<u>**Module -2.**</u>

<u>**CORROSION SCIENCE**</u>

Syllabus:

Definition and scope of corrosion, Dry and wet corrosion; Direct chemical corrosion, Electrochemical corrosion and its mechanisms; Types of electrochemical corrosion, (differential aeration, galvanic, concentration cell); Typical Electrochemical corrosion like Pitting, Inter-granular, Soil, Waterline; Factors affecting corrosion, Protection of corrosion.

Course Outcome: Utilize the knowledge of electrochemistry and corrosion science in preventing engineering equipments from corrosion.

Objectives:
- **To know about the basic nature of corrosion and its processes**
- **To identify types of corrosion**
- **To recognize the various factors affecting corrosion**
- **To understand about the various protective measures against corrosion**

1.0 Introduction

Whenever a design engineer choose a metal for any application, he/she consider the various properties of materials like mechanical, physical, chemical, etc. But, it is also true that a construction engineer gives importance to mechanical and physical properties of a metal and completely ignores the chemical properties, i.e., *effect of interaction of a metal with its environment.* For example, in construction we usually concentrate on the mechanical strength of metallic rods and normally ignore its chemical reactivity towards the environment. However, the interaction of metals & alloys with its environment plays an important role in selection and hence the performance of materials for any purposes. So, effective use of any constructional materials depends on mechanical, physical and chemical properties of materials.

For example, lead (Pb) pipes are not used for plumbo-solvent water(soft water) as concentration of Pb beyond 0.05 ppm is highly toxic and galvanized iron containers are not used for storing food stuff as zinc salts obtained via chemical interaction are toxic to human beings.

This lesson largely confined to interaction of metal with its environment, factors affecting such interaction and various way to control their interaction.

1.1 What is Corrosion?

Corrosion is "A process of loss of metallic materials from its surface through an undesirable chemical or electrochemical attack by its environment". It is a naturally occurring process, i.e., a thermodynamically feasible process for which $\Delta G < 0$.

Examples of corrosion: (1) R*usting of iron:*

Fe (substrate) + O_2 (environment) + H_2O (electrolyte) → Fe_2O_3. xH_2O (rust)
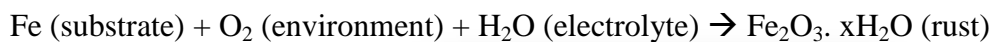
Fig. 1. Rusting of iron pipe

(2) *Tarnishing of silver:*

$2Ag + H_2S$ → Ag_2S (black layer on the Ag-surface) + H_2
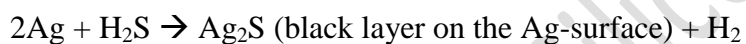

Ag$_2$S

Fig. Tarnished silver articles

(3) *Greenish layer on copper articles:*

$2Cu + CO_2 + H_2O + O_2$→ $CuCO_3 + Cu(OH)_2$

(Green layer; basic copper carbonate)
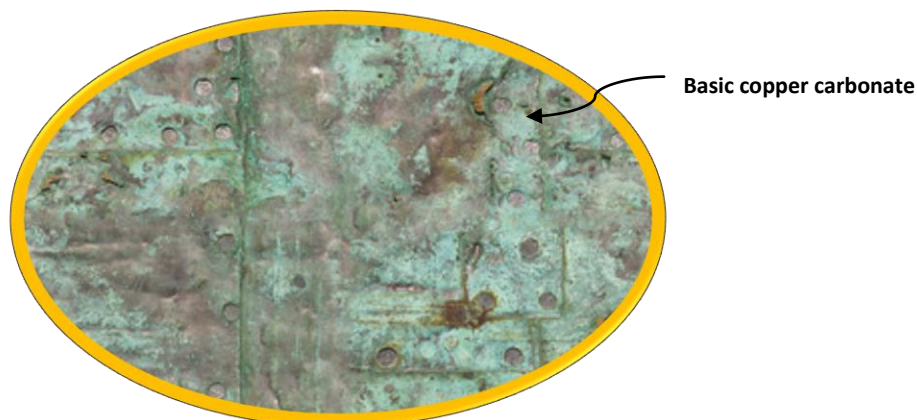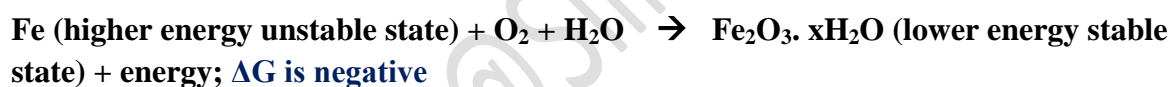
Basic copper carbonate
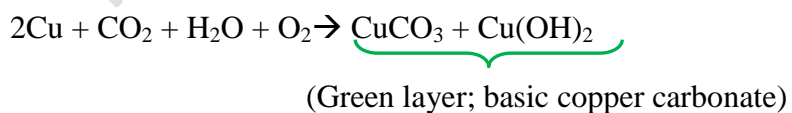
Fig. Green layer on the surface of a copper strip

1.2 Why corrosion occurs in metal?

We know that metals are extracted from their ores (i.e., combined form of metals) by the expense of huge amount of energy. It means that ores are energetically stable than pure metal. In other words, isolated pure metals are lies in excited state (a higher energy state) than their corresponding ores. For example, as pure Ca metal has a higher energy than its combined state, it prefers to lies in a lower energy & higher stability state, i.e., $CaCO_3$. So, when metals (possessing higher energy) are exposed to various environments (such as gases, moisture, liquids, etc.) during their uses, they interact with environment chemically or electrochemically cause loss of metal from its surface in the combined form (lower energy state). So in conclusion, the stability matter. We term such interaction as corrosion.

Fe (higher energy unstable state) + O_2 + H_2O → Fe_2O_3. xH_2O (lower energy stable state) + energy; ΔG is negative

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In the above reaction, the rust (Fe_2O_3. xH_2O) formed is thermodynamically more stable than the pure iron metal.

In general, corrosion leads to loss in many useful properties like mechanical strength, luster, ductility, conductivity, etc. of the pure metal.

1.3 Consequences of corrosion

Corrosion is a big problem. It is a costly process in terms of costly to repair, costly in terms of contaminated product, in terms of environmental damage, and costly in terms of human safety. The various effects of corrosion are as follows:

A. *Production related consequences are*:

(i) Loss in some important properties (like mechanical strength, ductility, etc.) of metals
(ii) Increase in maintenance cost (repair/replace) resulting in an increase in the overall production cost
(iii) Decrease in production rate

B. *Health related consequences are:*

(i) Contamination of foods
(ii) Leakage of toxic gases, liquids from the cylinder/pipes
(iii) Contamination of drinking water (water pollution)
(iv) Contamination of medicines
(v) Infection caused by rusted iron articles

C. Safety related consequences are:

(i) Sudden collapse of bridges, buildings results in loss of life/resources
(ii) Unpredicted failure of machineries/ machineries parts

So, by adopting suitable protection measures one can reduce this cost considerably. One can also check the rate of corrosion to a great extent by *regular inspection and maintenance of equipments*. For example, some equipment requires regular repainting and occasional inspection but equipment used in power plants, processing plants, aircraft, marine, etc. needed extensive maintenance schedules.

N.B.: Corrosion is not always unwanted. It is required in various processes like electroplating, surface finishing/smoothening, for sample preparation, etc.

Q.1 Mention some health related issues with corrosion.

Ans. Some of the health related issues due to corrosion are:

(i) Contamination of foods
(ii) Leakage of toxic gases, liquids from the cylinder/pipes
(iii) Contamination of drinking water (water pollution)
(iv) Contamination of medicines
(v) Infection caused by rusted iron articles

Q.2 **Mention some production related consequences with corrosion.**

Ans. *Production related consequences are*:

(i) Decrease in production rate
(ii) Increase in maintenance cost (repair/replace) resulting in an increase in the overall production cost
(iii) Loss in some important properties of metals

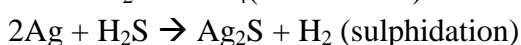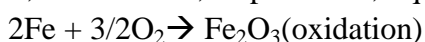Q.3 **Mention some safety related outcomes with corrosion.**

Ans.

(i) Sudden collapse of bridges, buildings results in loss of life/resources
(ii) Unpredicted failure of machines/ machineries parts

1.4 Types of corrosion

Corrosion affects the metal in various ways that depends on the nature metal itself and the nature of the immediate environment. One can classify corrosion in various ways which are as follows:

Based on the nature of the environment, corrosion is classified as (i) *dry corrosion and (ii) wet corrosion*.

(i) *Dry corrosion/Chemical corrosion:* This class of corrosion occurs mainly by direct chemical action of the environment (oxygen, hydrogen sulphide, sulphur oxide, chlorine, anhydrous inorganic liquids, etc.) on the surface of the metal. It occurs usually in absence of moisture and at high temperature. Example includes oxidation corrosion, chlorination, sulphidation, liquid metal corrosion, etc.

$$2Fe + 3/2O_2 \rightarrow Fe_2O_3 \text{(oxidation)}$$
$$Sn + 2Cl_2 \rightarrow SnCl_4 \text{(chlorination)}$$
$$2Ag + H_2S \rightarrow Ag_2S + H_2 \text{ (sulphidation)}$$

(ii) *Wet/Electrochemical corrosion:* This class of corrosion occurs when a metal comes in contact with a conducting liquid or when two different metals or alloys are either immersed or dipped partially in a solution. It occurs via formation of electrochemical cells in presence of moisture. It is otherwise known as *aqueous corrosion*. Wet corrosion is more common than dry corrosion. Examples are rusting of iron in an aqueous medium, Galvanic corrosion, etc.

Q.4 Differentiate between chemical and electrochemical corrosion.

Chemical/ Dry Corrosion	Electrochemical/Wet Corrosion
It occurs in dry or non-aqueous medium (in absence of moisture)	It occurs in wet condition or in presence of moisture
It occurs via direct chemical attack	It occurs via formation of electrochemical cells
It is uniform in nature (non localized)	It is not uniform. Localized in nature
It is a slow process	It is a fast process
It occurs on both homogeneous and hetero generous surfaces	It occurs only on heterogeneous surfaces
Corrosion product accumulates at the place of corrosion	Corrosion occurs at anode but product accumulated near the cathode
Example: Oxidation	Example: rusting of iron in an aqueous medium

1.5 Chemical or Dry Corrosion:

Dry corrosion of metals occurs in non-aqueous solution and in non-humid (dry) atmosphere. It occurs due to direct chemical interaction between the surfaces of metal and corrosive environment like atmospheric gases (e.g., O_2, H_2S, Cl_2, etc.) or anhydrous liquid like HCl, H_2SO_4, etc.

Most common type of dry corrosion is **Oxidation Corrosion.**

Oxidation Corrosion: It occurs when a reactive metal is exposed to O_2 in absence of moisture. Upon oxidation a thin layer of oxide formed on the surface of metal

- **(i)** $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
- **(ii)** $Ca + 1/2O_2 \rightarrow CaO$
- **(iii)** $Mg + 1/2O_2 \rightarrow MgO$

1.5.1 Nature of Oxide layer

A thin layer of oxide formed on the surface of metal can be non-porous, porous, unstable or volatile.

- (i) *Non-porous oxide layer*: It is stable, impervious and tightly sticks on the surface. It acts as a protective coating and prevents further corrosion.
  Example: Metals like Cu, Al, and Cr forms protective oxide layer such as CuO, Al_2O_3, Cr_2O_3, respectively.
- (ii) *Unstable oxide layer:* Such layer is formed by gold (Au) and platinum (Pt). As oxide layer decomposes back to metal and oxygen, Au and Pt do not undergo oxidation corrosion.
  Example: $4Au + 3O_2 \rightarrow 2Au_2O_3$
- (iii) Volatile oxide layer: The moment it is formed it gets volatilized and the metal surface is again gets exposed for further attack leading to continuous and rapid corrosion.
  Example: $2Mo + 3O_2 \rightarrow 2MoO_3$ Molybdenum oxide (volatile oxide layer)

  $2V + 2.5O_2 \rightarrow V_2O_5$ Vanadium oxide (volatile oxide layer)

- ✓ *This is the reason why Molybdenum and Vanadium undergo rapid corrosion in oxygen atmosphere.*
- *(iv)* *Porous oxide layer*: Due to porous nature, oxygen attacks the metal through pores and corrosion continues till the entire metal is converted into metal oxide.
  Metals like Fe, Ca, Mg, K, etc. form porous oxide layer.

Q.5 Define oxidation corrosion with a suitable example.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Q.6. How many types of oxide layer can be formed on the surface of metal?

Ans. Four type (Porous, non-porous, unstable, Volatile)

Q.7.Which type of oxide results in rapid and continuous corrosion?

Ans. Volatile

Q.8 Name a metal which can form a volatile oxide layer (mention reaction).

Ans. Molybdenum (Mo); $2Mo + 3O_2 \rightarrow 2MoO_3$

Q.9Name two metals which form porous oxide layer.

Ans. Na, K

Q.9 Name two metals which form non-porous oxide layer.

Ans. Al and Cr

Q.9 Name two metals which form unstable oxide layer.

Ans. Au and Pt

Q 10. Corrosion resistance of iron can be significantly improved by alloying with aluminum. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Al is that alloying element forms a protective layer of Al_2O_3 on the surface of host metal.

Q 10. Corrosion resistance of iron can be significantly improved by alloying with chromium. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Cr is that alloying element forms a protective layer of Cr_2O_3 on the surface of host metal.

Q 11. Stainless steel maintains its luster for a longer period of time. Give reason.

Ans. Stainless steel is an alloy of iron with alloying elements like Al, Cr, etc. This alloying elements upon exposure to oxygen form a protective layer of Al_2O_3/Cr_2O_3 on the surface of it to prevent formation of rust.

Q.13. Which type of oxide film is more protective against corrosion?

Ans. Al_2O_3 form by Al is Non-porous.

1.5.2 Piling-Bedworth Rule (PBR)

PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide film is porous.

[N.B: **Specific Volume Ratio SVR = (Volume of metal oxide/n.Volume of metal)**]

Where 'n' is no of metal per oxide molecule. For example for MgO, n =1.

In general,If,

- SVR $\geq$ 1 but < 2; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, SnO_2etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.), usually less than or equal to 2
- SVR >>>1 (SVR>2); Oxide layer is less protective in nature (usually > 2), example, Fe_2O_3

SVR: Al_2O_3 (1.27); Cr_2O_3 (2); MgO (0.8), ZnO (1.58), NiO (1.42), etc.

Q. 12. What is PBR?

Ans. PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the SVR; greater is the rate of oxidation corrosion.

Q 13. What is specific volume ratio (SVR). Mention its significance.

Ans. Specific Volume Ratio SVR = (Volume of metal oxide formed/n x Volume of metal)

Where n = no of metal per oxide molecule

In general, If,

- SVR $\geq$ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is less protective in nature (usually > 2), example, Fe_2O_3

Numerical on SVR:

Example-1 What is the nature of the oxide layer (MO) formed on the surface of a metal 'M'? Given that: density of Metal and Metal oxide is 1.74 & 3.65 g/cc, respectively. The At. Mass of Metal is 24 and molecular mass of metal oxide is 40.

Ans. SVR =(**Volume of metal oxide formed/n x Volume of metal**), **here, n = number of metal per metal oxide, here n = 1**

Volume of MO = Mass of MO/Density of MO = (40/3.65) =10.958

Volume of Metal = **Mass of Metal/Density of Metal =** (24/1.74) =13.793

Now, **SVR = 10.958/(1x13.793) = 0.7944** which is less than 1. So, oxide layer is porpus and non-protective in nature.

Example-2 What is the nature of the Zinc oxide layer formed on the surface of Zinc? Given that: density of Zn and ZnO are 7.13 & 5.61 g/cc, respectively. The At. Mass of Zn is 65 and molecular mass of Zinc oxide is 81.

Ans. SVR =(Volume of metal oxide formed/n x Volume of metal), here, n = number of metal per metal oxide, here n = 1

Volume of MO = Mass of MO/Density of MO = (81/5.61) =14.438

Volume of Metal = **Mass of Metal/Density of Metal =** (65/7.13) =9.116

SVR = (14.438)/(1x9.116) = 1.583 >1 => Oxide layer is non-porous and Protective

Example-3 What is the nature of the Aluminum oxide layer formed on the surface of aluminum? Given that: density of Al and Al_2O_3 are 2.7 & 4.0 g/cc, respectively. The At. Mass of Metal is 27 and molecular mass of metal oxide is 102.

Ans. SVR = **(Volume of metal oxide formed/n x Volume of metal), here, n = number of metal per metal oxide, here n = 2**

SVR= 1.27 >1

=>The oxide layer is protective

Example-4 What is the nature of the Chromium oxide layer formed on the surface of chromium? Given that: density of Cr and Cr_2O_3 are 7.19 & 5.22 g/cc, respectively. The At. Mass of Cr is 52 and molecular mass of metal oxide is 152.

Ans. SVR = **(Volume of metal oxide formed/n x Volume of metal), here, n = number of metal per metal oxide, here n = 2**

SVR= 2.02>1

=>oxide layer is protective

Other Numerical

Q.1. How much rust ($Fe_2O_3.3H_2O$) will be formed when 10 kg of iron (Fe) have completely rusted away? (At. mass: Fe = 56, H =1, O =16)

Ans. Mol. Mass of rust ($Fe_2O_3.3H_2O$) = 214 g

Here, rust contains 2 Fe-atoms.

So, 214g of rust contains 2 x 56 = 112 g Fe

Or, 112 g Fe produces 214 g rust

Then, 10 kg = 10,000g of Fe will form = (214/112) x 10,000 = 19107 g = 19.1 kg.

Q.2. An iron piece has formed 30 Kg of rust ($Fe_2O_3.3H_2O$) after complete corrosion. Find the weight of iron piece. (At. mass: Fe = 56, H =1, O =16)

Ans. Mol. Mass of rust ($Fe_2O_3.3H_2O$) = 214 g

Here, rust contains 2 Fe-atoms.

So, 214g of rust is formed by 112 g Fe

Or, Then, 30 kg = 30,000g of rust will be formed by = (112/214) x 30,000 = 157009 g = 15.7 kg Fe.

Assignment:

Nickel, with an atomic mass of 59, forms an oxide layer (NiO) with a molecular mass of 75. The density of the metal is 8.9 g/cc, and the density of the oxide layer is 6.67 g/cc. Can nickel be used as a coating to control the corrosion of iron?

Wagner's diffusion mechanism of Oxidation Corrosion

Let us discuss the mechanism of formation of magnesium oxide (MgO) on the surface of magnesium metal.

The various steeps involved are as follows:

Step-1 Metal gets oxidized to generate metal ions and electrons. It's an oxidation process.
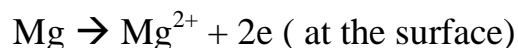
$$Mg \rightarrow Mg^{2+} + 2e \text{ (at the surface)}$$

Step-2 Electrons so released by Mg is captured by atmospheric O_2 and forms oxide anion (O^{2-}) near the interface (metal-atmosphere). It's a reduction process.

$$\frac{1}{2} O_2 + 2e \rightarrow O^{2-} \text{ (in the atmosphere near metal surface)}$$

Step-3 The O^{2-} ions are moved towards the metal-atmosphere interface and combine with Mg^{2+} ions to form metal oxide (MgO) at the surface.

$$Mg^{2+} + O^{2-} \rightarrow MgO \text{ (formed at the surface)}$$
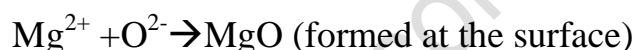
Here, MgO is a porous layer, so further oxidation occurs till whole metal is converted into oxide.

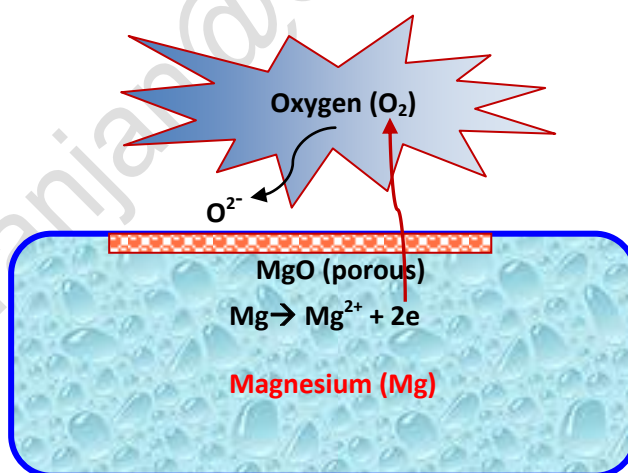**Fig. Mechanism of oxidation corrosion**

But in case of Al, it forms a protective layer of Al_2O_3 and hence it resists further oxidation process.

Q. Define oxidation corrosion. Discuss its mechanism.

Ans. . It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2.
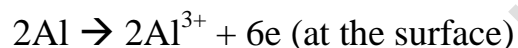
$$Mg + 1/2O_2 \rightarrow MgO$$

For mechanism, refer above

Q. Write the mechanism of formation of aluminum oxide Al_2O_3 on the surface of Al.

Ans. The various steeps involved are as follows:

Step-1 Al metal gets oxidized to generate metal ions and electrons. It's an oxidation process.

$$2Al \rightarrow 2Al^{3+} + 6e \text{ (at the surface)}$$

Step-2 Electrons so released by Mg is captured by atmospheric O_2 and forms oxide anion (O^{2-}) near the interface (metal-atmosphere). It's a reduction process.

$$3/2 \ O_2 + 6e \rightarrow 3O^{2-} \text{ (in the atmosphere near metal surface)}$$

Step-3 The O^{2-} ions are moved towards the metal-atmosphere interface and combine with Al^{3+} ions to form metal oxide (Al_2O_3) at the surface.

$$2Al^{3+} + 3O^{2-} \rightarrow Al_2O_3 \text{ (formed at the surface)}$$
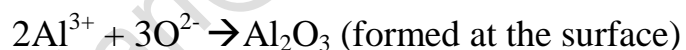
As Al_2O_3 is a non-porous layer, no further oxidation will occur.

Electrochemical or Wet corrosion

Wet corrosion of metals occurs in aqueous solution and in humid atmosphere through formation of a large number of minute electrochemical cells. The mechanism of corrosion can be explained by *electrochemical theory*. It involves anodic dissolution (oxidation) of metal and cathodic reduction of oxidants (e.g. oxygen) present in the solution/electrolyte.

Condition for wet corrosion

1. **Two different metals are joined and exposed to an electrolyte (Galvanic Corrosion)**
2. **A metal is exposed to different concentration of oxygen and exposed to an electrolyte (O_2 concentration cell corrosion)**
3. **A metal with different stress concentration and exposed to an electrolyte (Stress corrosion)**

1.6.1 *Electrochemical theory of wet corrosion:*

According to this theory, the various steps involved in wet corrosion are as follows:

Step 1: Formation of anodic and cathodic areas

Step 2: Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example Fe^{2+} from metal Fe

Step 3: Generation of non-metallic anions like hydroxyl anion (OH^-) by absorption of electrons(e^-) by oxidants like O_2

Step 4: Formation of corrosion product near cathode

Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with either (i) absorption of oxygen or (ii) evolution of hydrogen.

1.6.2 Mechanism of wet corrosion

A. Oxygen absorption mechanism in neutral medium:

Rusting of iron (Fe) in *a neutral aqueous medium* of electrolyte (such as NaCl) with dissolved oxygen or oxygen in the atmosphere follows oxygen absorption mechanism.

Let us consider that an iron piece is exposed to a humid environment that is not acidic in nature. Also assume that a small piece of metal (nickel) with lower oxidation potential (relative to Fe) is placed on its surface. Under this situation, pure iron with higher oxidation potential acts as anode and undergoes corrosion/rusting.
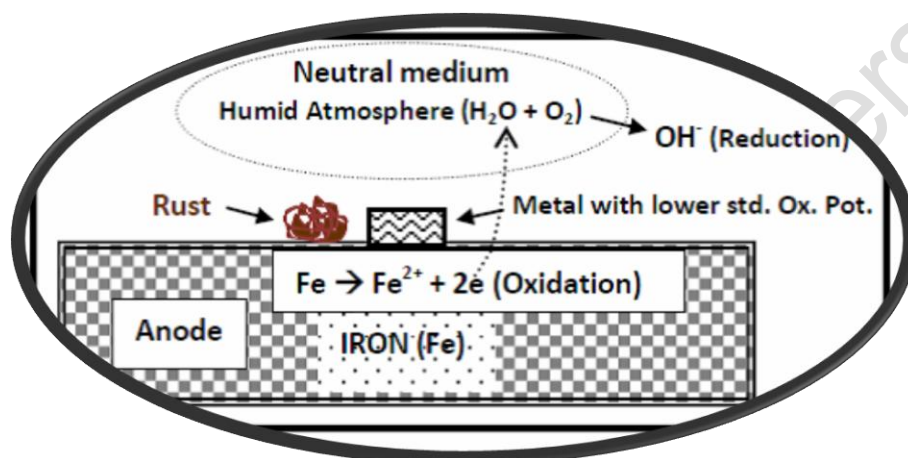

Fig. 2. Mechanism of wet corrosion by oxygen absorption.

The mechanism of rusting of iron piece in neutral medium involves the following steps:
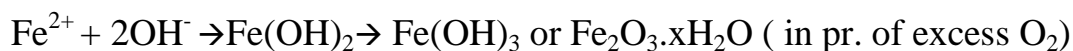
(i)   Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.
        At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ ------   (oxidation)

(ii)   The liberated electrons are captured by the oxidants (O^2) at the cathode to form non-metallic ions (OH^-)
        At Cathode: $1/2 O_2$ (oxidant) $+ H_2O + 2e^- \rightarrow 2OH^-$ -----   (reduction)
        (O_2 absorption occurs)

(iii)   The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O \text{ (in pr. of excess } O_2)$$

N.B.: In limited oxygen environment, ferrous hydroxide converted into a blackish oxide Fe_3O_4 (Ferrous ferric oxide, $FeO.Fe_2O_3$)

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe_3O_4 \text{ (limited supply of } O_2)$$

B. *Hydrogen Evolution mechanism in acidic medium*

Rusting of iron (Fe) *in an acidic medium* (such as HCl) follows **H_2 evolution** mechanism.
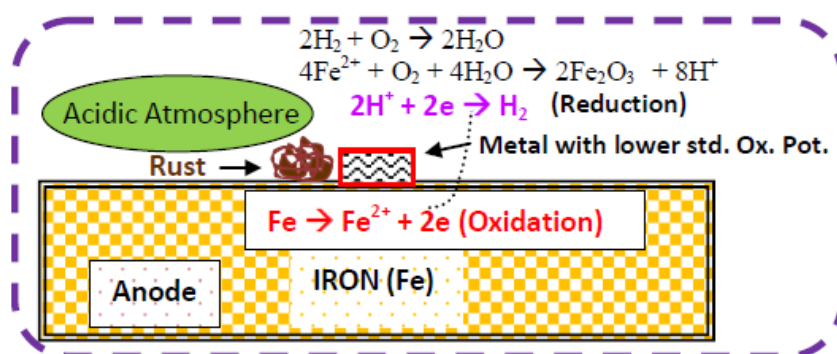

Fig. 3. Mechanism of wet corrosion by hydrogen evolution.

Let us consider that an iron piece is exposed to an acidic environment. Also assume that a small piece of metal with lower oxidation potential (relative to Fe) is placed on its surface. Under this situation, pure iron acts as anode and undergoes corrosion/rusting.
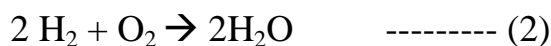
The mechanism of rusting of iron piece in an acidic environment involves the following steps:

(i)   Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

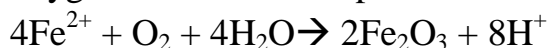   **At Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation or anodic reaction)

(ii)   At the cathode, the liberated electrons are captured by the hydrogen ions (H^+-ions) to form H-atoms and later form H_2 molecules. The H_2 molecules combine with dissolved oxygen forms water.

      At Cathode: $4H^+ + 4e^- \rightarrow 2H_2$ (Reduction) ----- (1)

                              (H_2 evolution occurs)

$$2 H_2 + O_2 \rightarrow 2H_2O \quad \text{--------- (2)}$$

Net cathodic reaction (1) + (2) : $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

(iii) As the ferrous ions are unstable, they are oxidized by atmospheric oxygen to form rust as per the following reactions.

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$$

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O \ (\text{rust})$$

Factors affecting the rate of rusting: The various factors are:

a. Amount of dissolved oxygen
b. Presence of acid and electrolytes
c. Deposition of rust on its surface
d. Potential difference between iron and the metal placed on its surface
e. % moisture in the atmosphere
f. Conductivity of the medium

Long Questions

Q.1. Define wet corrosion. Discuss the mechanism of rusting of iron in a neutral or alkaline medium.

Ans. Wet corrosion of metals occurs in aqueous solution and humid atmosphere through formation of a large number of minute electrochemical cells.

Mechanism of rusting of iron: refer section 1.6.2 A

Q.2. Discuss the mechanism of rusting of iron in an acidic medium.
Ans. refer section 1.6.2 B

Short Questions

Q.1 Mention the factors affecting rusting of iron.

Ans. The various factors are:

1. Amount of dissolved oxygen
2. Presence of acid and electrolytes
3. Deposition of rust on its surface

4. Potential difference between iron and the metal sat on its surface
5. % moisture in the atmosphere

Q.2 Write the chemical reaction occurs at cathode during rusting of iron in a neutral medium.

Ans. $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Q. 3.Write the chemical reaction occurs at cathode during rusting of iron in an acidic medium.

Ans. : $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

Q.4. Mention the conditions needed for a wet corrosion.

Ans. The various conditions are as follows:

1. **Two different metals are joined and exposed to an electrolyte (Galvanic Corrosion)**
2. **A metal is exposed to different concentration of oxygen and exposed to an electrolyte (O$_2$ concentration cell corrosion)**
3. **A metal with different stress concentration and exposed to an electrolyte (Stress corrosion)**

Medium Question

Q.1 Discuss the electrochemical theory of wet corrosion.
Ans. See section 1.6.1

Electrochemical or Wet corrosion

Wet corrosion of metals occurs in aqueous solution and in humid atmosphere through formation of a large number of minute electrochemical cells. The mechanism of corrosion can be explained by *electrochemical theory*. It involves anodic dissolution (oxidation) of metal and cathodic reduction of oxidants (e.g. oxygen) present in the solution/electrolyte.

Condition for wet corrosion

1. **Two different metals are joined and exposed to an electrolyte (Galvanic Corrosion)**
2. **A metal is exposed to different concentration of oxygen and exposed to an electrolyte (O_2 concentration cell corrosion)**
3. **A metal with different stress concentration and exposed to an electrolyte (Stress corrosion)**

1.6.1 Electrochemical theory of wet corrosion:

According to this theory, the various steps involved in wet corrosion are as follows:

Step 1: Formation of anodic and cathodic areas

Step 2: Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example Fe^{2+} from metal Fe

Step 3: Generation of non-metallic anions like hydroxyl anion (OH^-) by absorption of electrons(e^-) by oxidants like O_2

Step 4: Formation of corrosion product near cathode

Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with either (i) absorption of oxygen or (ii) evolution of hydrogen.

1.6.2 Mechanism of wet corrosion

A. Oxygen absorption mechanism in neutral medium:

Rusting of iron (Fe) in *a neutral aqueous medium* of electrolyte (such as NaCl) with dissolved oxygen or oxygen in the atmosphere follows oxygen absorption mechanism.

Let us consider that an iron piece is exposed to a humid environment that is not acidic in nature. Also assume that a small piece of metal (nickel) with lower oxidation potential (relative to Fe) is placed on its surface. Under this situation, pure iron with higher oxidation potential acts as anode and undergoes corrosion/rusting.
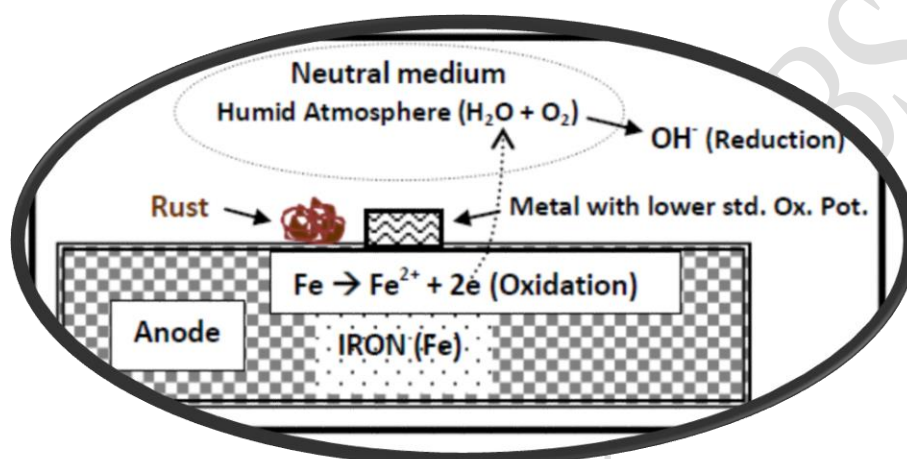

Fig. 2. Mechanism of wet corrosion by oxygen absorption.

The mechanism of rusting of iron piece in neutral medium involves the following steps:
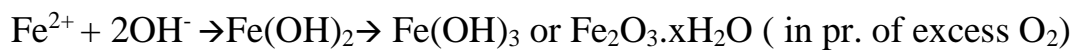
(i) Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ ------ (oxidation)

(ii) The liberated electrons are captured by the oxidants (O^2) at the cathode to form non-metallic ions (OH^-)

At Cathode: $1/2 O_2$ (oxidant) $+ H_2O + 2e^- \rightarrow 2OH^-$ ----- (reduction) (O_2 absorption occurs)

(iii) The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3$ or $Fe_2O_3.xH_2O$ (in pr. of excess O_2)

N.B.: In limited oxygen environment, ferrous hydroxide converted into a blackish oxide Fe_3O_4 (Ferrous ferric oxide, $FeO.Fe_2O_3$)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe_3O_4$ (limited supply of O_2)

B. *Hydrogen Evolution mechanism in acidic medium*

Rusting of iron (Fe) *in an acidic medium* (such as HCl) also follows H_2 evolution mechanism.
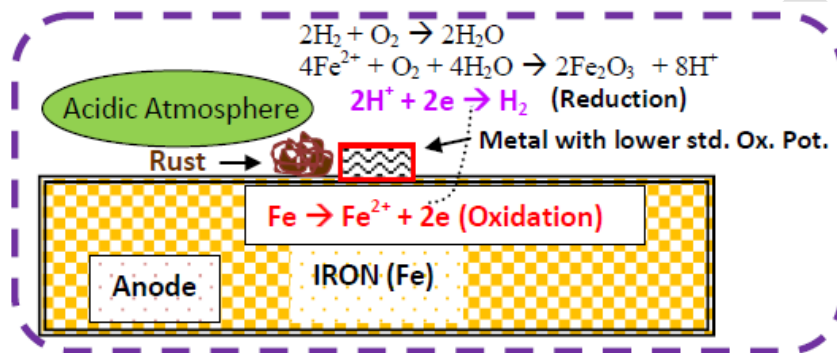

Fig. 3. Mechanism of wet corrosion by hydrogen evolution.

Let us consider that an iron piece is exposed to an acidic environment. Also assume that a small piece of metal with lower oxidation potential (relative to Fe) is placed on its surface. Under this situation, pure iron acts as anode and undergoes corrosion/rusting.
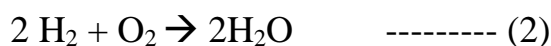
The mechanism of rusting of iron piece in an acidic environment involves the following steps:

(i)   Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

      At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation or anodic reaction)

(ii)   At the cathode, the liberated electrons are captured by the hydrogen ions (H^+-ions) to form H-atoms and later form H_2 molecules. The H_2 molecules combine with dissolved oxygen forms water.

      At Cathode: $4H^+ + 4e^- \rightarrow 2H_2$ (Reduction) ----- (1)

                                      (H_2 evolution occurs)

$$2 H_2 + O_2 \rightarrow 2H_2O \qquad \text{--------- (2)}$$

Net cathodic reaction (1) + (2) : $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

(iii) As the ferrous ions are unstable, they are oxidized by atmospheric oxygen to form rust as per the following reactions.

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$$

$$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 \cdot xH_2O \text{ (rust)}$$

Factors affecting the rate of rusting: The various factors are:

a. Amount of dissolved oxygen
b. Presence of acid and electrolytes
c. Deposition of rust on its surface
d. Potential difference between iron and the metal placed on its surface
e. % moisture in the atmosphere
f. Conductivity of the medium

Long Questions

Q.1. Define wet corrosion. Discuss the mechanism of rusting of iron in a neutral or alkaline medium.

Ans. Wet corrosion of metals occurs in aqueous solution and humid atmosphere through formation of a large number of minute electrochemical cells.

Mechanism of rusting of iron: refer section 1.6.2 A

Q.2. Discuss the mechanism of rusting of iron in an acidic medium.
Ans. refer section 1.6.2 B

Short Questions

Q.1 Mention the factors affecting rusting of iron.

Ans. The various factors are:

1. Amount of dissolved oxygen
2. Presence of acid and electrolytes
3. Deposition of rust on its surface

4. Potential difference between iron and the metal sat on its surface
5. % moisture in the atmosphere

Q.2 Write the chemical reaction occurs at cathode during rusting of iron in a neutral medium.

Ans. $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Q. 3. Write the chemical reaction occurs at cathode during rusting of iron in an acidic medium.

Ans. : $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

Q.4. Mention the conditions needed for a wet corrosion.

Ans. The various conditions are as follows:

1. **Two different metals are joined and exposed to an electrolyte (Galvanic Corrosion)**
2. **A metal is exposed to different concentration of oxygen and exposed to an electrolyte (O$_2$ concentration cell corrosion)**
3. **A metal with different stress concentration and exposed to an electrolyte (Stress corrosion)**

Medium Question

Q.1 Discuss the electrochemical theory of wet corrosion.
Ans. See section 1.6.1