

CORROSION

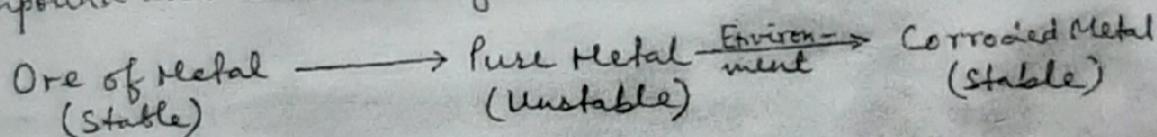
Definition

Corrosion is the process of gradual deterioration of a metal from its surface due to the chemical or electrochemical interaction of metal with its environment.

A typical example of corrosion is the rusting of iron which is a reddish scale of iron oxide (Fe_3O_4) formed on the surface of iron when exposed to the atmospheric conditions.

Cause and Problem of Corrosion

Metals have a tendency to go to the thermodynamically stable state. This they do by interacting chemically or electrochemically with their environment to form stable compound and thus undergo corrosion.



Due to corrosion, many useful properties of metals such as malleability, ductility, and electrical conductivity are lost.

Types of Corrosion

1. DRY OR CHEMICAL CORROSION
2. WET OR ELECTROCHEMICAL CORROSION

1. DRY CORROSION : This type of corrosion is due to the chemical action of atmospheric gases, such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen, or anhydrous liquid, on metal surfaces in their close proximity.

Dry corrosion is of three main types, viz.,

- (i) Corrosion by oxygen
- (ii) Corrosion by other gases
- (iii) Liquid metal corrosion

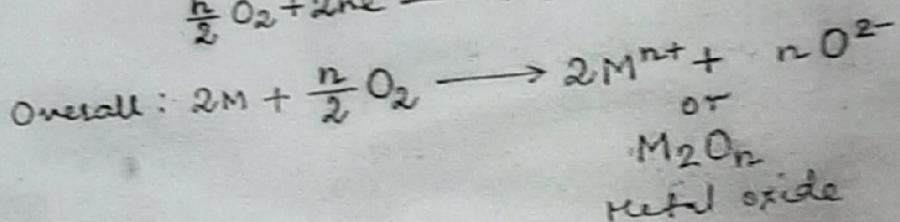
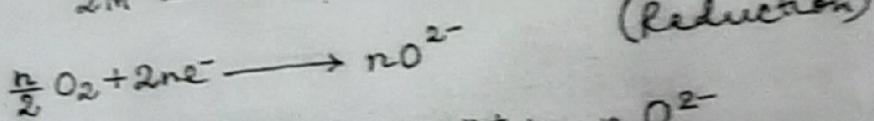
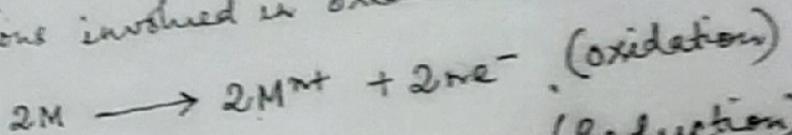
(i) Corrosion by oxygen (also called oxidation corrosion) —

It is caused due to the direct action of oxygen at low or high temperatures on metals, in the absence of moisture.

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Example, alkali metals ($\text{Li}, \text{Na}, \text{K}, \text{Rb}$, etc) and alkaline earth metals ($\text{Be}, \text{Ca}, \text{Sr}$, etc) are rapidly oxidized at low temperatures. At high temperature, almost all metals (except $\text{Ag}, \text{Au}, \text{Pt}$) are oxidized.

The reactions involved in oxidation corrosion are as below:



Mechanism: It is necessary to consider the mechanism of formation of metal oxide. First, oxidation of metal takes place and the electrons thus released lead to the reduction of oxygen (O_2). Formation of metal oxide takes place at the point of meeting of M^{n+} and O^{2-} . The resulting metal oxide scale forms a barrier restricting further oxidation. For oxidation to continue, either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. As the size of M^{n+} is much smaller than that of O^{2-} , hence outward diffusion of M^{n+} is faster than the inward diffusion of O^{2-} . This allows for the oxidation to continue, of course it depends much on the porosity of the metal oxide scale.

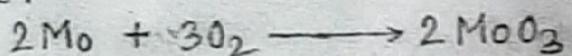
Depending on the nature of the metal oxide scale, further action of oxygen on metal would be decided. A thin layer of oxide formed on the surface of metal could be stable, unstable, volatile, or porous.

(a) Stable: A stable layer is one which gets adhered tightly to the metal surface and is impervious in nature. Such an oxide layer acts as a protective coating and prevents further corrosion of metal. Example,

the oxide films on Cu, Al, Sn, etc. are stable in nature.

(b) Unstable : An unstable layer of oxide is one that on formation decomposes back to metal and oxygen. Thus, oxidation corrosion is not possible in such case. Typical examples of metals that do not undergo corrosion are Ag, Au, and Pt.

(c) Volatile : Metal oxide on formation may volatilize easily, thereby leaving metal surface exposed for further oxidation. This would cause rapid and continuous corrosion. An example is the oxide of molybdenum (MoO_3) that is volatile.



Thus Mo undergoes excessive corrosion.

(d) Porous : An oxide layer may have pores and cracks. This would facilitate attack by atmospheric oxygen of the underlying metal surface, and corrosion would thus continue till the entire metal is converted into its oxide. Example, oxides of alkali metals (Li, Na, K, etc) and alkaline earth metals (Be, Ca, etc) are porous in nature.

(ii) Corrosion by other gases -

Gases like SO_2 , CO_2 , Cl_2 , H_2S , F_2 , etc. cause corrosion. The extent of corrosion depends on the chemical affinity between metal and the gas involved. The degree of attack depends on the formation of protective or non-protective films on metal surface.

(a) If the film formed is protective or non-porous, the extent of attack decreases, because the film protects the metal from further attack. For example, AgI film formed from the attack of Cl_2 on Ag is a protective film.

(b) If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed. For example, Cl_2 attacks Sn forming SnCl_4 which is volatile in nature and escapes immediately leaving fresh Sn surface for further attack.

(iii) Liquid metal corrosion—

This type of corrosion is due to the chemical action of liquid metal flowing at high temperature on solid metal or alloy. It leads to weakening of solid metal due to (a) its dissolution in liquid metal or (b) internal penetration of liquid metal into the solid metal. An example is the corrosion of Cd metal in nuclear reactor due to liquid Na metal used as a coolant.

2. NET CORROSION:

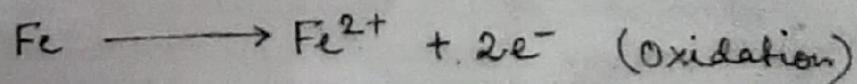
This type of corrosion occurs due to the electrochemical action of moisture and oxygen on metals. Corrosion of very important metal iron takes place due to electrochemical attack.

The corrosion involves:

- (i) Separate anodic and cathodic parts between which current flows through the conducting medium.
- (ii) Oxidation occurs at anodic parts, which generates metal ions.
- (iii) Non-metallic ions like OH^- , O_2^- are formed at cathodic parts.
- (iv) The metallic and non-metallic ions diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.

Mechanism: The mechanism of wet corrosion is illustrated taking the example of the rusting of iron. The processes occurring at the anodic and cathodic parts are:

At Anode: The reaction involved in the anode area is the dissolution of metal (here Fe) into its corresponding ions (Fe^{2+}) with the release of electrons.

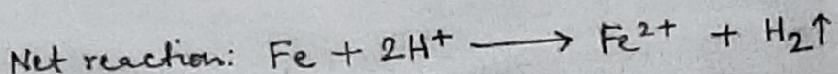
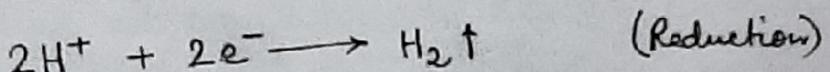


At Cathode: The electrons released at the anode are conducted to the cathode and are responsible for various cathodic reactions. Depending on the nature of the chemical

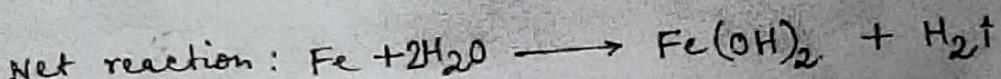
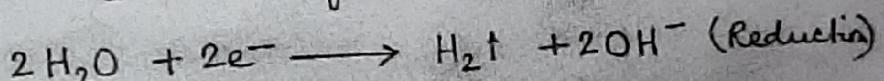
environment in the cathodic area, cathodic reaction is accompanied with either (a) evolution of hydrogen, or (b) absorption of oxygen.

(a) Evolution of hydrogen: It occurs in acidic environments or basic environments, in the absence of oxygen.

When the atmosphere is acidic and contains no oxygen, H_2 will be given out.

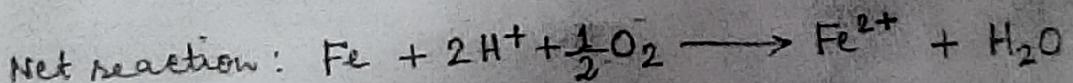
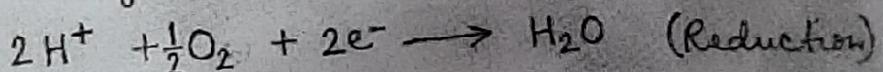


When the atmosphere is basic or neutral and contains no oxygen, OH^- and H_2 will be given out.

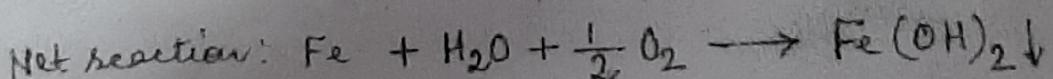
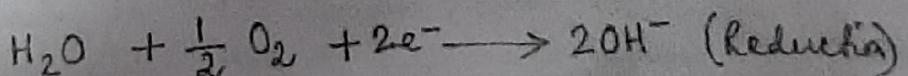


(b) Absorption of oxygen: This type of corrosion occurs in the acidic or basic environments, in the presence of dissolved oxygen.

When the atmosphere is acidic and contains oxygen, water will be given out.

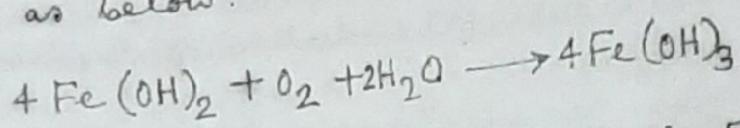


When the atmosphere is basic or neutral and contains more oxygen, OH^- will be given out.



If enough oxygen is present, $Fe(OH)_2$ is oxidised to

Fe(OH)_3 , as below.



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

Some Terms We Should Know

1. PILLING - BEDWORTH RULE.

According to this rule, whether a metal oxide is protective (non-porous) or non-protective (porous) is decided by the ratio of the volume of the oxide to the volume of the ~~present~~ metal. If the ratio is smaller, greater will be the oxidation corrosion because ~~then~~ the film will be porous allowing easy diffusion of oxygen. On the other hand, if the ratio is large, the oxide film will be non-porous and hence corrosion will be hindered. The reason ascribed to this is that for the volume of the oxide smaller than the volume of the metal, when the ratio is smaller, the oxide layer faces considerable stress and strains. Thus, the oxide develops cracks and pores in its structure. Porous oxide layer allows diffusion of oxygen easily to the underlying metal surface for fresh action and thus corrosion continues. In case where the oxide volume is greater than or equal to the volume of the metal, there is no stress or strain and consequently the oxide is tightly-packed devoid of cracks or pores. Example of metals that have smaller ratio of volume of oxide to volume of metal are alkali and alkaline earth metals ($\text{Li}, \text{Na}, \text{K}, \text{Mg}$); metals like Al, Cu form oxides of volume greater than the volume of metals.

2. PITTING CORROSION

Pitting corrosion is a localized accelerated attack resulting in the formation of cavities, pits, and pin-holes in the metal. It occurs as a result of the breakdown or cracking of the protective film on a metal at specific points. Once a small pit is formed, the rate of corrosion will be enhanced. The corrosion leads to the formation of small anodic and large cathodic areas. This sets up differences of potential at localized spots to pit, which produces corrosion current. The presence of impurities like sand, dust, scale, etc. embedded on the surfaces of metals also lead to pitting.

To gain insight, let us consider a drop of water resting on the surface of metal. The metal surface which is covered by the drop has low concentration of oxygen and thus acts as an anode. The uncovered metal surface due to high oxygen concentration acts as cathode. Intense corrosion occurs just below the water droplet. This is illustrated pictorially below.

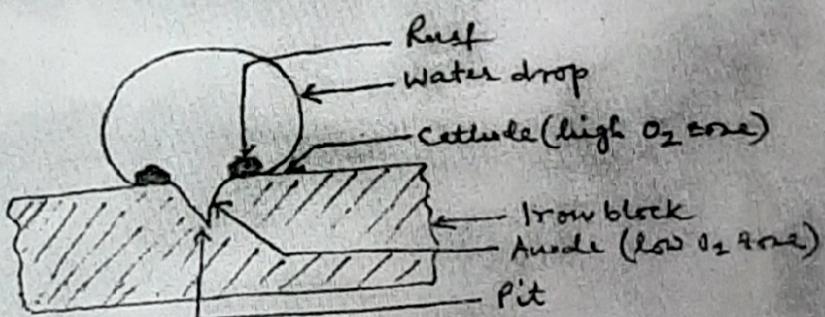
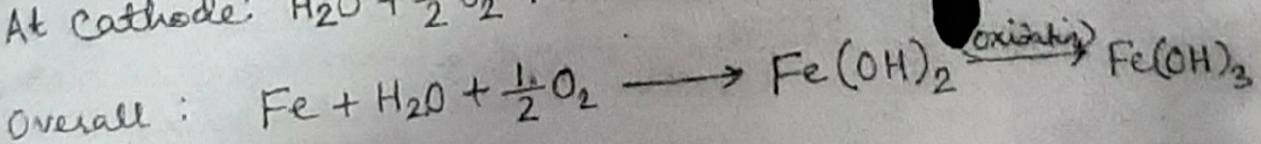
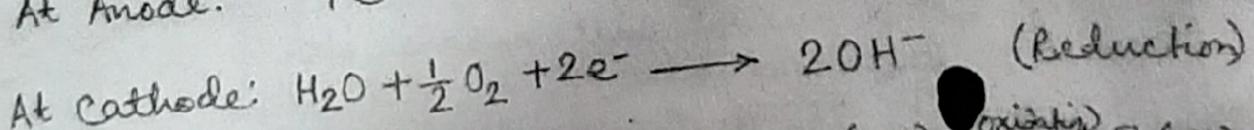
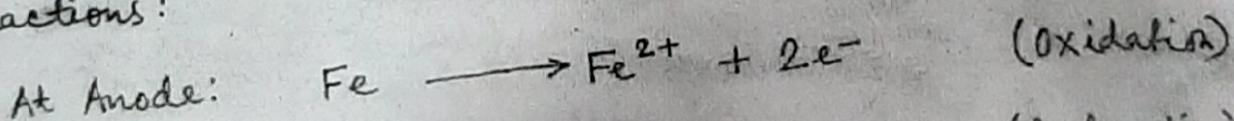


Fig. Pitting corrosion
at the surface of iron

Reactions:



3. WATER-LINE CORROSION

When water is stored in a steel tank, it is found generally that the maximum amount of corrosion occurs along a line just below the level of water meniscus. This is because the concentration of oxygen above the water surface is greater than that under the surface. As a result, an oxygen concentration cell is generated. In this cell, the area above the water-line acts as the cathode that remains unaffected to corrosion. Corrosion occurs at the anodic part, the metal below the water-line.

Reactions:

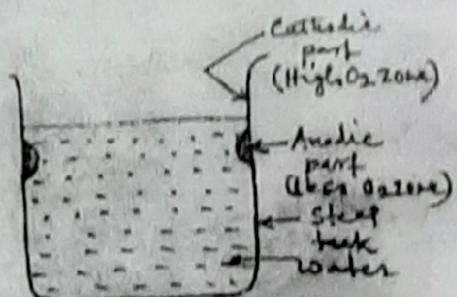
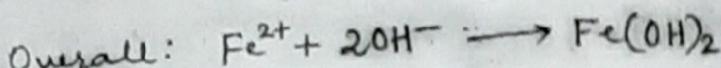
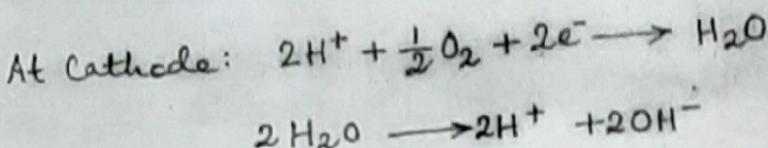
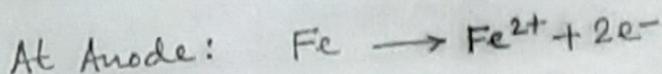


Fig. water-line corrosion

Corrosion does take place if the water is acidic. However, if the water is relatively free from acidity, little corrosion takes place.

4. PASSIVITY / PASSIVATION

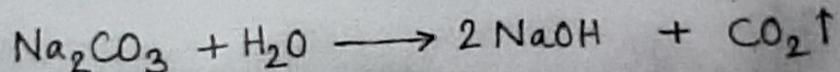
It is a phenomenon by which a metal (or alloy) shows high corrosion resistance due to the formation of a highly protective, very thin (~ 0.0004 mm thick) and quite invisible film on the metal surface. The film is insoluble, non-porous (protective) and of a 'self-healing nature' that when broken, the metal will repair itself on re-exposure to oxidising conditions.

For example, Ti, Al, Cr, and a variety of stainless steel alloys containing Cr exhibit outstanding corrosion resistance in the presence of oxygen. This is due to the formation of this, protective oxide film on their surfaces.

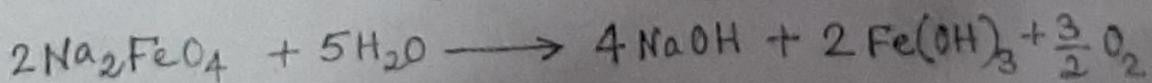
If any damage occurs, this film is automatically repaired in oxidizing environments. But in reducing environments, the passive metals and alloys become chemically active and are rapidly corroded. For instance, Al metal is not attacked by concentrated HNO_3 , but iron gets rapidly corroded even by dilute HNO_3 . In sharp contrast, stainless steel, due to the presence of Cr in it, maintains protective oxide film so exhibits high corrosion resistance in HNO_3 solution over a wide range of concentrations.

5. CAUSTIC EMBRITTLEMENT

It is ^{one} form of stress corrosion occurring in mild steel exposed to alkaline solutions at high temperatures and stresses. The phenomenon of caustic embrittlement is often associated with steam boilers and heat-transfer equipment in which waters of high alkalinity are used. Boiler water usually contains a certain proportion of sodium carbonate added during the softening of water; and this Na_2CO_3 decomposes to give sodium hydroxide that makes the water caustic/alkaline.



This caustic water flows into the minute hair-cracks, present in the boiler, due to the capillary action. On continuous evaporation of water the dissolved caustic soda concentration increases thereby dissolving iron of boiler as sodium ferrate (Na_2FeO_4). This causes embrittlement of boiler walls, joints, rivets, etc. causing even failure of the boiler. Na_2FeO_4 again decomposes to regenerate NaOH thereby enhancing further corrosion.



Caustic embrittlement occurs due to the setting up of a concentration cell. With the iron surrounded by dilute NaOH acting as the cathode, while the iron

in contact with rather concentrated NaOH acting as the anode. It is the iron in the anodic part that gets dissolved or corroded.

Prevention of caustic Embrittlement: It can be prevented by : (i) using sodium phosphate (Na_3PO_4) as softening reagent, instead of sodium carbonate (Na_2CO_3) in the external treatment of water.

(ii) adding tannin or lignin to boiler water, which blocks the hair-cracks in the boiler walls.

(iii) adding sodium sulphate (Na_2SO_4) to boiler water, which also blocks the hair-cracks.

+]_{TON} | Concentrated NaOH | dilute NaOH | Iron

CORROSION CONTROL

Sacrificial Anodic Protection Method

It is a cathodic protection method, the principle being that the metal to be protected against corrosion is forced to behave like a cathode. Since there will not be any anodic area on the metal, corrosion will not occur.

In this technique, a more active metal is connected to the metallic structure (to be protected) by a wire, so that all the corrosion is concentrated at the active metal. The active metal gets slowly corroded, while the parent metal is protected. The more active metal so used is called "sacrificial anode". The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are Mg, Zn, Al, and their alloys.

Important applications of sacrificial anodic method include protection of buried pipelines, underground cables, ship-hulls, water tanks, piers, etc.

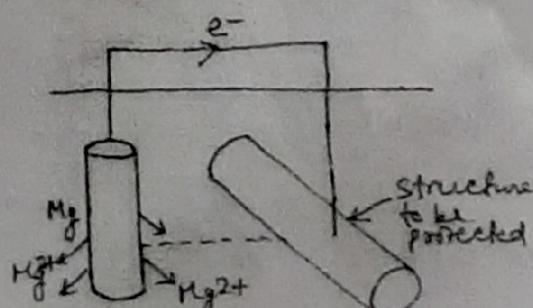


Fig. Sacrificial anodic protection