrosion	Corrosion occurs at the anode while the products are formed elsewhere.
5.	It is a self controlled process.	It is a continuous process.
6.	It adopts adsorption mechanism.	It follows electrochemical reaction.
7.	Formation of mild scale on iron surface is an example.	Rusting of iron in moist atmosphere is an example.

Factors influencing corrosion

Metallic factors
- Relative areas of cathode and anode
- Potential difference of electrodes
- Over voltage
- Physical state of metal
- Purity of metal
- Nature of surface film
- Solubility of corrosion products

Environmental factors
- pH of the medium and temperature
- Humidity of air
- Presence of impurities in atmosphere
- Presence of suspended particles in atmosphere
- Nature of ions present
- Conductance of the corroding medium
- Formation of oxygen concentration cell
- Polarization of electrodes

Relative areas of cathode and anode

➢ Smaller anode area w. r. t. cathode area induce severe and faster corrosion rate at the anodic area.

Cathodic area $\propto$ rate of corrosion

or

Anodic area $\propto \dfrac{1}{\text{rate of corrosion}}$

Potential difference of electrodes

➢ Greater the electrode potential difference of metal, faster is the rate of corrosion.

➢ Eg. Corrosion of Zn is severe in Zn–Cu (electrode potential difference, 1.1 V) system than in Zn–Fe (electrode potential difference, 0.78 V).

Overvoltage

➤ Decomposition voltage of an electrolyte varies with the nature of the electrodes employed for the electrolysis – it is considerably higher than calculated from the difference of the reversible electrode potentials – overvoltage.

Rate of corrosion $\propto$ 1/overvoltage

➤ EMF of standard Cl_2–H_2 cell is 1.36 V. But unless one use a platinized Pt electrode, the decomposition voltage required to generate H_2 and Cl_2 by electrolysis of the electrolyte is considerably greater than 1.36 V. This extra voltage above cell voltage is overvoltage.

➤ Consider dissolution of pure Zn in dil.HCl. The SEP of Zn is –0.76 V it should readily dissolve in dil. HCl with evolution of H_2. But in practice it is not so because hydrogen overvoltage on Zn is 0.70 V.

➢ When few drops of $CuSO_4$ added, the corrosion of Zn is observed because some Cu get deposited on the Zn metal, forming minute cathode, where the H_2 overvoltage over Cu is only 0.3 V.

➢ Reduction in overvoltage plays important part in accelerating corrosion.

Magnitude of overvoltage

➢ Low on – Pt, Au and Ag

➢ Intermediate on – Fe, Ni, Co, C and Cu

➢ High on – Zn, Hg, Cd and Pb.

➢ Overvoltage is low on rough, abraded metal surface than smooth and polished surface.

Temperature $\propto$ 1/overvoltage

Purity of metal

Rate of corrosion $\propto$ 1/Purity of metal

Impurities in metals form tiny galvanic cells – corrosion

Eg. Zn containing impurity, Pb or Fe cause corrosion.

Metal	%purity	corrosion rate
Zn	99.999	1
Zn	99.99	2650
Zn	99.95	5000

➤ Corrosion resistance of metal improved with purity.

Physical state of metal

➤ Grain size, orientation of crystals, stress etc. affects rate of corrosion.

➤ Smaller grain size – greater solubility – greater is the rate of corrosion.

➤ Area under stress, even in pure metal, affected by corrosion.

Nature of surface film

➢ Greater the specific volume ratio – lesser is the oxidation corrosion rate.

➢ Eg. Specific volume ratio of Ni, Cr and W are 1.6, 2.0, 3.6 respectively. Rate of oxidation is least in W even at elevated temperature.

➢ Oxide film render thicker by prolonged heating, chemical oxidizing agents and by anodizing.

➢ If the oxide film is volatile – excessive corrosion.

Solubility of the corrosion product

➢ Rate of corrosion faster if corrosion product formed is soluble in the medium to which it is immersed eg. Pb not attacked by pure air-free water – readily corroded by water containing dissolved air– $Pb(OH)_2$ soluble in water.

➢ If the corrosion product insoluble it may cover electrode surface as thin film and inhibits corrosion.

➢ Eg. Pb in aerated water contains CO_3^{2-} or SO_4^{2-} salt they form insoluble coating of $PbCO_3$ or $PbSO_4$ on the surface and prevent corrosion.

➢ Eg. Pb in H_2SO_4 form $PbSO_4$–insoluble thin film–inhibits corrosion.

Environmental factors

Temperature

Rate of corrosion $\propto$ temperature

- Increase in temperature – increases rate of reaction, rate of diffusion, decrease in polarization – increases rate of corrosion
- Increase in temperature reduces dissolved O_2 which affects the formation of oxide film – passive metal become active
- Caustic embrittlement – high temperature

Humidity

- Humid environment favors corrosion of metals.
- Corrosion of Fe rather slow in dry air-increase rapidly in moist air.
- Moisture acts as solvent for gases (O_2, SO_2, CO_2 etc.) and salts to furnish electrolyte for corrosion cell.

pH of the medium

- Acidic media – more corrosion than alkaline and neutral media.
- Eg.Zn corrode even in H_2CO_3 solution but corrodes min. at pH= 11
- Rate of corrosion of metal increases with increase in [H^+] (i.e pH<7)
- Increase in [H^+], increases the solubility of corrosion product.

Presence of impurities in atmosphere

➤ Atmosphere in industrial area contains corrosive gases, CO_2, H_2S, SO_2 and fumes of HCl, H_2SO_4 etc.

➤ The presence of above mentioned impurities under humid condition sets a electrochemical cell and induce corrosion.

➤ Similarly in marine environment presence of NaCl and other salts under humid condition speed up the corrosion.

➤ Suspended impurities like charcoal deposit on metal can absorb sulfur gas and moisture and enhance corrosion rate.

Nature of ions present

➤ Silicate anion (SiO_4^{2-}) leads to formation of insoluble product which inhibit further corrosion.

➤ Chloride (Cl^-) ions, destroy protective and passive surface film and thereby induce corrosion.

➤ Presence of traces of Cu in mine water, accelerates the corrosion of iron pipes.

➤ Many metals including Fe undergoes rapid corrosion when corroding medium contains NH_4^+ salts due to formation of more soluble $M(NH_3)_n$ complex.

Conductance of the corroding medium

- High conductance – more corrosion.
- Corrosion of metallic structure in underground depend on conductance of the medium.
- Dry sandy-soil – lower conductance – low corrosion.
- Clay and minerals – high conductance – high corrosion.

Formation of oxygen concentration cell

- Exposing moist-metal to oxygen promotes corrosion.
- Metal part exposed to high oxygen – cathode, less oxygen – anode and lead to formation of oxygen concentration cell.
- Oxygen concentration cell promotes corrosion, but corrosion occurs where oxygen concentration is less.
- Eg. Waterline corrosion, buried pipelines and cables passing from one type of soil to another and crevice corrosions

Polarization $\propto$ 1/corrosion rate

➢ During electrolysis – if ions are not transported to or from an electrode as rapidly as they are consumed or created – concentration polarization exists.

➢ Concentration of corroded material is high near anode and less near cathode – concentration difference between electrode surface and bulk solution – polarization – reduce potential difference.

➢ For corrosion to occur electrolyte species must be supplied to cathode and it should be removed from anode continuously – Both process occur by diffusion – retarded – slow rate of corrosion.

➢ Greater polarization, Stagnant solution, low concentration of electrolyte and low temperature reduces diffusion rate and decreases corrosion.

➢ Overvoltage and passive film – cause polarization – decrease corrosion – More adherent passive film acts as barrier between electrode and electrolyte and reduces rate of diffusion of reactant and product of the electrode reaction.

➢ Inhibitors binds electroactive species and reduces its concentration near electrodes –cause polarization – reduces corrosion.

End of Module 3