

MODULE - 4 - WATER CHEMISTRY

2

OXIDATION - REDUCTION

Reactions

WATER

- * Water is used as coolant in power and chemical plants
- * Most important use of water is steam generation.

Sources of water

(i) SURFACE WATER

- Rain water
- River water
- Lake water
- Sea water

UNDERGROUND WATER

- * spring and well water
- * organic impurity is negligible

TYPES OF IMPURITIES IN WATER

(a) PHYSICAL IMPURITIES

- (i) Colour → due to dissolved salts of iron, Mn, Cr etc
- (ii) Turbidity → clay, silt,
- (iii) Taste → presence of NaHCO_3 , Al_2SO_4 , FeSO_4
- (iv) Odour
↓
It is caused due to presence of organic chemicals like phenols, ester, ketones etc.

- (ii) CHEMICAL Impurities : They are due to
- (a) Inorganic and Organic chemicals Released from Insecticides, Pesticides etc.
 - (b) CO_2 , SO_2 present in water bodies
 - (c) Biological Impurities due to fungi, virus, Pathogens etc.

EFFECTS OF CHEMICAL Impurities

- (i) Biological Oxygen Demand (BOD) & Chemical Oxygen Demand (COD) Increases.
- (ii) Growth of Pathogens.
- (iii) Eutrophication due to enrichment of Nutrients (Dissolved Oxygen Decreases)
- (iv) Heavy Metals
 - (a) Mercury (Hg) → Responsible for Minamata disease
 - (b) Lead (Pb) → Toxic as it replaces calcium in bones
 - (c) Cadmium (Cd) → causes Itai-Itai Disease
 - (d) Arsenic (As)
 - It causes
 - Anaemia, liver Damage, skin cancer, black foot disease

BOILER - FEED WATER

Water used for cooling may not be of high quality but water required for boiler feed purposes (steam generation) should be of very high quality and requires lots of treatment.

Problem Due to Impurities Present Inside Boiler

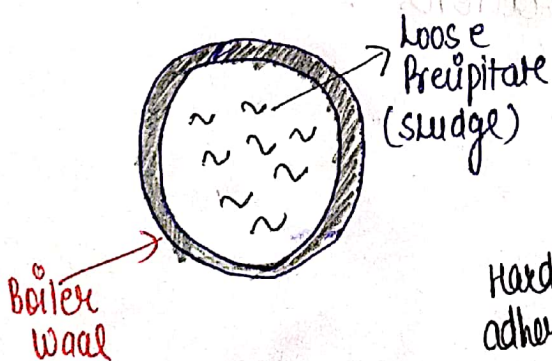
- (i) SCALE & SLUDGE FORMATION
- (ii) BOILER CORROSION
- (iii) CAUSTIC EMBRITTLEMENT
- (iv) PRIMING & FOAMING

v.v. Important

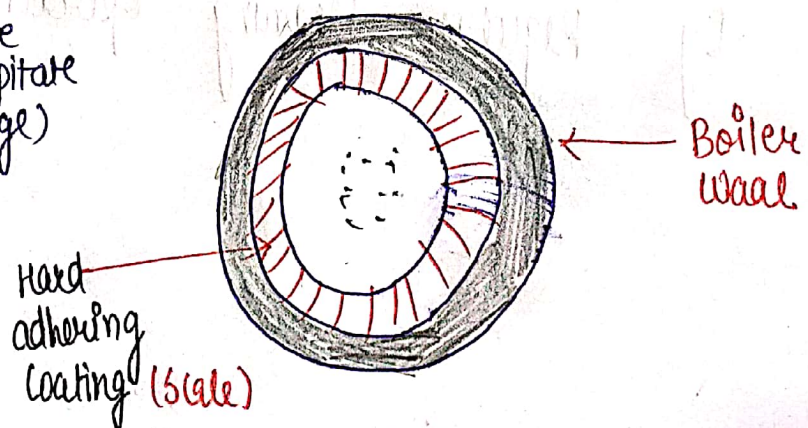
(i) SCALE AND SLUDGE FORMATION IN BOILERS

- Water is converted into steam in a boiler
- Evaporation of water increases concentration of dissolved salts.
- When this salt concentration increases beyond SATURATION POINT Dissolved SALTS start precipitating out

SLUDGES



SCALES IN Boiler wall



Ques.

SLUDGES

1. When precipitation of dissolved salts take place in form of loose, NON-ADHERENT SLIMY PRECIPITATE is called SLUDGE.
2. It is due to CaCl_2 , MgCO_3 , CaSO_4 , MgCl_2 & MgSO_4 and SiO_2 .
3. formed by substance having greater solubility in Hot water than in cold water.

Disadvantage of SLUDGE FORMATION

- (i) Wastage of fuel - Sludges are poor conductors of Heat-
- (ii) Decreased efficiency of Boilers - Poor conduction $\downarrow$ efficiency
- (iii) CHOKING OF PIPELINES - Water circulation $\downarrow$

PREVENTION OF SLUDGE

- * Using soft water instead of hard water
- * By Regular cleaning operations.

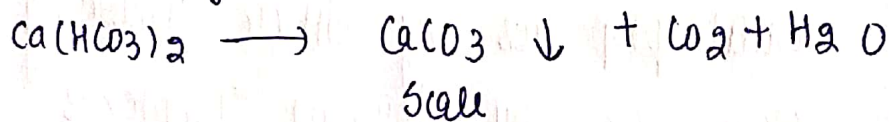
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SCALE FORMATION

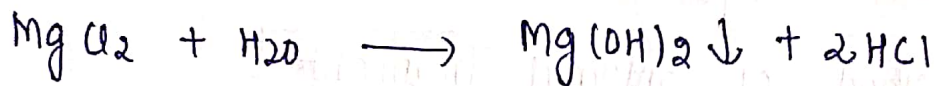
When the Precipitation of dissolved salt take place in Form of HARD, ADHERENT CRUST COATING ON INNER WALLS OF BOILERS it is called SCALES.

Formation is due to

(a) Decomposition of Bicarbonates



(b) Hydrolysis of Magnesium salt



(c) Deposition of Calcium sulfate

(d) Presence of silica (CaSiO_3 & MgSiO_3)

Disadvantages of Scale formation

(a) Wastage of fuel - scales have low Thermal conductivity

(b) Bagging - Distortion of boiler material is known as Bagging.

(c) Decrease in efficiency - Scales get deposited in valves and condensers of Boilers & choke them Partially.

(d) Danger of Explosion -

Uneven expansion of scale may lead to cracking of scale
cracking of scale leads to formation of huge steam pressure.

PREVENTION OF SCALE FORMATION

• EXTERNAL TREATMENT

It includes softening of water

• Internal Treatment

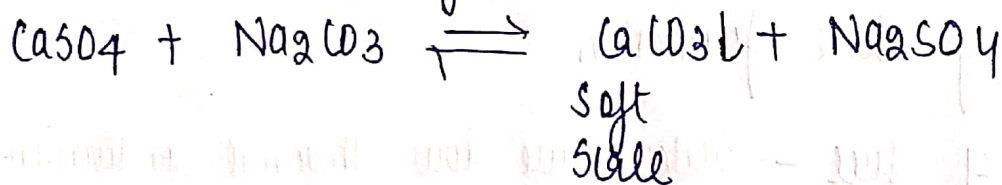
Treatment within Boiler is called internal treatment - or
"SEQUESTRATION"

Sequestration is a process in which ion is prohibited to exhibit its usual properties by either converting it to some other form or by forming complexes with some other compound.

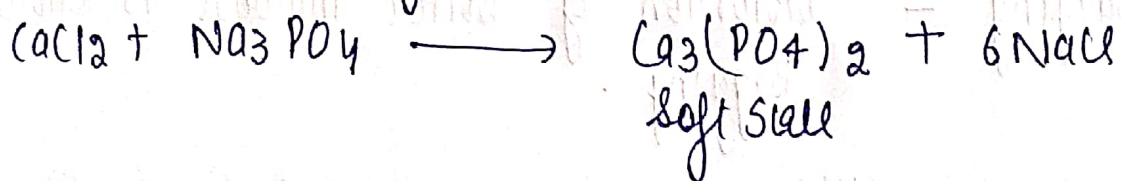
Method of Internal Treatment

(a) Colloidal Conditioning → Kerosene, glue, Tanin are used

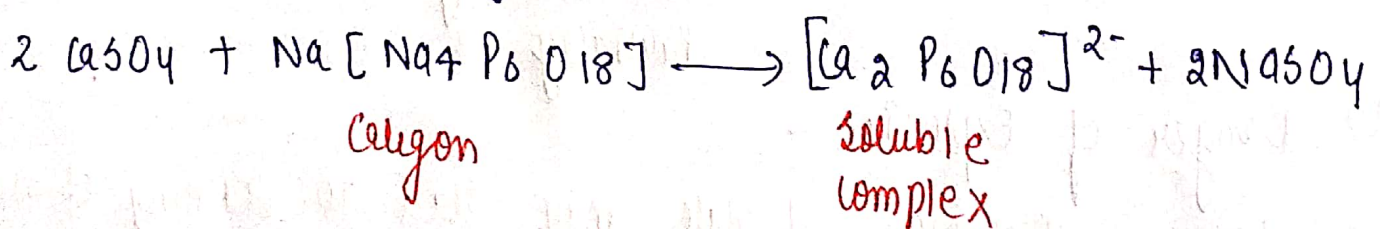
(b) Carbonate Conditioning



(c) Phosphate Conditioning



(d) Calgon Conditioning → soluble complex is formed



* BOILER CORROSION

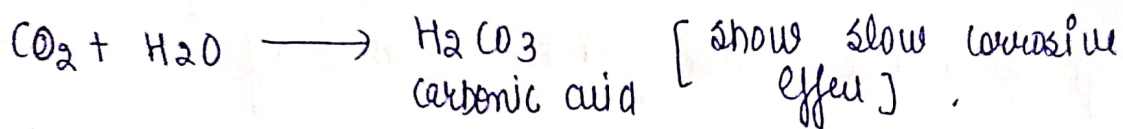
It is decay of boiler material by certain chemicals to form oxides or sulphides or electrochemical attack by its environment.

Main Reason for boiler corrosion

1. Presence of Dissolved Oxygen



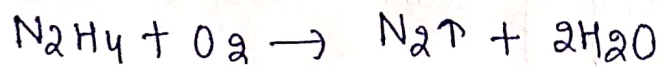
2.) Presence of Dissolved CO_2



3.) Presence of Mineral acids like HCl .

Prevention of Boiler Corrosion

① Removal of Dissolved O_2 by using chemicals like Na_2SO_3 , Na_2S or Na_2H_4



② Removal of CO_2 by using NH_4OH (ammonium hydroxide)

CAUSTIC EMBRITTLEMENT

Corrosion due to presence of highly alkaline water in boiler. Matter of boiler becomes brittle due to accumulation of caustic substance.

Prevention of Caustic Embrittlement

- ① using sodium phosphate for water softening instead of sodium carbonate
- ② addition of Tannin or lignin
- ③ addition of Na_2SO_4

} Both Black Hairline cracks
&
Punctⁿ infiltration of NaOH

④ Priming and Foaming

Process of wet steam formation in association with liquid water droplet is called priming

Reasons of Priming

- 1.) High steam velocities
- 2.) High water level in boiler
- (3). Faulty boiler design
- (4). Sudden boiling

Foaming - Formation of small persistent bubbles or foams in water

oil and grease are mainly responsible for formation of foaming

Disadvantages of Priming & Foaming

- ① Decrease in efficiency of turbine blades & heater
- ② Reducing life of machinery
- ③ Difficulty in maintaining boiler pressure

Prevention of Priming

- * Maintain low level of water
- * Reducing steam velocities
- * Improving Boiler Design

Prevention of Foaming

- * Adding Anti-Foaming agent like castor oil.
- * Removing oil from boiler feed water
- * Adding coagulating Agent $\text{Al}(\text{OH})_3$

CORROSION

* Corrosion is defined as process by which metals have tendency to stay in combined state such as Oxides, carbonates, sulphides, chlorides etc.

* It is degradation or deterioration of metal by chemical or electrochemical ~~Reduction~~ Reaction.

Effect of Corrosion

- 1.) Weakening of material due to loss of cross-sectional area
- 2.) Decaying of surface of metals
- 3.) Loss of properties like malleability & ductility

Common Example $\Rightarrow$ Rusting of Iron (due to Fe_2O_3) (2) Tarnishing of Silver (due to Ag_2O formation)

Most Imp

THEORIES OF CORROSION

(i) DRY CORROSION
OR
CHEMICAL CORROSION

It is of Three types

- (a) Oxidation corrosion
- (b) Corrosion by gas
- (c) Liquid-metal corrosion

(ii) WET CORROSION
OR
ELECTROCHEMICAL CORROSION

It is of 6 types

- 1.) Galvanic
- 2.) Pitting
- 3.) Crevice
- ④ Waterline
- ⑤ Stress corrosion
- ⑥ Differential aeration corrosion

DRY CHEMICAL CORROSION ^{Imp}

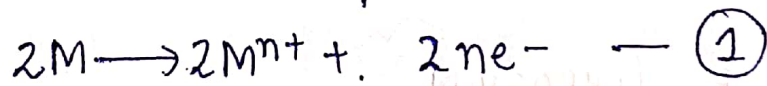
- * It Takes place by direct chemical attack on metal surface.
- * Oxygen, Nitrogen, Halogen, H₂S are Responsible for this.
- Metal is consumed and Properties of metal changes.

(I) Oxidation Corrosion

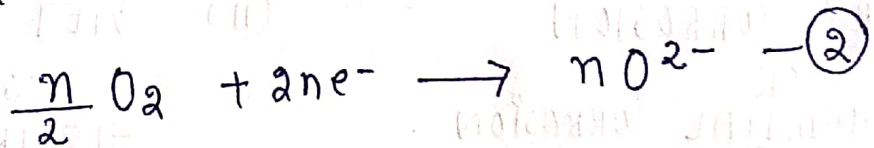
- * It takes place via chemical action of Oxygen at High and Low Temp.
- * Group I (Li, Na, K) & Group II (Ca, Be, Sr) are oxidized Rapidly.
- * Ag, Au and Pt are oxidized at High Temperature.

Mechanism of Action

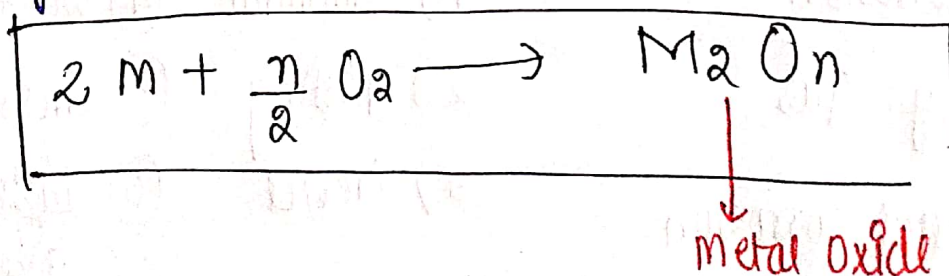
(i) Metal gets oxidized as temp rises



(ii) Oxygen gets Reduced to oxide ion



Combining 1 & 2



~~Not so Imp~~

PILLING - BEDWORTH RULE

An oxide layer will be protective or Non protective depending upon Ratio of Volume of metal oxide formed to Volume of metal which is consumed in oxide formation.

$$\text{Pilling - Bedworth Ratio} = \frac{\text{Volume of Metal oxide formed}}{\text{Volume of metal consumed}}$$

~~Imp~~ (II) CORROSION BY GASES.

* Other Gases such as CO_2 , SO_2 , Cl_2 , H_2S and F_2 have corrosion effect

* Extent of corrosion depend upon chemical affinity b/w metal and corresponding gas involved.

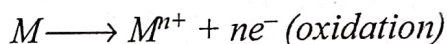
~~Imp~~ (II) Liquid - metal corrosion

cause due to action of flowing ^{Liquid} metal at High Temperature on solid metal or alloy.

8.4 WET OR ELECTROCHEMICAL CORROSION (THEORY)

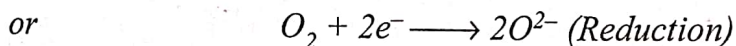
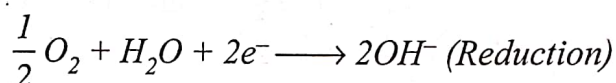
Wet corrosion is more common than dry corrosion. It occurs mostly under wet or moist conditions through the formation of electrochemical cells and is therefore, referred to as electrochemical corrosion. The **mechanism/theory** of electrochemical corrosion involves:

- (i) The existence of separate anodic and cathodic areas between which current flows through the conducting solution.
- (ii) Oxidation (loss of electrons) take place at the anodic area and the metal is destroyed by either dissolution or combination with oxygen. Hence corrosion always takes place at the anode.



M^{n+} forms compounds such as oxides or dissolves in solution.

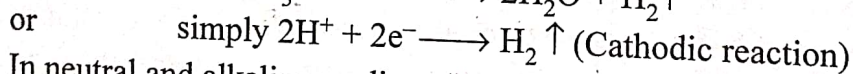
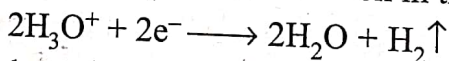
- (iii) Reduction (gain of electrons) takes place at the cathode. The electrons from the anode are accepted by the dissolved oxygen forming ion such as OH^{-} or O^{2-} ions.



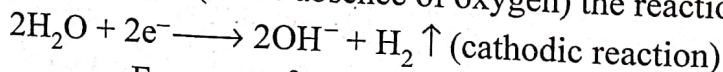
- (iv) The metallic ions formed at the anode and non-metallic ions formed at the cathode diffuse through the conducting medium and combine to form the corrosion product some where between anodic and cathodic area.

Wet corrosion involves flow of electron current, between the anodic and cathodic areas. The anodic reaction involves dissolution of metal as corresponding metallic ions with the liberation of free electrons. Whereas, the cathodic reactions accept electrons by two ways: (i) evolution of hydrogen or (ii) by absorption of oxygen. The evolution of hydrogen and absorption of oxygen in cathodic reaction depends on the nature of corrosive environment.

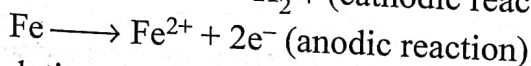
- (i) **Evolution of Hydrogen:** The process of corrosion in which H_2 is liberated is called *evolution of hydrogen type corrosion*. This type of corrosion usually takes place in acidic environment. Thus, acidic medium (absence of oxygen) hydrogen ions acquire electrons with the liberation of H_2 gas cathodic reaction, whereas in the anodic reaction metal atoms lose their electrons to the environment and pass into solution in the form of +ve ions.



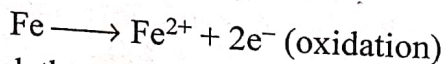
In neutral and alkaline medium (in the absence of oxygen) the reaction taking place will be



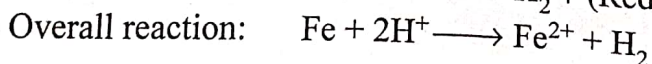
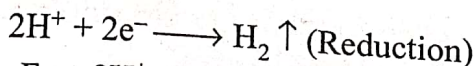
whereas



e.g., if iron metal is used, the dissolution of iron as Fe^{2+} ions with the evolution of electrons in anodic reaction.



These electrons flow through the metal, from anode to cathode, where H^{+} ions of acidic solution are eliminated as H_2 .



Therefore, this type of corrosion cause displacement of hydrogen ion from the acidic solution by metal ions.

The above statements can be easily understood from Fig. 8.1.

Thus, from the diagrams, it is clear that anodic areas are very large in comparison to cathodic areas. All the metals, above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous liberation of hydrogen.

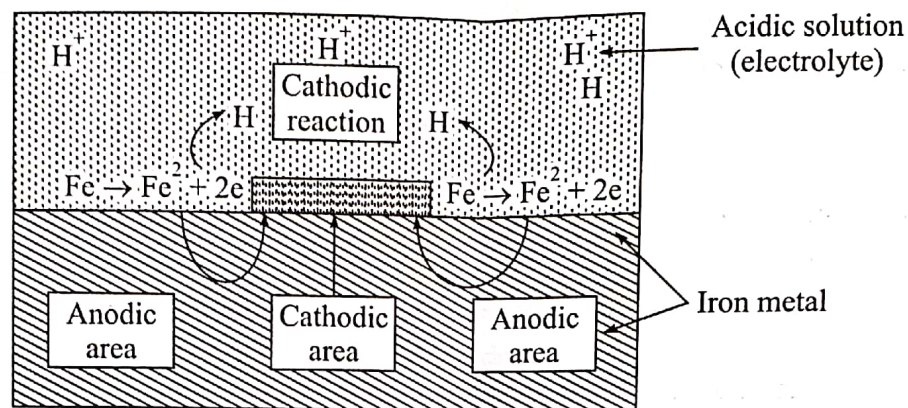


Fig. 8.1 Mechanism of wet corrosion by hydrogen evolution

(ii) Absorption of Oxygen: This type of corrosion occurs in neutral environment (such as NaCl solution used as electrolyte). The popular examples of absorption of oxygen type corrosion is rusting of iron in neutral aqueous solution of NaCl in the presence of atmospheric oxygen.

The surface of iron is usually covered with a film of iron oxide. If there are some cracks in iron oxide film, an anodic area is developed on the surface, whereas the wet metal part act as cathodic area. In this corrosion reaction cathodic area is much more large in comparison to anodic area.

The above overall reaction mechanism is represented diagrammatically in Fig. 8.2.

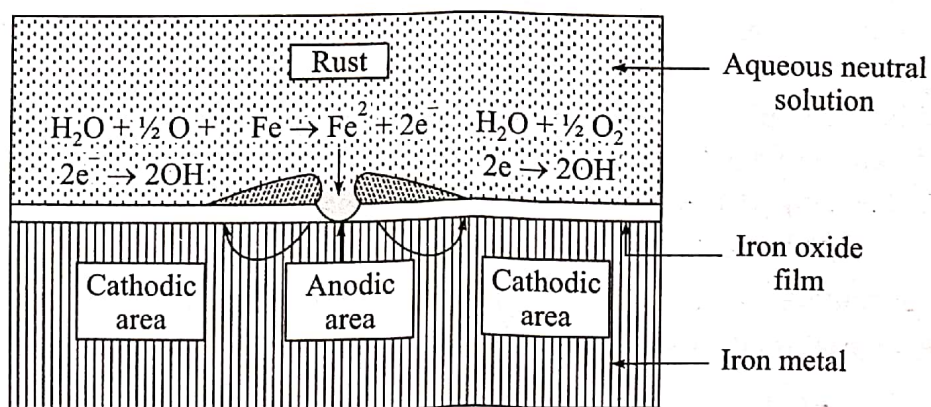
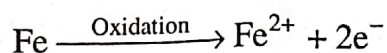


Fig. 8.2 Mechanism of wet corrosion by absorption of oxygen type corrosion

Thus, from the above diagram it is clear that at the cathodic area, iron metal dissolves with the liberation of electrons as



The above evolved electrons flow from anodic areas through iron metal where electrons are taken up by the dissolved oxygen as

8.4.1 Comparison of Chemical with Electrochemical Corrosion

The comparison of these two main types of corrosion of metals has been summed up in the following Table 4.1

Table 8.1 Comparison of chemical with electrochemical corrosion

<i>Chemical corrosion</i>	<i>Electrochemical corrosion</i>
1. It occurs in dry condition. 2. It involves the chemical attack of oxygen or other gases on the surface of metal. 3. It can occur at homogeneous as well as heterogeneous metal surfaces. 4. It is uniform in nature throughout the surface of the metal. 5. It is a slow process taking place by chemical reaction of atmospheric gases. 6. Corrosion products accumulate at the place where corrosion occurs i.e., at the anode. 7. Its mechanism is explained on the basis of absorption.	1. It occurs in wet condition in the presence of moisture and electrolyte. 2. It involves electrochemical attack of corrosive environment on the surface of the metal. 3. It occurs only on heterogeneous metal surface. 4. It is not uniform. If the area of anode is small, pitting corrosion takes place. 5. It is a fast electrochemical process. It proceed through the formation of electrochemical cells. 6. Corrosion products accumulate some where between the area of anode and cathode. 7. Its mechanism is explained on the basis of electrochemical reactions.

4.44 FACTORS INFLUENCING CORROSION

Corrosion happens due to a number of factors and can be divided into two basic groups (1) Internal factors such as grade and kind of metal, i.e., the nature of metal and (2) External factors such as nature of surrounding medium.

4.44.1 Nature of the Metal

The rate of extent of corrosion depends on a number of properties of the metal.

(a) **Position in galvanic series** : When two metals are in electrical connection in an electrolytic solution, the metal higher up in the galvanic series becomes anodic and suffers corrosion.

(b) **Purity of metal** : The rate of corrosion increases with increase in concentration of impurities. Impurities in a metal generally cause 'heterogeneity' and form minute electrochemical cells and the anodic parts get corroded.

(c) **Physical state of the metal** : The rate of corrosion is highly influenced by the physical state of metal such as grain size, orientation of grains, grain structures, localized stresses, scratches etc.

(d) **Relative area of anodic and cathodic part** : If the area of the cathode is large compared to that of the anode the corrosion of anode is rapid and severe. The reason being that the current density at a smaller anodic area is much greater and the demand of electrons by the large cathodic areas can be met by smaller anodic areas only by undergoing "corrosion more briskly".

4.44.2 Environmental Factors

The nature of aggressiveness of the environment determines to a large extent the degree of corrosion. Some of the common environmental variables are:

(a) **Temperature** : The rate of corrosion increases with increase in temperature.

(b) **Humidity** : One of the important environment variables in corrosion is relative humidity. With increase in humidity of the atmosphere the corrosion rate increases.

4.44.3 Presence of Impurities in Atmosphere

Atmospheric corrosion gets enhanced if it contains polluted gases like CO_2 , H_2S , SO_2 and fumes of HCl and H_2SO_4 which are usually observed in the vicinity of industrial areas.

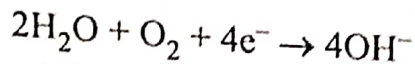
- Presence of polluting gases increases the acidity of the liquid adjacent to the metal surface and hence increases its conductivity. This increases rate of corrosion.
- Dust particles if present in the atmosphere absorb SO_2 and enhance corrosion process.
- In the marine atmosphere due to presence of NaCl as well as other chlorides the conductivity of the liquid layer in contact with metal surface increases and speeds up corrosion.

(d) **Effect of pH** : In acidic media ($\text{pH} < 7$) corrosion rate is faster than in alkaline ($\text{pH} > 7$) or neutral media ($\text{pH} = 7$). Zn easily corrodes even in weakly acidic solutions such as carbonic acid (H_2CO_3) and suffers minimum corrosion at $\text{pH} = 11$. Amphoteric metals like Zn, Al, Pb etc., however suffer corrosion in highly alkaline solutions due to formation of complex ions.

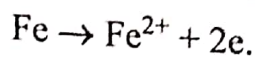
(e) **Nature of ions present** : The nature of ions present in solution has a marked effect on corrosion.

(i) **Formation of oxygen concentration cell** : The rate of corrosion increases due to differential aeration by the formation of concentration cell. The part less exposed to oxygen behaves as anode and the more oxygen exposed part as cathode and 'oxygen concentration cell is formed' and anodic parts suffer corrosion.

At cathode



In case of corrosion of the metal, like iron, which is the anodic part.



The formation of oxygen concentration cell thus promotes corrosion. Waterline corrosion of buried pipelines and cables, passing from one type of soil to another type of soil and crevice corrosion are due to the formation of differential oxygen concentration cell.

4.45 CORROSION CONTROL *Imp*

The rate of corrosion may be slow but the loss is enormous. Economy of a country can be drastically improved if corrosion is prevented. But corrosion is inevitable; only thing one can do is to minimize the rate i.e. to control it. The various methods which can be applied to control corrosion are –

- ✓ 1. Protection by proper design and fabrication procedure.
 - ✓ 2. Proper material selection.
 - ✓ 3. Change in environmental condition.
 - ✓ 4. Modifying the properties of metal.
 - ✓ 5. Application of inhibitors.
 - ✓ 6. Use of protective coatings.
 - ✓ 7. Cathodic protection or electrochemical protection.
- Imp*

4.45.1 Cathodic Protection or Electrochemical Protection

For structures immersed in soils or electrically conducting liquids, the cathodic protection is the best way to control corrosion.

The principle involved is to make the metal to be protected as a cathode, so that corrosion is in the lowest level. The cathodic protection can be achieved in two ways.

- (i) Sacrificial anodic protection (galvanic protection)
- (ii) Impressed current cathodic protection.

Imp (i) **Galvanic protection** : In galvanic protection or sacrificial anodic protection, the metallic structure to be protected is connected by a wire to a more anodic metal.

The more active metal so-employed is called "sacrificial anode". The sacrificial anode is replaced by a fresh one when it is consumed completely. Metals commonly employed as sacrificial anodes are magnesium (Mg), zinc (Zn), aluminium (Al) and their alloys.

The important applications of sacrificial anodic protection method include protection of buried pipelines, underground cables, marine structures, water tanks etc.

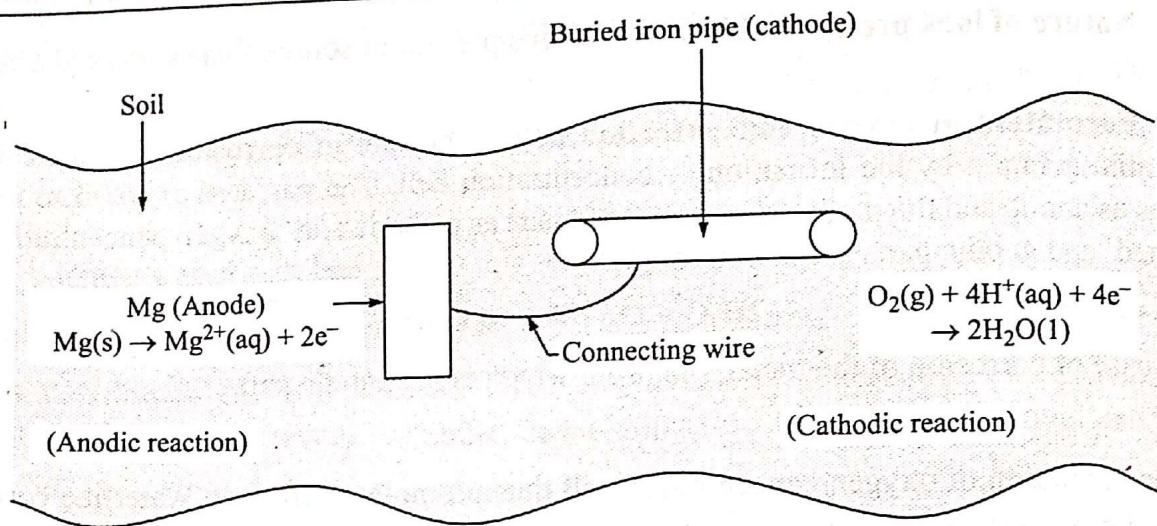


Fig. 4.28 Galvanic protection using sacrificial anode

(ii) Impressed current cathodic protection : In this method, an impressed current is applied in the opposite direction to nullify the corrosion current, and converting the corroding metal from anode to cathode. The object to be protected is made cathode by connecting it to the negative terminal of DC source. The positive terminal is connected to an insoluble anode, buried in the soil or immersed in the corroding medium like graphite, scrap iron or platinum and kept adjacent to the metal which is to be protected. These are placed in such a manner that a uniform potential is obtained over the metal surface. The electrons flow to the metal structure and as a result it acts as a cathode and is protected.

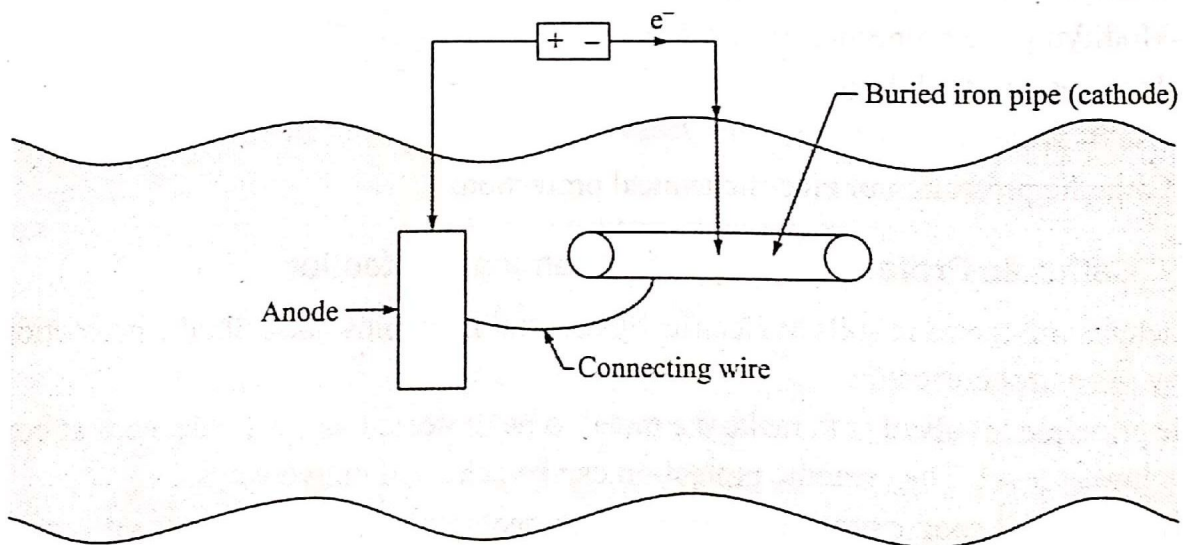


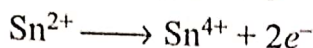
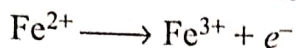
Fig. 4.29 Cathodic protection by impressed current

(3) Passivation : Passivation or passivity is the “phenomenon in which a metal exhibits a much higher corrosion resistance than expected from its position in the electrochemical series”. Such a metal is said to be passive in a corrosion environment. Passivity of a metal is due to formation of a highly protective, but very thin film (of the order of 4×10^{-4} mm thickness) on the surface of the metal under a definite environmental condition. The film so formed makes the metal or alloy behave as a noble metal.

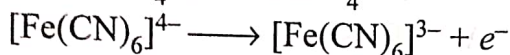
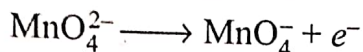
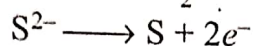
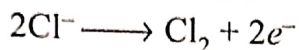
5.12 OXIDATION AND REDUCTION

Oxidation: Earlier oxidation was treated as any process involving addition of oxygen or removal of hydrogen from a substance. However, these days oxidation is defined as a process which involves the loss of electrons by a substance. Consequently, there is an increase in positive charge or decrease in negative charge of the atom or ion which undergoes oxidation. For example,

(i) *Loss of electrons resulting in an increase in positive charge*

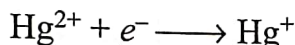
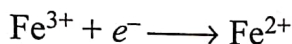
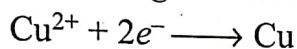


(ii) *Loss of electrons resulting in a decrease in negative charge*

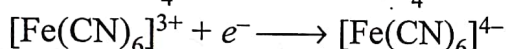
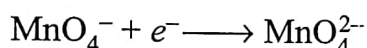
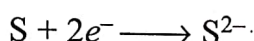
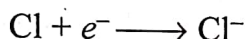


Reduction: Earlier, reduction was treated as a process involving addition of hydrogen or removal of oxygen from a substance. However, these days, reduction is defined as a process which involves the gain of electrons by a substance. Consequently, there is a decrease in positive charge or increase in negative charge of the atom or ion which undergoes reduction. For example,

(i) *Gain of electrons resulting in a decrease in positive charge*

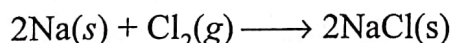


(ii) *Gain of electrons resulting in a increase in negative charge*



Further, in a chemical reaction, there is no net loss or gain of electrons. Therefore, loss and gain of electrons from one substance to another must take place simultaneously. In other words, in a chemical reaction, a substance can gain electrons only if another substance which can lose electrons is also present in the system. This means oxidation can take place only if reduction also takes place at the same time and vice versa.

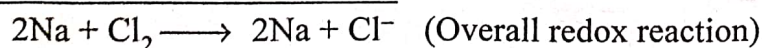
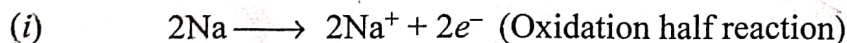
Therefore, oxidation and reduction always occurs side by side. To illustrate this, let us consider reaction between sodium metal and chlorine gas to form sodium chloride.



Now this reaction consists of two distinct, though simultaneous processes, which take place in such a way that:

Number of electrons lost = Number of electrons gained

These are represented below:

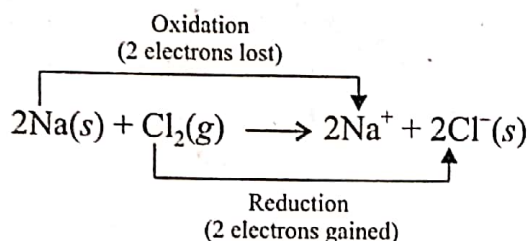


Thus, the overall reaction involves the transfer of electrons from sodium metal to chlorine. It means that sodium metal gets oxidized to Na^{+} ion while chlorine gets reduced to Cl^{-} ions so that overall reaction involves oxidation and reduction and is known as **redox reaction**.

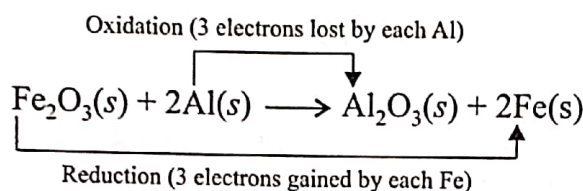
Therefore, a redox reaction may be defined as a reaction in which electrons are transferred from one to another reactant.

Every electron transfer reaction or redox reaction is the sum of oxidation half reaction in which electrons are lost and a reduction half reaction in which electrons are gained as shown above. The sum of the two half reactions in the total or net reaction known as redox reaction.

We may depict the above redox reaction in another way



Another example of the redox reactions is:



5.12.1 Oxidising and Reducing Agents

On the basis of electron transfer, an oxidizing agent may be defined as the substance which can accept electrons and a reducing agent as that which can lose electrons. The oxidizing agent itself, however, gets reduced while the reducing agent gets oxidized. In the formation of NaCl from sodium and chlorine, chlorine acts as oxidizing agent and sodium acts as reducing agent.

Some common examples of oxidising agents also called *oxidants* are KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, oxygen, Ozone, HNO_3 and SO_2 etc.

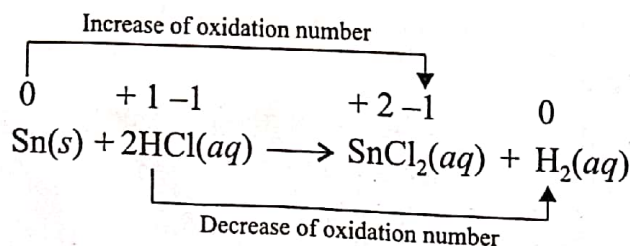
Some common examples of reducing agents also called *reductants* are: Ferrous salt, oxalic acid and oxalates, HBr, HI, H_2S and C etc.

There are some substances which act as *oxidants as well as reductants* depending upon the conditions of the reaction e.g., H_2O_2 , HNO_2 etc.

5.12.2 Redox Reaction in Terms of Oxidation Number

An atom undergoes *oxidation* when it increases its oxidation number. It undergoes *reduction* when its oxidation number decreases. Since the number of electrons in a chemical reaction remains the same, reduction of one atom must accompany the oxidation of another.

Therefore, any reaction involving changes in oxidation numbers is an oxidation reduction or Redox reaction. For example, consider the reaction.



As may be seen, Sn is converted to Sn^{2+} (aq) by losing two electron and gets oxidized. On the other hand H^+ ions gains one electron and gets reduced. It may also be seen that oxidation number of Sn increases from 0 to +2 when it gets oxidized. The oxidation number of H^+ decreases from +1 to 0 when it is reduced. Therefore, *oxidation is an increase in oxidation number while reduction is decrease in oxidation number*. In the above reaction, HCl acts as *oxidising agent* while Sn acts as *reducing agent*.