ENGINEERING CHEMISTRY

COURSE CODE: 18CY1BSCHY/ 18CY2BSCHY

UNIT - 2

CORROSION AND METAL FINISHING

Corrosion - Definition, Electrochemical theory of corrosion, Types of corrosion - differential metal, differential aeration (pitting and water line corrosion) and stress corrosion; Factors affecting the rate of corrosion; Corrosion control: inorganic coatings – anodizing and phosphating; Metal coatings - galvanization, tinning; Cathodic protection – Sacrificial anode, Impressed current method, Electroplating of Chromium,

CORROSION

Definition: "Gradual deterioration/destruction of metal at its surface by chemical or electrochemical reaction between the metal and the surrounding environment (air, moisture) is called corrosion".

- Corrosion is surface phenomenon
- Most metals, except noble metals such as gold and platinum, undergo corrosion
- Eg.: **Rusting of iron**: reddish brown deposition on iron and steel objects due to hydrated ferric oxide ($Fe_2O_3.nH_2O$)
- Eg.: **Green scales** on copper vessels due to the formation of basic cupric nitrate ($Cu(NO_3)_2 + Cu(OH)_2$)
- Corrosion can be slow or fast based on the nature of metal and the surrounding environment

Why study of corrosion is important?

- The corrosion process, although slow, affects the metal drastically.
- Corrosion of metals causes a loss of 2 to 2.5 billion dollars per annum all over the world.
- The common consequences of corrosion are as follows:
  1. Corrosion causes severe economic loses and hampers the safety of equipment.
  2. Metal loses its strength and can become brittle, leading to the failure of machine parts.
  3. Frequent replacement and maintenance of the corroded parts leads to indirect financial loses, which include production loss during replacement and maintenance.
  4. Corroded pipes may lead to leakage of inflammable and toxic gases resulting in fire hazards, environmental pollution and affect the human and animal population adversely.

5. It causes contamination of the products. (Eg.: traces of metals may alter the color of dyes; Food articles in corroded containers may get spoilt due to contamination).
6. Nearly 25% of the annual production of iron is wasted because of corrosion.

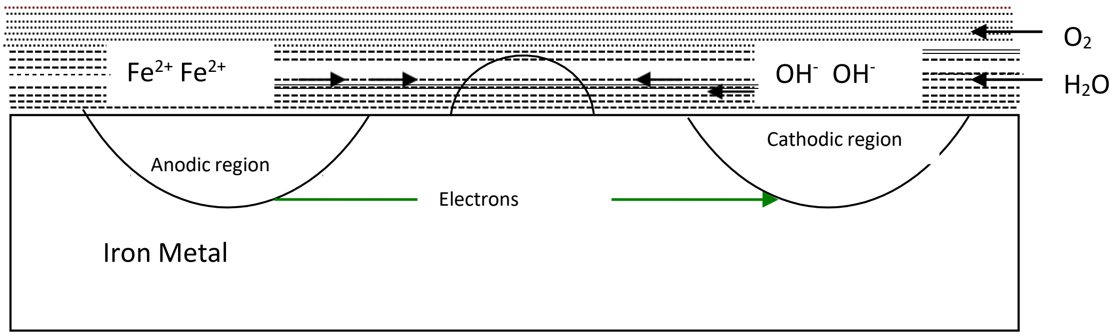
Therefore, the study of corrosion and its prevention is essential for both engineers and metallurgists.

Why metals undergo corrosion?

- Naturally, metals are present in their oxidized form in their ores.
- During their extraction, lot of energy is put to reduce metal ions to metal atoms. Hence, metals are always in higher energy sate and thermodynamically unstable. Metals try to lower their energy by spontaneously reacting with chemicals present in their surrounding environment like O_2 and H_2O. This process of loss of metal is termed as metallic corrosion.

Electrochemical theory of corrosion by taking iron as example or Rust formation of iron (diagram with labeling is important)

- Rust formation on iron can be explained by Electrochemical theory of corrosion.
- According to this theory, when iron is exposed to atmosphere air (O_2) & moisture (H_2O), the following changes occur leading to corrosion;
    - > Formation of large number of minute anodic and cathodic areas on the metal surface (galvanic cells).



At anodic area:

- Oxidation takes place and iron (Fe) is oxidized into ferrous ions (Fe^{2+}) liberating electrons.

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

- Thus, metal is lost or destroyed at the surface due to dissolution.
- The electrons released at anodic area move to the cathodic area through metal.

At Cathodic area

- Chemical species present on the metal surface get reduced.
- Cathodic area of the iron just provides the surface for reduction but remains unaffected.

- Depending upon the environment, the following reduction reactions are possible;

- At cathode, there are three possible reduction reactions depending upon the environment

a) If the metal is exposed to moisture (H_2O) and air (O_2) under neutral conditions,

$$1/2\, O_2 + H_2O + 2e^- \longrightarrow 2\, OH^-$$

b) If the metal is exposed to only moisture under neutral condition in the absence of air,

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

c) If the metal surface is exposed to acidic medium,

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

Fe^{2+} ions released at anodic area move towards cathode on the surface of metal.

- Similarly, **OH^-** ions formed at cathode move towards anode.
- They meet near the cathode forming ferrous hydroxide

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

- Ferrous hydroxide further reacts with H_2O and O_2 forming hydrated ferric oxide, brownish red corrosion product called rust

$$2\,Fe(OH)_2 + 1/_2\,O_2 + H_2O \longrightarrow \underset{\text{Rust}}{[Fe_2O_3 \cdot 3H_2O]}$$

Electrochemical Series

- The tendency of metal to undergo oxidation is a measure of its tendency to corrode.
- The oxidation tendency of metal can be known from its standard electrode potential (E^o) value.
- E^o value of all the electrode is measured with respect to Standard Hydrogen Electrode (SHE) and arranged in an increasing order in a series which is called as EMF or electrochemical series.
- Lower the electrode potential, higher the tendency of metal to undergo oxidation.
- Rate of corrosion not only depends upon the tendency to undergo oxidation but also upon other environmental factors.

M^{n+}/M	**E^o in Volts**
Li^+/Li	-3.02
Na^+/Na	-2.71
Mg^{2+}/Mg	-2.34
Ti^{2+}/Ti	-1.75
Al^{3+}/Al	-1.67
Zn^{2+}/Zn	-0.76
$Cr^{3+}Cr$	-0.71
Fe^{2+}/Fe	-0.44
Cd^{2+}/Cd	-0.40
H^+/H_2	***0.0***
Cu^{2+}/Cu	0.34
Ag^+/Ag	0.79
Pt^{2+}/Pt	1.20
Au^{3+}/Au	1.42

TYPES OF CORROSION

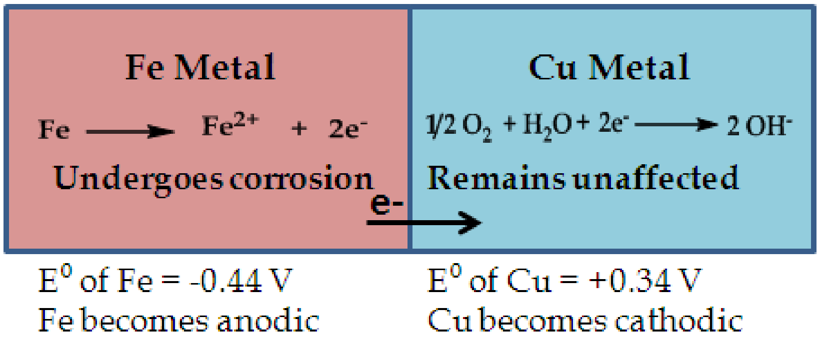
There are 3 types of corrosion;

1. Differential Metal Corrosion (Galvanic Corrosion/Bimetallic Corrosion)
2. Differential Aeration Corrosion (Concentration cell corrosion)
3. Stress Corrosion

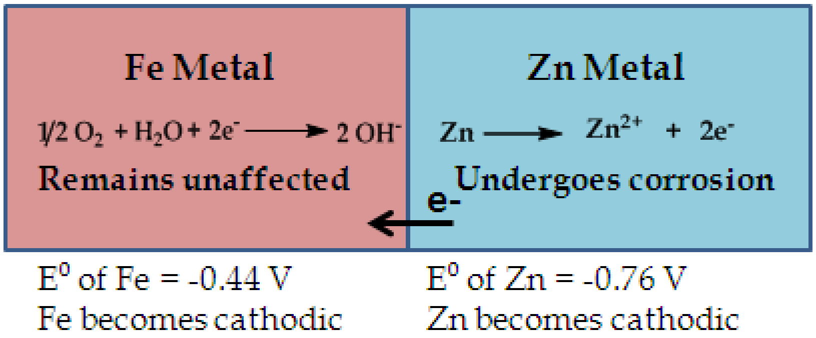
I. Differential Metal Corrosion (Galvanic Corrosion/Bimetallic Corrosion)

- It occurs when 2 dissimilar metals are in contact with each other in a corrosive environment
- Metal with lower electrode potential becomes anodic and undergoes oxidation; i.e. metal with lower electrode potential undergoes corrosion
- Whereas, metal with higher electrode potential becomes cathode and hence remains unaffected

Example 1:



- Standard electrode potential of Fe (-0.44 V) is lower than Cu (+0.34 V). Therefore, when Fe and Cu are in contact with each other, iron becomes anodic and undergoes corrosion and Cu remain unaffected.



Example 2:

- Standard electrode potential of Zn (-0.76 V) is lower than Fe (-0.44 V). Therefore, when Fe and Zn are in contact with each other, Zn becomes anodic and undergoes corrosion and Fe remain unaffected.

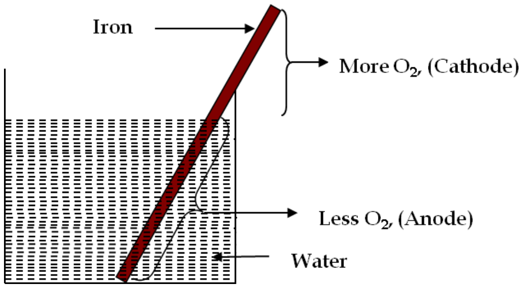
II. Differential Aeration Corrosion (Concentration cell corrosion)

- This type of corrosion occurs when a metal is exposed to different concentrations of air (O_2).
- Here, the part of the metal exposed to **lower concentration of O_2** will have lower electrode potential; therefore, it becomes anodic and **undergoes corrosion**.
- The part of the metal exposed to **higher concentration of O_2,** will have higher electrode potential; it becomes cathodic and **remains unaffected**.

Example: Iron rod partially dipped in water

- The part of iron dipped in water is exposed to less oxygenated environment or low O_2 concentration
- Therefore, the dipped part of iron acts as anode and undergoes corrosion

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



- The part of iron not dipped in water is exposed to higher O_2 concentration.
- So, it becomes cathodic, undergoes reduction reaction and remains unaffected in the corrosion process.

$$1/2\,O_2 + H_2O + 2e^- \longrightarrow 2\,OH^-$$

Other examples for Differential Aeration Corrosion (Concentration cell corrosion)

- Part of the nail inside the wall
- Window rods inside the frame
- Partially buried pipeline in soil
- Paper pins inside paper

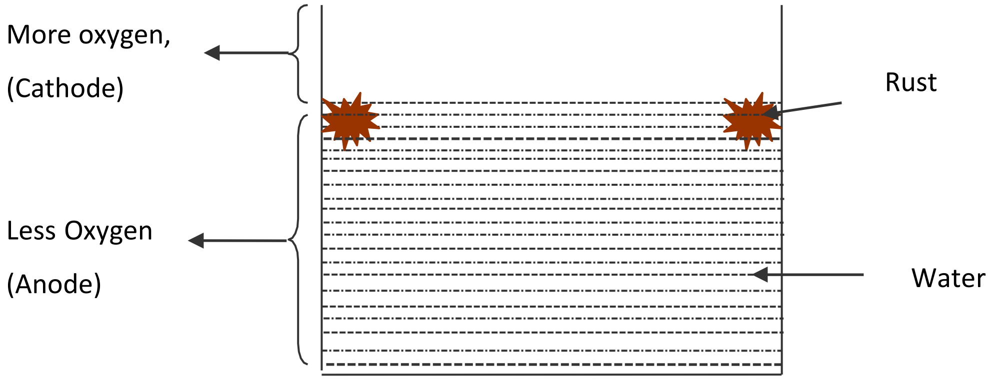
Differential aeration corrosion can be seen in;

1. Water line corrosion
2. Pitting corrosion

1. Water line corrosion

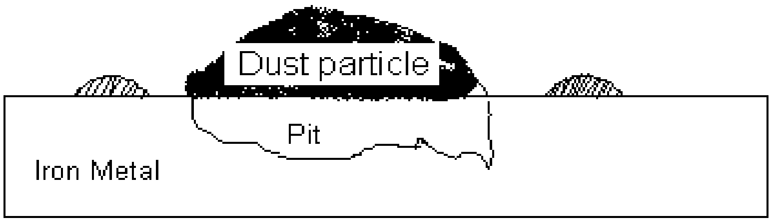
- It is a type of differential aeration corrosion.
- Generally, observed in steel/iron tanks partially filled with water and ships in ocean.

- In water tanks, part of the tank which is below water line (part which is filled with water) is exposed to less O_2 concentration environment. So, it acts as anode, undergoes corrosion.
- The part of water tank which is above water line is exposed to high O_2 concentration. So, it becomes cathodic and remains unaffected.



2. Pitting Corrosion

- It is a type of differential aeration corrosion process.
- Pitting corrosion is observed when dust particles or oil drops get deposited over the surface of metal.



- The portion of the metal which is covered is less aerated (less oxygenated) acts as anode, undergoes corrosion.
- Thus metal is lost underneath (below) the surface of dust particle forming deep, narrow pit (hole).
- The area which is not covered by dust is exposed to higher concentration of O_2; it becomes cathodic and hence remains unaffected.

Note: Pitting corrosion is a more dangerous form of corrosion. Because, once pit is formed, the concentration rate is accelerated due to further decrease in concentration of O_2 within pit. Hence, in a short duration, a narrow pit is formed resulting in the sudden breakdown of the metal.

III. Stress corrosion

- It is a type of corrosion that occurs when some part of the metal is under stress and exposed to specific corrosive environment.
- As a result, stressed part becomes more reactive (anodic). When this portion is exposed to specific corrosive environment, chemicals get chemisorbed on these sites and initiates corrosion.
- Stress corrosion decreases ductility, increases brittleness and results in cracking of metal surface which is called **stress corrosion cracking**.

Example: Caustic embrittlement in boilers

Caustic embrittlement in Boilers

- Caustic embrittlement is a form of stress corrosion that occurs in boilers operating at high pressure, at the stressed regions of the boiler.
- Caustic soda (NaOH) is the specific corrosive environment required for stress corrosion of water boiler. Therefore, this type of corrosion is called caustic embrittlement.
- Boilers are made up of mild steel, they undergo corrosion at the stressed portion when exposed to hot concentrated alkaline solution (or caustic soda, NaOH)
- Na_2CO_3 is added to boiler to reduce scaling.
- When boiler feed water is boiled, Na_2CO_3 undergoes hydrolysis forming NaOH.

$$Na_2CO_3 + H_2O \longrightarrow 2\,NaOH + CO_2$$

- NaOH formed flows into hairline cracks by capillary action and gets accumulated there.

- When the concentration of NaOH reaches > 10%, it reacts with Fe and forms Na_2FeO_2, which decomposes into Fe_3O_4 and NaOH.

$$Fe + 2\,NaOH \longrightarrow \underset{\text{sodium ferrite}}{Na_2FeO_2} + H_2$$

$$3\,Na_2FeO_2 + 4\,H_2O \longrightarrow \underset{\text{Ferrosoferric oxide}}{Fe_3O_4} + 4\,H_2 + 6\,NaOH$$

- NaOH formed further reacts with iron to cause corrosion cracking.
- As a result, boiler parts become brittle leading to boiler failure.

Factors affecting/influencing the rate of corrosion

The following factors which affects the rate of corrosion

1. Nature of metal

- In general, metals with lower electrode potential are more reactive and are susceptible for corrosion.
- Active metals like K, Na, Mg, Zn, etc. having lower electrode potential are more susceptible for corrosion.
- The metals having higher electrode potential are less reactive. Therefore, noble metals like Ag, Au, Pt, etc. are less susceptible for corrosion.

2. Electrode potential difference

(**Difference in potential between anodic and cathodic region**)

- The rate of corrosion depends on potential difference between anodic and cathodic regions.
- Generally, metal with lower the electrode potential has higher tendency for oxidation and hence higher tendency for corrosion.
- When two dissimilar metals are in contact, the metal with lower electrode potential becomes anode and undergoes corrosion.
- Whereas, the metal with higher electrode potential, becomes cathode and remains unaffected.

- Higher the potential difference between two metals, higher is the corrosion current (flow of electrons formed by oxidation) and higher will be the rate of corrosion of anodic metal.
- Therefore, when the metals are placed far away in the electrochemical series (EMF series), larger is the potential difference and greater is the rate of corrosion.

Example: Iron (-0.44 V) in contact with copper (+0.34 V) has a potential difference of 0.78 V; and iron in contact with tin (-0.14 V) has a potential difference of -0.30 V. Since, the potential difference between iron and copper is larger, iron in contact with copper undergoes corrosion at faster rate.

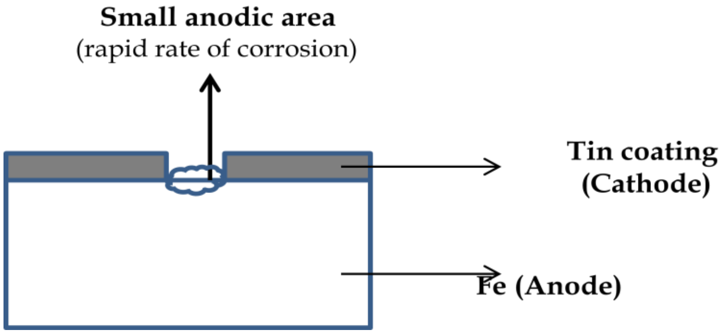
3. Relative anodic and cathodic area

- The rate of corrosion is greatly influenced by relative anodic and cathodic area.
- When metal corrodes, a part of it becomes anode and another part becomes cathode.
- If the surface area of anode is smaller and area of cathode is larger, then corrosion rate is intense (faster).

Reason:

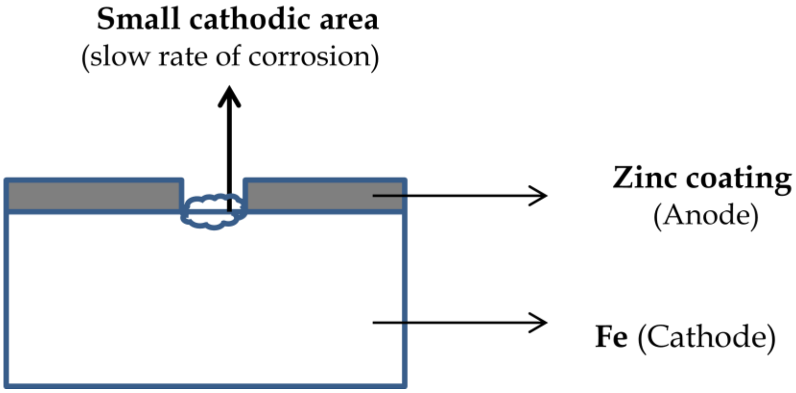
- Cathode is the region where reduction occurs by consuming the electrons.
- When the size of cathode is larger, the demand for electrons will be higher.
- This leads to rapid liberation of electrons at anode by oxidation to fulfil the demand of cathode.
- Thus, the corrosion rate is increased at smaller anode.
- When anode is larger and cathode is smaller, demand for electrons is less; therefore, corrosion occurs in a slower rate.

Example: (i) Coating of tin on iron



- When tin is coated onto iron metal surface, tin becomes cathodic (-0.14 V) and Fe is anodic (-0.44 V)
- If some part of iron is not covered (or peeled off), it results in small anodic area and large cathodic (Tin) area
- In this case, intense corrosion can be observed at smaller anodic Fe.

Example: (ii) Coating of zinc on iron



- When Zn is coated onto iron surface, Zn (-0.76 V) becomes anodic and Fe (-0.44 V) becomes cathodic.
- If some part of iron is not covered (or peeled off), it results in smaller cathodic (Fe) area and larger anodic (Zn) area.
- Therefore, in this case, corrosion rate is slower.

4. Anodic and Cathodic polarization

- Polarization is the process in which variation of electrode potential takes place due to insufficient movement of ions.
- Polarization at anode and cathode decreases the rate of corrosion.

Anodic Polarization:

- At anodic area, metal is oxidized liberating metal ions.
- If metal ions do not move freely towards cathodic area due to lower conductivity and higher resistance, they get concentrated at anodic region.
- This increases the potential of anode and decreases the rate of oxidation (Higher electrode potential at anode, lower the tendency for oxidation).
- The phenomenon of increasing potential of anodic area due to insufficient movement of ions over metal surface is called anodic polarization and the potential is called anodic polarization potential.

At anode: Metal undergoes oxidation

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

Potential of anodic area is calculated by,

$$E = E^0 + \frac{2.303RT}{nF} \log [Fe^{2+}]$$

Therefore, increase in the concentration of metal ions at anodic area due to polarization results in higher electrode potential and slower corrosion rate.

Cathodic Polarization:

- In case of cathodic polarization, there will be insufficient movement of OH^- ions, and they accumulate in the cathodic area
- Cathodic polarization is the phenomenon of decreasing potential of cathodic area due to insufficient movement of ions over metal surface and the potential is called cathodic polarization potential
- Therefore, anodic and cathodic polarization reduces the rate of corrosion

5. Nature of corrosion product

- Nature of the corrosion product largely decides the further rate of corrosion in metal
- The corrosion product formed on the metal surface may or may not prevent further corrosion
- Most metals form their oxides as corrosion products
- A thin film /layer of oxide is formed on the surface metal surface
- If the oxide is highly insoluble, stable, non-porous, conductivity, then the oxide layer acts a protective layer/ over metal surface, and prevents further corrosion of metal
- Eg.: The corrosion products of Al, Cr, Ti, etc. form passive oxide layers over the metal surface preventing further corrosion of metal
- If the oxide is highly soluble, unstable, porous it cannot prevent further corrosion of metal
- Eg.: The corrosion products of Fe, Zn, Mg, etc. unstable and therefore, do not prevent further corrosion of metal

6. Hydrogen overvoltage

- A metal with low hydrogen overvoltage on its surface is more susceptible for corrosion
- Here, hydrogen evolution takes place in the cathodic reaction
- This occurs in the metals which are exposed to acidic medium in the absence of oxygen
- Hydrogen overvoltage affects the corrosion current flow at the cathode
- When hydrogen overvoltage is lower on the metal surface,
  - faster will be the cathodic reaction i.e. release of H_2
  - faster will be the rate of corrosion
- When hydrogen overvoltage is higher on the metal surface,
  - slower will be the cathodic reaction

> slower will be the rate of corrosion

For understanding: Overvoltage is the excess voltage/potential/energy required to drive a cell reaction than thermodynamically expected value. So, when H_2 overvoltage is lower, evolution of H_2 is easy; therefore, cathodic reaction is faster, leading to faster corrosion rate.

7. pH

- "The rate of corrosion increases with decrease in pH".
- The pH of the solutions (acidic, alkaline or neutral) decides the type of cathodic reaction.

pH < 4

- When pH of a solution to which metal exposed is below 4, the concentration of H^+ ions will be more.
- So, liberation of H_2 will be higher at cathode, resulting in corrosion at faster rate.

$$2H^+ + 2e^- \longrightarrow H_2$$

pH between 4 and 10:

- When pH is between 4 and 10, rate of corrosion depends upon the availability of O_2 on cathodic area.

$$1/2\, O_2 + H_2O + 2e^- \longrightarrow 2\,OH^-$$

- If the concentration of O_2 is higher, higher is the corrosion rate.

pH > 10:

- When pH > 10, corrosion partially ceases (stops) due to formation of metal hydroxides on meat surface.

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

Generally, acidic medium is more corrosive than alkaline/neutral medium. But some metals like Al, Zn etc. undergo corrosion in alkaline medium in a faster rate.

8. Temperature

"Rate of corrosion increases with increase in temperature"

Reason: Increase in temperature causes increase in conductance (movement of ions) of the medium. This decreases polarization (accumulation of ions), hence corrosion progresses faster.

Example: Rate of O_2 reduction is doubled for every 30 °C rise in temperature
Rate of H_2 evolution is doubled for every 10 °C rise in temperature

9. Conductance of medium

"Rate of corrosion increases with increase in the conductance of the medium"

Reason: Higher the conductivity of the medium, migration of ions between the anodic and cathodic regions is faster. This causes decrease in polarization, which in turn results in increase in rate of corrosion.

Example: Metal immersed in sea water undergoes faster corrosion than the metals dipped in river water/normal water/distilled water. This is because sea water contains high concentration of salt, Na^+ and Cl^- ions. This increases the conductivity of the medium and migration of ions between the anodic and cathodic regions is faster. As a result, corrosion rate increases.

10. Humidity

"Higher humidity in environment to which metal is exposed, faster is corrosion"

Reason:

- This is because, humidity or moisture in atmosphere acts as electrolyte and provides conducting medium for the formation of galvanic cell and the movement of ions.
- Also, the gases like CO_2, SO_2, etc. dissolved in the moisture in atmosphere form electrolyte causing galvanic corrosion.

Example: Iron exposed to humid environment combines with O_2 and H_2O forming ferrous hydroxide, which can combine with atmospheric CO_2 forming ferrous bicarbonate. This results in faster corrosion of iron.

$$Fe + O_2 + H_2O \longrightarrow 2\,Fe(OH)_2$$

$$2\,Fe(OH)_2 + CO_2 \longrightarrow Fe(HCO_3)_3$$

Whereas, iron exposed to dry air undergoes slow corrosion.

CORROSION CONTROL

"Corrosion control is more realistic than corrosion prevention"

- Corrosion occurs due to oxidation and reduction reactions taking place at anode and cathode, respectively.
- These two reactions (oxidation and reduction) are simultaneous and interdependent
- Therefore, by preventing or decreasing the rate of one reaction, the overall corrosion process rate of can be controlled
- The following methods are commonly used to control corrosion;
    1. Protective coating
    2. Cathodic protection
    3. Anodic protection
    4. Corrosion inhibitors
    5. Design and selection of materials

1. Protective coatings

- Corrosion occurs mainly due to exposure of metal surface to environment containing O_2 and H_2O.
- Therefore, protective coatings prevent corrosion by acting as a barrier between metal surface and the corrosive environment.
- The following protective coatings are commonly used to prevent corrosion;

    A) Inorganic coating

        i) Metal coating

            a) Galvanizing (Anodic metal coating)

            b) Tinning (Cathodic metal coating)

ii) Surface conversion coating

a) Anodizing

b) Phosphating

Inorganic Coatings

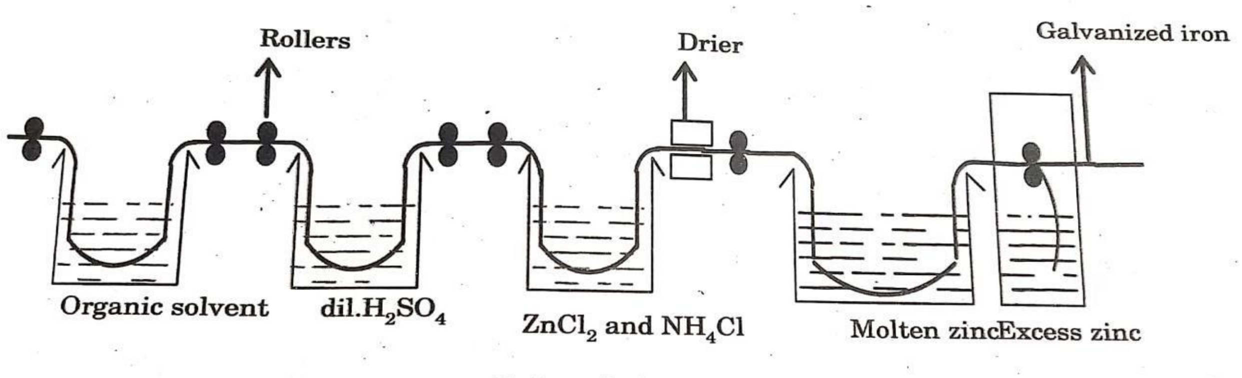
I. Metal coating: Metal coating can be anodic or cathodic depending on the base metal (metal to be protected).

a) Anodic metal coating (Galvanization):

"It is the coating of a layer of metal which is anodic to base metal".

Eg: Coating of zinc (more active metal) on iron (base metal).

Galvanization is a process of coating a layer of zinc on iron by hot dipping method.



Galvanizing

Galvanizing process involves following steps;

- Iron sheet is passed through organic solvent to remove oil & grease impurities present on it (degreasing process).
- The degreased iron sheet is washed with dil. H_2SO_4 to remove rust (any oxide layer) present on the iron surface (Pickling process).
- Then, the iron sheet is treated with aqueous solution of $ZnCl_2$ and NH_4Cl which acts as flux and then dried.
- Once the surface of iron is cleaned by these steps, it is then dipped in Molten Zinc at 450 °C
- The excess zinc present on the iron sheet is removed by passing it through rollers

(**Flux** is a cleaning or purifying chemical agent. It is a substance that is added to molten metal to bond with impurities that can be readily removed)

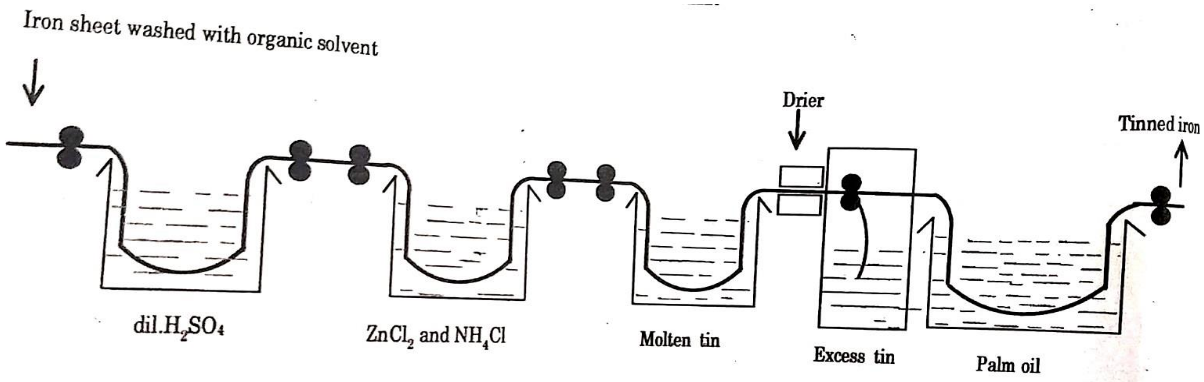
Applications of Galvanization/anodic metal coating:

- Galvanizing is a most widely used method to protect iron articles because of low cost and eases of application.
- Galvanizing is used to protect iron in roofing sheets, fencing wire, buckets, bolts, nuts, bails, screws, pipes, tubes, etc.
- Galvanized steel is used in building constructions, where high degree of corrosion resistance required.

b) Cathodic metal coating:

"It is the coating of a layer of metal which is cathodic to base metal".

Tinning is a process of coating a layer of tin metal on iron by hot dipping method.



Tinning

Tinning process involves following steps;

- Iron sheet is passed through **organic solvent** to remove oil & grease impurities present on it (degreasing process).
- The degreased iron sheet is washed with **dil. H_2SO_4** to remove rust (any oxide layer) present on the iron surface (Pickling process).
- Then, the iron sheet is treated with aqueous solution of **$ZnCl_2$ and NH_4Cl** which acts as flux and then dried.
- Once the surface of iron is cleaned by these steps, it is then dipped in **molten tin** at 230 °C.

– The excess tin present on the iron sheet is removed by passing it through rollers and then it is immersed in palm oil to prevent surface oxidation of tin.

Applications of Tinning/Cathodic metal coating:

> Tinning is used to coat iron articles for storing food stuffs such as jam, instant food, milk products, pickle, etc.

> Tin coated cans can be used to store kerosene.

> Tin is non-toxic in nature, so tin coated copper can be used for cooking and storing food.

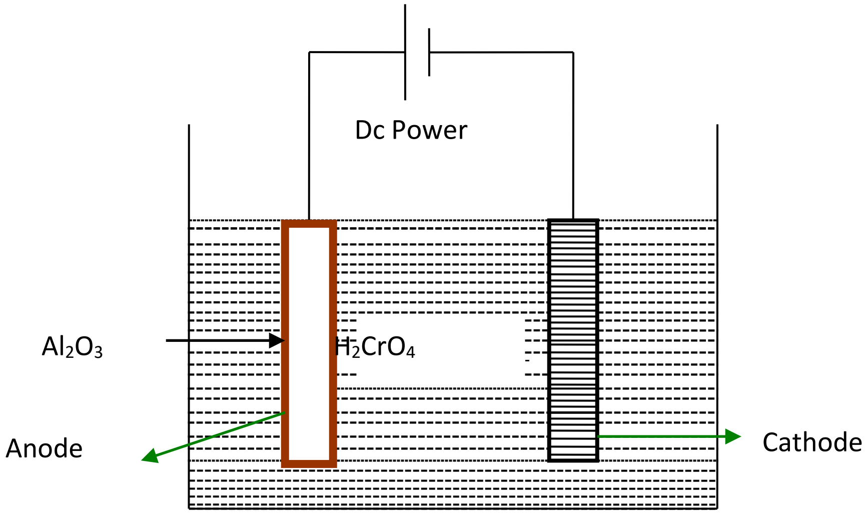
II. Surface conversion coating

It is a method in which surface of the base metal is converted into a protective coating by appropriate chemical modification.

a) Anodizing:

"It is the process of oxidation of outer layer of metal to its metal oxide by electrolysis". The oxide layer formed over metal surface acts as protective layer, preventing further corrosion.

Anodizing of Aluminium: (Converting the surface of Al metal into passive layer of Al_2O_3).



- In the anodizing process, Aluminium is cleaned, degreased and polished.
- Then, it is then taken as anode in an electrolytic cell.
- Steel or copper is taken as cathode.
- The electrodes are dipped in an electrolyte solution of 5 – 10% chromic acid (H_2CrO4).
- The temperature in bath is maintained at 35 °C.
- A current density of 100 A/m^2 is applied, which oxidizes a layer of Al to Al_2O_3 that gets deposited over the metal.
- The oxide layer formed is porous, so the metal is dipped in hot deionized water to seal the pores forming $Al_2O_3 \bullet H_2O$. This process is called sealing.
- The oxide layer becomes less porous and more protective preventing further corrosion of aluminium metal.

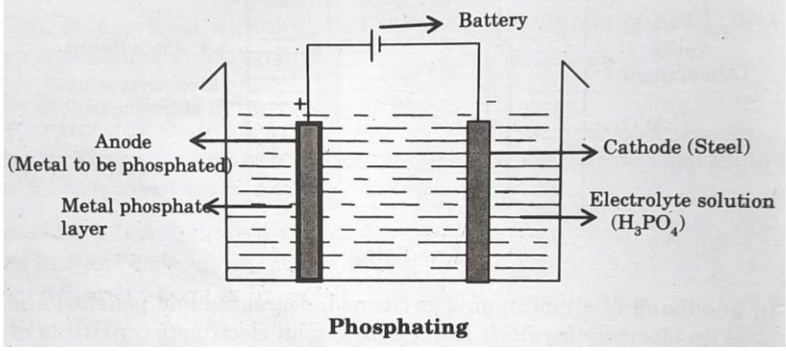
Applications of Anodizing:

> Anodized aluminium is used as an attractive, highly durable and corrosion resistant material in exterior for roofs, walls, buildings, home appliances, consumer products.

> Anodized articles are used in tiffin carriers, window frames etc.

b) Phosphating:

It is the process of coating metal phosphate on metal surface by oxidizing its outer layer in phosphoric acid medium.



Phosphating

- In phosphating process, metal to be phosphated is taken as anode in an electrolytic cell.
- An inert metal (steel) is taken as cathode.
- The electrodes are immersed in electrolyte, phosphoric acid (H_3PO_4).
- pH is maintained between 1.8 – 3.2 and the temperature 35 °C.
- The accelerators like NO^{3-}, ClO^{3-} are used to speed up the reaction.
- Direct current is passed through the cell to oxidize the outer layer.
- Metal ions thus formed combine with phosphate ions to give metal phosphate which gets deposited on the surface.

Applications of Phosphating:

- Phosphate coating is the first layer applied in the production of corrosion resistant automobile parts.
- It is used in steel sheet fabrications such as refrigerators and washing machines.
- Phosphate coatings are used mainly as base for paints and impart good paint adhesion quality to the surface of a metal.
- Phosphating of galvanized iron eases painting on its surface.

Cathodic Protection

It is the method of protecting metal against corrosion by making the entire metal cathodic by providing electrons from an external source. Here, corrosion can be prevented by eliminating the anodic area by converting the entire metal into cathode.

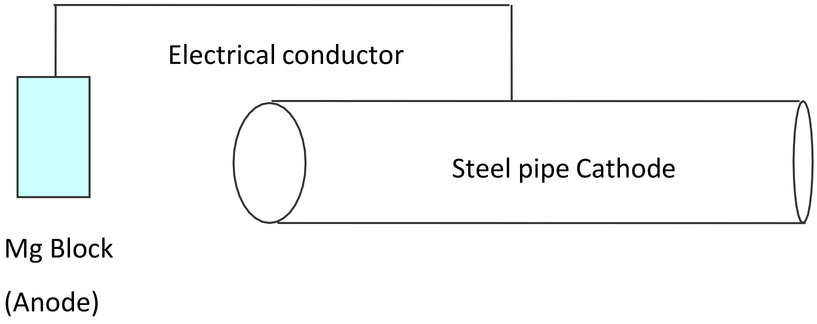
Cathodic protection of a metal can be done by 2 ways;

1) Sacrificial Anode method
2) Impressed Current method

1) Sacrificial Anode method:

- In this method, metal to be protected is connected to a more active metal (which will act as anode).
- For example, anodic metals like An, Mg, etc. can be used to protect iron articles.

- When an anodic metal (Zn, Mg) is in contact with iron, a galvanic cell is set up, where anodic metal becomes anodic area and whole iron article becomes cathodic area.
- Anodic metal undergoes oxidation and provides electrons to the specimen (iron).
- Hence, the entire specimen becomes cathodic and thus protected from corrosion.
- In the process, anodic metal undergoes corrosion by scarifying itself to protect the specimen (iron). Therefore, it is called sacrificial anode.
- Sacrificial anodes have to be replaced frequently.

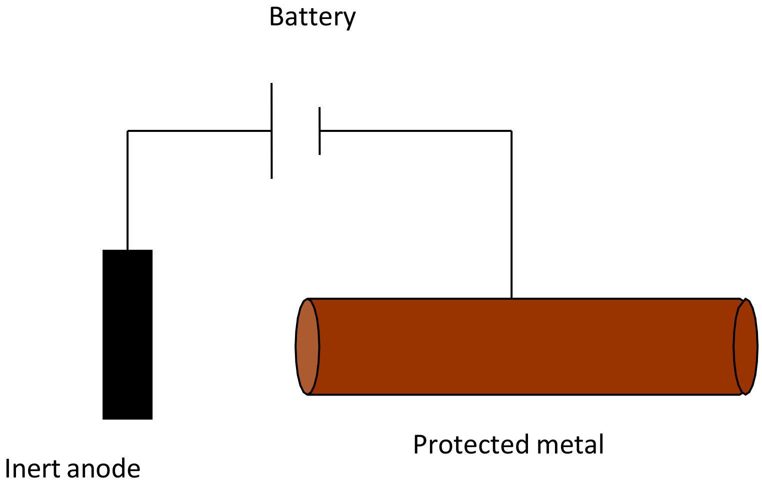


Eg: Mg bars are fixed to the sides of ships to act as sacrificial anode. Mg blocks are connected to bury pipe lines.

2) <u>Impressed Current method:</u>

- In this method, the electrons are supplied to the metal to be protected from an external source.
- The metal to be protected is connected to the negative terminal of a direct current (DC) source.
- The positive terminal of battery is connected to an inert anode like graphite to complete the circuit.
- In corrosion process, metal (acts as anode) undergoes oxidation liberating electrons.

- But in the impressed current method, the metal is protected by supplying the electrons to it in the reverse direction by applying a potential greater than potential of anodic reaction.
- In such condition/set up, metal acts as cathode, does not undergo corrosion and remains unaffected.



Impressed current method

Electroplating:

It is a process in which a layer of metal is deposited on the surface of another metal by applying electric current.

The common metals used for electroplating are Zn, Cu, Ni, Cr, Ag, Pt, Au, etc.

Electroplating of Chromium:

Chromium is one of the widely used metals for electroplating.

There are two types of Chromium coatings

1. Decorative Chromium coating (Not in the part of the syllabus)
2. Hard Chromium coating

Hard Chromium coating:

- It is a process of coating chromium on the surface of another metal (with a thickness of 2.5 to 300 μm) by applying electric current.
- It is carried out in an electrolytic cell consisting of two electrodes; the metal to be coated is taken as the cathode.
- The electrodes are dipped in the electrolytic solution under the following conditions;

Bath composition : 250 g of chromic acid (H_2CrO_4) + 2.5 g of H_2SO_4 (100:1 ratio)
Temperature : 45 – 55 °C
Current density : 290 – 580 A/ft^2
Current efficiency : 17 – 21%
Anode : Insoluble anodes like Pb-Sn or Pb-Sb
Cathode : Article to be plated/coated

Reactions involved in electroplating of chromium:

- Formation of chromic acid by the reaction of chromium trioxide (CrO_3) with water.

$$CrO_3 + H_2O \longrightarrow H_2CrO_4$$

- Chromic acid is in equilibrium with dichromic acid.

$$H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O$$

- Electrons supplied to the cathode reduce the salt of chromium to metallic chromium.

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

$$2\,Cr^{3+} + 6\,e^- \longrightarrow 2\,Cr$$

<u>Role of PbO_2:</u>

- PbO_2 checks the concentration of Cr^{3+} in the solution by oxidizing it to Cr^{6+}. Because, excess Cr^{3+} results in black or burnt deposition.

Why chromium anodes are not used in Cr plating?

Chromium anodes are not used in Cr plating because on oxidation, it releases Cr^{3+} which increases the concentration of Cr^{3+} in solution which leads to burnt deposition on the metal.

Applications of Hard Cr coating/plating:

- Hydraulic cylinders and rods
- Diesel engine cylinders
- Printing industries
- Industrial rods
- Cutting tools