# Chapter 2

# Corrosion and Water Chemistry

## 2.1 Corrosion

### 2.1.1 Introduction

Any process of destruction (or deterioration) and consequent loss of a solid metallic material, through an unwanted chemical or electrochemical attack by its environment, starting at its surface, is called **corrosion.**

The most familiar example of corrosion is rusting of iron, when exposed to the atmospheric conditions. During this, a layer of reddish scale and powder of oxide ($Fe_3O_4$) is formed, and the iron becomes weak. Another common example is formation of green film of basic carbonate $[CuCO_3 + Cu(OH)_2]$ on the surface of copper, when exposed to moist-air containing carbon dioxide.

### Causes and Effects of corrosion

### Cause of Corrosion

Metals are exist in the form of oxides, sulphides, sulphates and carbonates. These chemically combined states of metal known as ore has low energy and is thus thermodynamically stable state for metal. The metals are extracted from these ores after supplying a large amount of energy. Metals in the uncombined condition have a higher energy and are in an unstable state. It is their natural tendency to go back to the low energy state i.e., combined state by recombining with the elements present in the environment. This is the main reason for corrosion

$$\begin{array}{ccccc} \text{Ore of metal} & \xrightarrow{\text{Metallurgical operation + energy}} & \text{Pure metal} & \xrightarrow{\text{environment}} & \text{Corroded metal} \\ \text{(Thermodynamically Stable state)} & & \text{(Thermodynamically unstable state)} & & \text{(Comparatively more stable than pure metal)} \end{array}$$

Although corroded metal is thermodynamically more stable than pure met but due to corrosion useful properties of a metal such as malleability, ductility an electrical conductivity are lost.

### Effects of corrosion

The effects of corrosion are the following;

1. Loss of useful properties of metal and thus loss of efficiency.
2. Replacement of corroded equipment.
3. High maintenance costs such as repainting.
4. Contamination of the product.
5. Due to failure, the plant shuts down.
6. Pollution due to a corrosion product affects the health.

Corrosion can be prevented by;

1. Proper design and use of suitable material.
2. Cathodic and anodic protection.
3. Treatment of metals.
4. External influences and
5. Environmental modifications.

## 2.1.2 Dry (or) Chemical corrosion

This type of corrosion occurs mainly through the direct chemical action environment/atmospheric gases such as oxygen, halogen, hydrogen sulph sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surface immediate proximity. *There are three main types of chemical corrosion.*

### Oxidation corrosion

Oxidation corrosion is brought about by the direct action of oxygen at low high temperatures on metals, usually, in the absence of moisture. At ordin temperatures, metals, in general, are very slightly attacked. However, alkali me (Li, Na, K, Rb, etc.) and alkaline-earths (Be, Ca, Sr, etc.) are even rap oxidized at low temperatures. At high temperatures, almost all metals (ex Ag, Au, and Pt) are oxidized.

The reaction in the oxidation corrosion are:

$$2M \longrightarrow \underset{\text{Metal ions}}{2M^{n+}} + 2ne^- \quad \text{(Loss of electrons)}$$

$$\frac{n}{2}O_2 + 2ne^- \longrightarrow \underset{\text{Oxide ions}}{nO^{2-}} \quad \text{(Gain of electrons)}$$

$$2M + \frac{n}{2}O_2 \longrightarrow \underbrace{\underset{\text{Metal ions}}{2M^{n+}} + \underset{\text{Oxide ions}}{nO^{2-}}}_{\text{Metal oxide}}$$

## Mechanism

Oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier that tends to restrict 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. Both transfers occur, but the outward diffusion of metal is, generally, much more rapid than the inward diffusion of oxygen, since the metal ion is appreciably smaller than the oxygen iron and consequently, of much higher mobility.

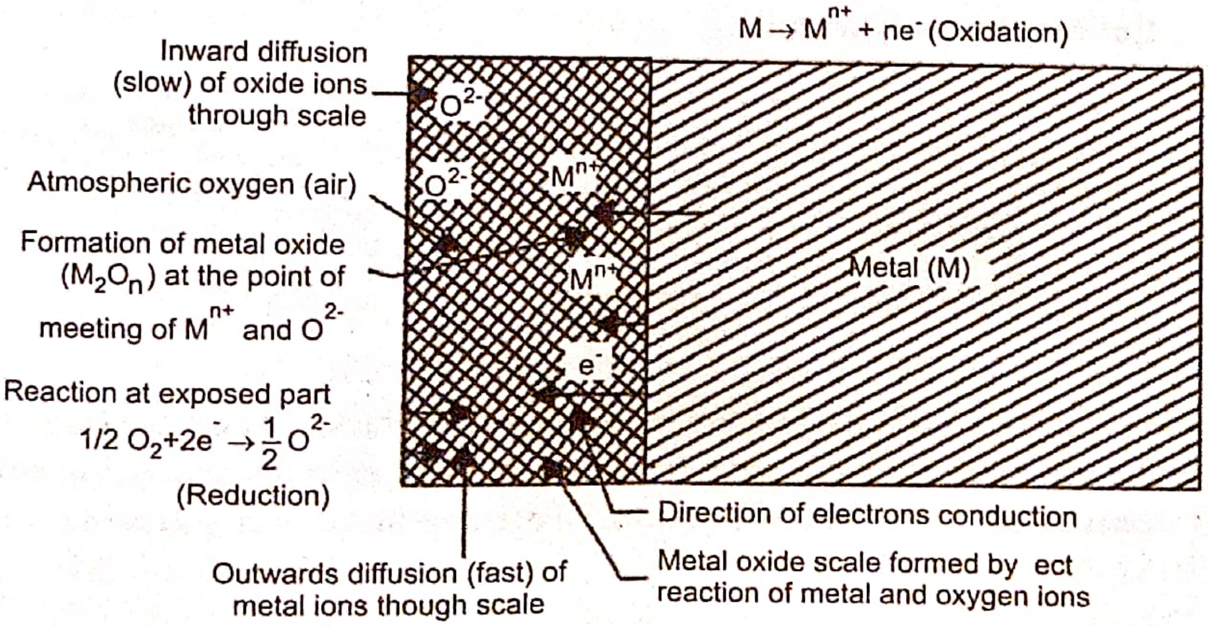


**Figure. 2.1 Mechanism of oxidation corrosion**

Nature of the oxide formed plays an important part in oxidation corrosion process.

Metal + Oxygen ⟶ Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. If the film is:

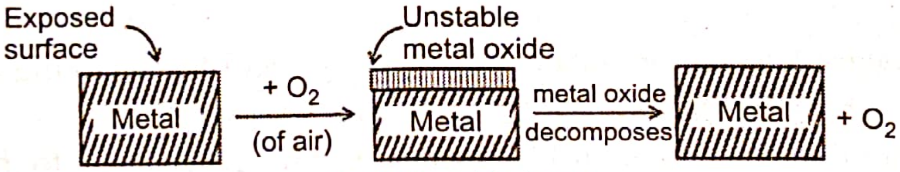
(i) **Stable:-** The corrosion forms stable oxide film which is impervious or tightly adhering. This impervious coating will prevent further corrosion.

**Ex:** Al, Sn, Pb, Cu, etc.

(ii) **Unstable:-** Sometimes the oxide film decomposes back to metal and oxygen. In such conditions the corrosion is not possible. In this case the oxide layer formed decomposes back into the metal and oxygen.

**Ex:** Ag, Au and Pt.

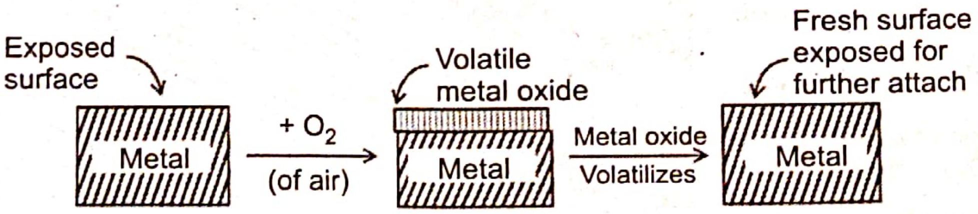
Metal oxide = Metal + Oxygen



Unstable oxide layer

(iii) **Volatile:-** In some metal surfaces, the oxide film gets volatized as soon as it is formed. This condition exposes the metal surface again and increases corrosion rapidly.

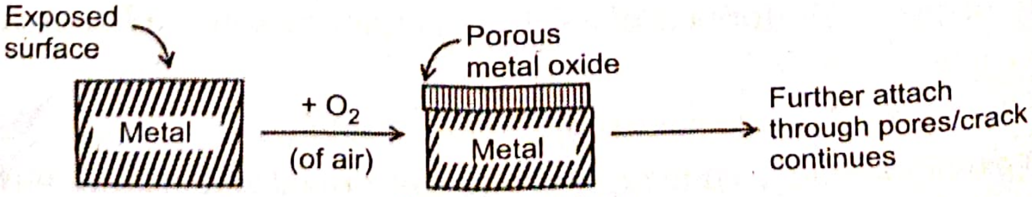
**Ex:** Mo ($MoO_3$ is volatile).



Volatile oxide layer

(iv) **Porous:-** If metal oxide layer having pores or cracks. At certain times the oxygen passes through pores or cracks of the layer to the underlying metal surface and continues corrosion till the entire metal is converted to metal oxide.

**Ex:** Alkali metals (Li, Na, Ka etc.)



Porous oxide layer

### Pilling-Bed worth rule

Pilling-Bed worth rule describes the porous and non-porous nature of metallic oxide which is formed during corrosion.

According to this rule the specific volume ratio is calculated as follows:

$$\text{specific volume ratio} = \frac{\text{volume of metal oxide}}{\text{volume of metal}}$$

a) If the specific volume ratio is smaller, then oxidation corrosion will takes place because the oxide films will be sufficiently porous for diffusion of $M^{n+}$ and $O^{2-}$.

b) If volume of the metal oxide $\geq$ volume of the parent metal, then it will be non-porous.

c) If the volume of the metal oxide $<$ volume of the parent metal, then it will be porous

The specific volume ratios of $Ni, Cr$ and $W$ are 1.6, 2.0 and 3.6 respectively. Hence, the rate of oxidation of tungsten (W) is least even at elevated temperatures.

### Corrosion by other gases

Corrosion by other gases like $SO_2, CO_2, Cl_2, H_2S, F_2$, etc. The extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non-protective films on the metal surface.

(a) If the film formed is protective or non-porous (e.g., AgCl film, resulting from the attack of $Cl_2$ on Ag), the intensity or extent of attack decreases, because the film formed protects the metal from further attack.

(b) If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed. For example, dry $Cl_2$ gas attacks on tin (Sn) forming volatile $SnCl_4$ (which volatilizes immediately), thereby leaving fresh metal surface for further attack. Similarly, in petroleum industry, $H_2S$ at high temperature attacks steel forming a FeS scale, which is porous and interferes with normal operations.

### Liquid metal corrosion

Liquid metal corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in devices used for nuclear power. The corrosion reaction involves either: (i) dissolution of a solid metal by a liquid metal or (ii) internal penetration of the liquid metal into the solid metal. Both these modes of corrosion cause weakening of the solid metal.

## 2.1.3 Theories of Corrosion

### Wet (or) Electrochemical corrosion

This type of corrosion occurs when

(i) metal contact with conducting liquid (or)

(ii) when two dissimilar metals or alloys are either immersed or dipped partially in a solution.

Under the above conditions, metals lead to form different anodic and cathodic areas resulting an electrochemical cell.

***At anode*** - Oxidation takes place (loss of electron), so anodic metal is destroyed. Hence, corrosion always occurs at anodic areas.

***At Cathode*** - reduction takes place (gain of electron), no affect on cathodic part. Since most metals cannot be further reduced.

Thus, we may sum up that electrochemical corrosion involves:

(i) The formation of anodic and cathodic areas or parts in contact with each other,

(ii) Presence of a conducting medium,

(iii) Corrosion of anodic areas only, and

(iv) Formation of corrosion product somewhere between anodic and cathodic areas.

### Mechanism:

In an electrochemical corrosion, the anodic reaction involves dissolution (oxidation) of metal to metal ion.

$$\text{At anode:}\quad \underset{\text{(Metal)}}{M} \longrightarrow \underset{\text{(Metal ion)}}{M^{n+}} + ne^{-} \quad \text{(Oxidation)}$$

$$\underset{\text{(Metal ion)}}{M^{n+}} \longrightarrow \text{Dissolved in solution}$$

$$\longrightarrow \text{Forms compound such as oxide}$$

The cathodic reaction involves reduction which depends on the nature of corroding environment.

If the medium is

(i) Acidic, cathodic reaction is accompanied by evolution of hydrogen.

$$2H^{+}2e^{-} \longrightarrow H_2 \uparrow \quad \text{(Reduction)}$$

(ii) Alkaline (or) neutral, cathodic reaction is accompanied by absorption of oxygen.

$$\frac{1}{2}O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-} \quad \text{(Reduction)}$$

(a) **Evolution of hydrogen-type:-** corrosion occurs, usually, in acidic environments. Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \text{ Oxidation)}$$

These electrons flow through the metal, from anode to cathode, where $H^+$ ions (of acidic solution) are eliminated as hydrogen gas.

$$2H^{+} + 2e^{-} \longrightarrow H_2 \uparrow \quad \text{(Reduction)}$$

The overall reaction is:

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

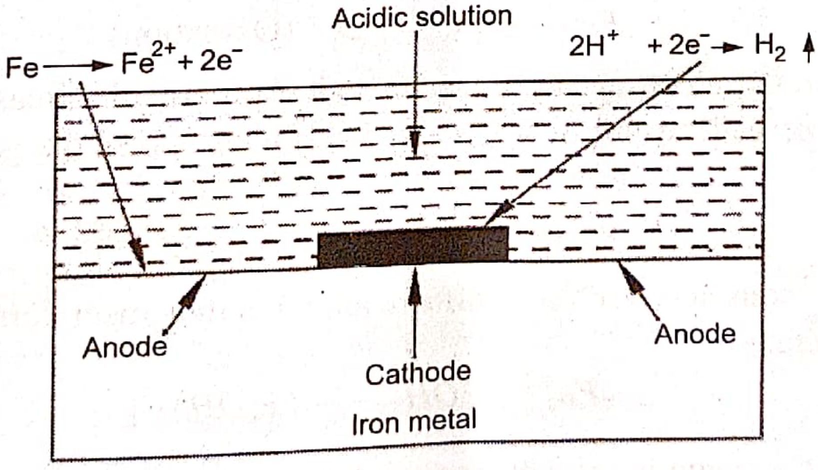


Figure. 2.2

Thus, this type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ions". Consequently, all metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

(b) **Absorption of oxygen:-** Rusting of iron in neutral aqueous solution of electrolytes (like NaCl solution) in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is, usually, coated with at thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface, while the well metal parts act as cathodes. It follows that the anodic areas are small surface parts, while nearly the rest of the surface of the metal forms large cathodes.

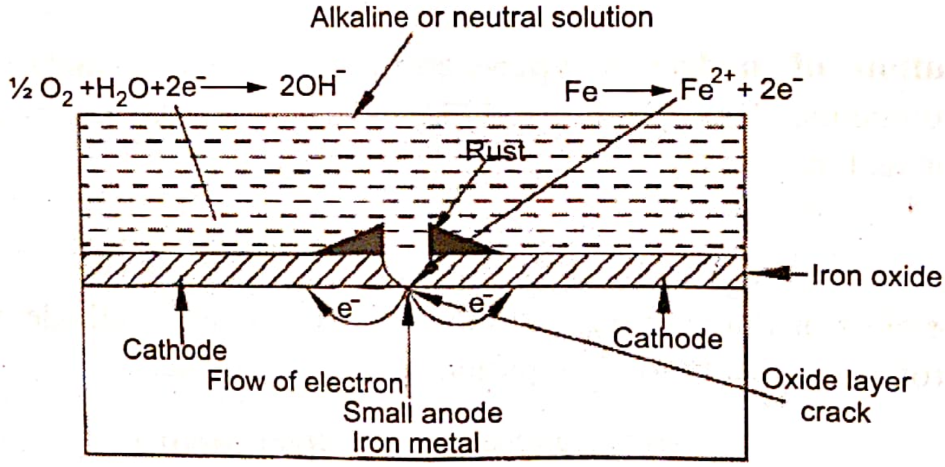


Figure. 2.3

At anodic areas of the metal (Fe) dissolve as ferrous ions with liberation of electrons.

$$Fe \longrightarrow Fe^{+2} + 2e^{-} \text{ (Oxidation)}$$

The liberated electrons flow from anodic to cathodic areas through iron metal, where electrons are intercepted by the dissolved oxygen as

$$\frac{1}{2}O_2 + H_2O + 2e^{-} \longrightarrow 2OH^{-} \text{ Reduction}$$

The $Fe^{+2}$ ions and $OH^{-}$ ions diffuse and then they meet, ferrous hydroxide is precipitated.

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

1. If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$$

This product is called Yellow rust actually corresponds to $Fe_2O_3.H_2O$

2. If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, $Fe_3O_4$.

### Difference between Chemical and Electrochemical corrosion

| S.No. | Chemical corrosion | Electrochemical corrosion |
|---|---|---|
| 1. | It occurs in dry condition. | It occurs in the presence of moisture or electrolyte. |
| 2. | It involves the direct chemical attack of metals by dry gases. | It involves the setting up of large number of electrochemical cells. |
| 3. | Corrosion products accumulate in the same spot of corrosion. | Corrosion occurs at the anode, products gather at the cathode. |
| 4. | Corrosion is uniform throughout the surface. | Corrosion is not uniform, which depends on anodic and cathodic. |
| 5. | It follows adsorption mechanism. | It follows mechanism of electrochemical reactions. |

## 2.1.4 Types of Corrosion

### Galvanic corrosion

When two dissimilar metals (e.g, *Zn* and *Cu*) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called **Galvanic Corrosion**. In the above example, *Zn* (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas *Cu* (lower) acts as cathode.

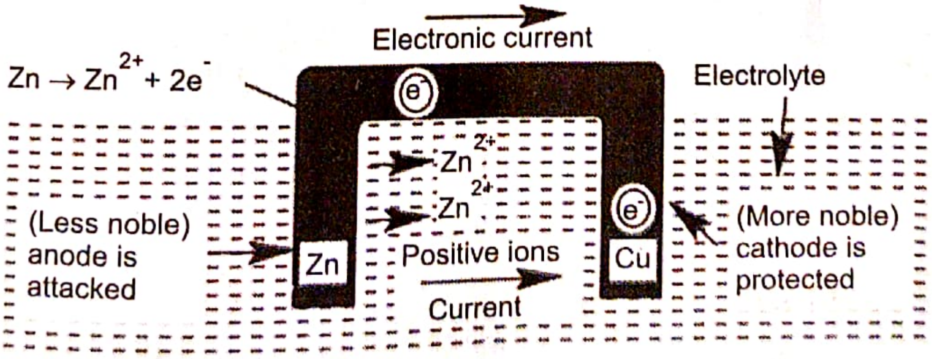


Figure. 2.4 Galvanic corrosion

### Mechanism

In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The current flows from anode to cathode.

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

Thus, it is evident that the corrosion occurs at the anodic metal; while the cathodic part is protected.

**Ex:-** 1. Steel screws in a brass marine hardware,

2. Pb-Sb solder around copper wire.

### Waterline corrosion:

When water is stored in a steel tank, it is generally found that the maximum amount of corrosion takes place along a line just beneath the level of the water meniscus .The area above the waterline (highly-oxygenated) acts as the cathodic and is completely unaffected by corrosion. However, if the water is relatively free from acidity, little corrosion takes place.

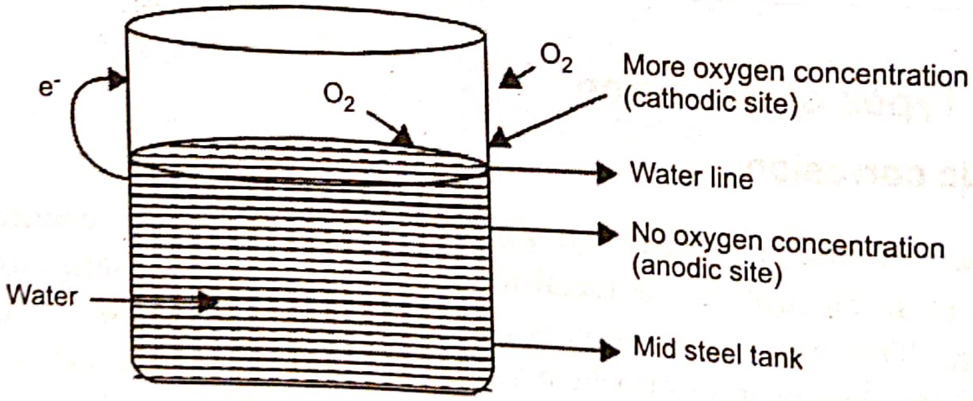


**Figure. 2.5 Waterline corrosion**

The problem of water line corrosion is also that concerns marine engineers. In the case of ships, this kind of corrosion is often accelerated by marine plants attaching themselves to the sides of ships. The uses of special antifouling paints restrict this to some extent.

## 2.1.5 Factors influencing corrosion

The rate and extent of corrosion, depends on the following factors:

### Nature of the metal

(i) **Position in galvanic series:-** When two metals or alloys are in electrical contact, in presence of an electrolyte, the more active metal (or higher up in the series) suffers corrosion. The rate and severity of corrosion, depends upon the difference in their positions, and greater is the difference, the faster is the corrosion of the anodic metal/alloy.

(ii) **Overvoltage:-** Corrosion rate is inversely proportional to the over voltage of the metal in a corrosive surroundings. e.g, the hydrogen over voltage of $Zn$ in 1M $H_2SO_4$ is 0.70 v. So the rate of corrosion is low. But when some $Cu$ impurity is present, the over voltage is reduced and corrosion rate increases.

(iii) **Relative areas of the anodic and cathodic parts:-** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.

(iv) **Physical state of metal:-** The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.). The smaller the grain-size of the metal or alloy, the greater will be its solubility and hence, greater will be its corrosion. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

(v) **Nature of surface film:-** In aerated atmosphere, practically all metals get covered with a thin surface film (thickness = a few Angstroms) of metal oxide. The ratio of the volumes of the metal oxide to the metal is known as a 'specific volume ratio'. Greater the specific volume ratio, lesser is the oxidation corrosion rate. The specific volume ratios of $Ni, Cr$, and $W$ are 1.6, 2.0 and 3.6 respectively. Consequently, the rate of oxidation of tungsten is least, even at elevated temperatures.

### ature of the corroding environment

(i) **Temperature:-** With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.

(ii) **Humidity of air:-** Humidity of airis the deciding factor in atmospheric corrosion. "Critical humidity" is defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply. The value of critical humidity depends on the physical characteristics of the metal as well as nature of the corrosion products. The reason why corrosion of a metal becomes faster in humid atmosphere is that gases ($CO_2$, $O_2$ etc) and vapours, present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical corrosion cell.

(iii) **Presence of impurities in a atmosphere:-** Atmosphere, in the vicinity of industrial areas, contains corrosive gases like $CO_2, H_2S, SO_2$, and fumes of $HCl, H_2SO_4$ etc. In presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases. This consequently, results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces.

(iv) **Influence of pH:-** Generally, acidic media (i.e. $pH < 7$) are more corrosive than alkaline and neutral media. However, amphoteric metals (like $Al, Zn, P$ etc.) dissolve in an alkaline solution as complex ions.

(v) **Conductance of the corroding medium:-** In corrosion of underground or submerged structures, the conductance of the medium is of prime importanc Conductance of dry sandy-soils is lower than those of clayey and mineraliz soils. Consequently, stray currents (from power leakages) will cause more severe damage to the metallic structures, buried under clayey and mineralize soils than those under dry sandy-soils.

(vi) **Formation of oxygen concentration cell:-** With the increase in supply of oxygen/air to the moist-metal surface, the corrosion is promoted. Less oxygen concentration (e.g. oxide-coated part or less-exposed part) parts becomes anodic; while the more-oxygenated regions (or parts more exposed to oxygen) becomes cathodic, thereby leading of the formation of "oxygen - concentration cell" in which the anodic part suffers corrosion.

## 2.1.6 Corrosion control methods (Protective coatings)

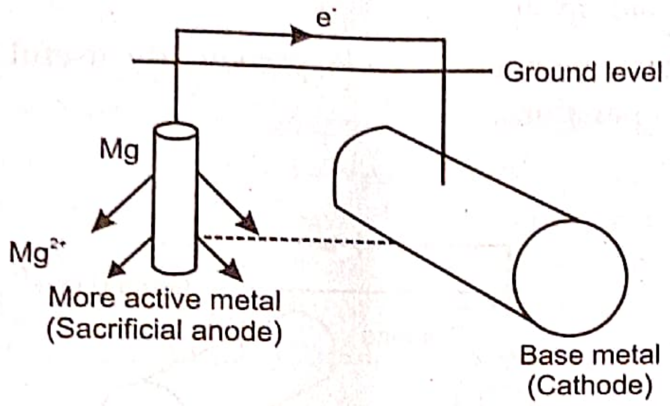
### Cathodic protection

The principle involved in this method is to force the metal to be protected to behave like a cathode. (i.e) The base metal to be protected can be converted into cathode, thereby corrosion does not occur. This is achieved by the following methods.

### (i) Sacrificial anodic protection method: -

- In this protection method, the metallic structure (to be protected) is connected by a wire to more active metal (anode), so that all the corrosion is concentrated at this more active metal.
- The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so-employed 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 magnesium, zinc, aluminum and their alloys.

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



Ex:- 1. Protection of pipe lines, cables from soil corrosion.
2. Protection of ship hulls from marine corrosion.

### Advantages

1. No need of external power supply.
2. Installation and maintenance cost is low.

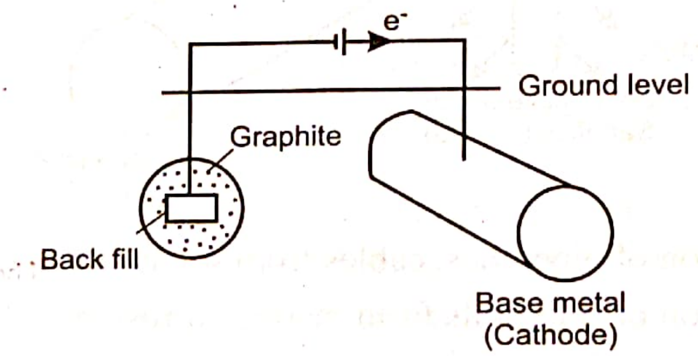
### Limitations

1. Not suited for large objects due to limited driving potential.
2. Uncoated parts cannot be protected.

### (ii) Impressed current cathodic protection:-

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- Usually, the impressed current is derived from a direct current source (like battery or rectifier on a.c. line) with an insoluble anode (like graphite, high silica iron, scrap iron, stainless steel or platinum).
- Usually, a sufficient D.C. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium), and connected to the metallic structure to be protected.

- The anode is, usually, in a backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil.
- This type of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc.
- This kind of protection technique is, particularly, useful for large structures for long-term operations.



### Advantages

1. Larger objects can be protected due to larger driving voltage.
2. Uncoated parts can be protected.

### Limitations

1. Larger installation cost.
2. Higher maintenance cost.

## 2.1.7 Methods of application of metal coatings

### Hot dipping:

Hot dipping is used for producing a coating of low-metal such as $Zn(m.p. = 419°C)$, $Sn(m.p. = 232°C)$, $Pb$, $Al$, etc. on iron, steel and copper, which have relatively higher melting points. The process, in general, consists of immersing the base metal in a bath of the molten coating-metal, covered by a molten flux layer (usually zinc chloride). The flux cleans the base metal surface and prevents the oxidation of the molten coating-metal. For good adhesion, the base metal surface must be very clean; otherwise it cannot be properly wetted by the molten metal. Two most widely applied hot dipping methods are:

### Galvanizing

Galvanizing is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. The process is carried out as follows: The iron or steel article (e.g., sheet, pipe, and wire) is first cleaned by pickling with dilute $H_2SO_4$ solution for 15-20 minutes at 60-90°C. This treatment also removes any scale, rust (oxide layer) and impurities. The article is then washed well and dried. It is then dipped in bath of molten zinc, maintained at 425-430°C. The surface of the bath is kept covered with a flux $[NH_4Cl]$ to prevent oxide formation. When the article is taken out, it is found to have been coated with a thin layer of zinc. It is then passed through a pair of hot rollers. This process removes any superfluous (excess) of zinc and produces a thin film of uniform thickness. Then, it is annealed at a temperature of 650°C and finally, cooled slowly.

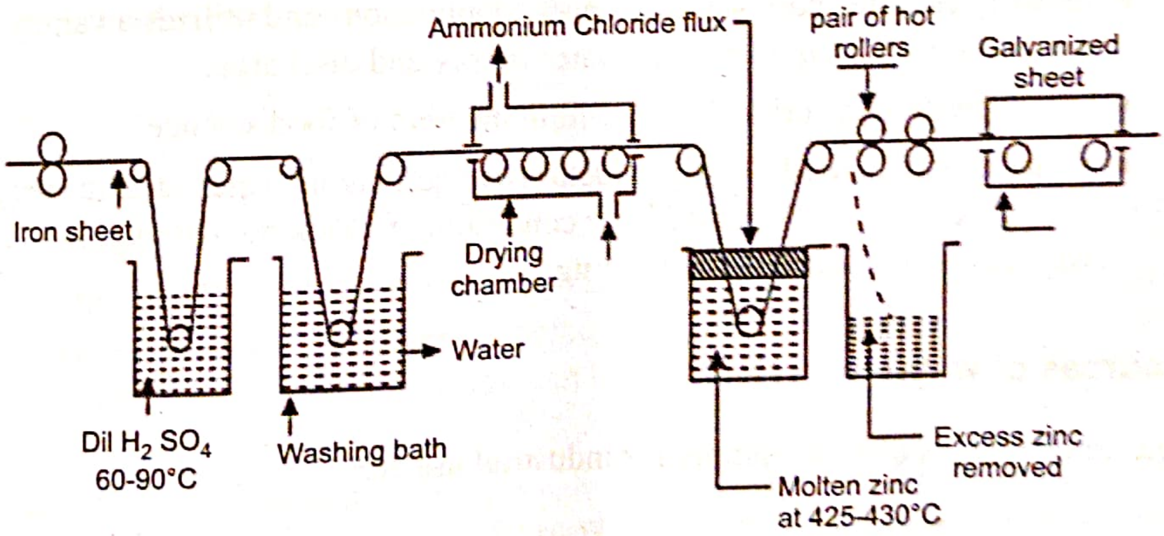


Figure. 2.6

**Uses:-** It is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes, etc. It may be pointed here that zinc gets dissolved in dilute acids to form highly toxic (or poisonous) compounds. Hence, galvanized utensils cannot be used for preparing and storing foodstuffs, especially acidic ones.

## 2.2 Water Chemistry

### 2.2.1 Introduction

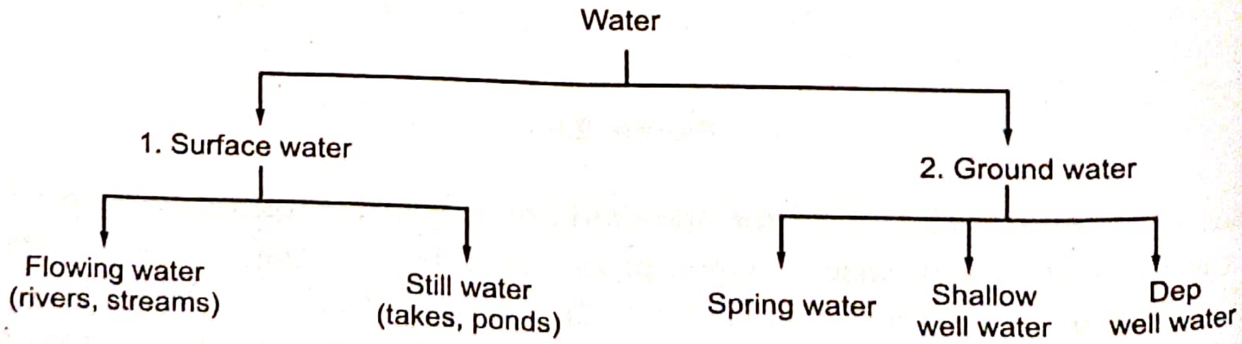
Water is the most useful, wonderful and abundant compound on earth. It is a vital component of the life forms. It is a proven theory that one can live without food for many number of days but one cannot live without water. Water is the important constituent of all the body fluids, without which all the cells or organisms are in crystalline or dead state. (For example, the human body contains 70%, land plants 50 - 75% and aquatic plants 95 -99%). Water is not only essential for the lives of animals and plants, but also occupies a unique position in industry.

## Industrial Purpose of Water:

- Water is used in power generation. As steam in steam turbines and as coolants.
- Blasting and water jet cutters. Very high pressure water guns are used for precise cutting. It is also used in the cooling of machinery to prevent over-heating, or prevent saw blades from over-heating.
- Industry requires pure water for many applications and utilizes a variety of purification techniques both in water supply and discharge.
- Water plays many critical roles within the field of food science.
- Water is widely used in the production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air conditioning, drinking, bathing, sanitary, washing, irrigation and fire-fighting etc.

## Sources of water

The chief sources of water supply for industrial use are:



- **Rain water:-** The purest form of water, collected on the roofs. Yet this method is seldom adopted in industry.
- **Surface water:-**
  - Flowing water, such as rivers, streams etc.
  - Still water, such as lakes, ponds etc.

- **Ground water:-**
    - Water from springs.
    - Water from shallow wells. In the case of shallow wells, the boring is done only through one geological stratum.
    - Water from deep wells. Here the boring is done through many geological strata.
- **Sea water:-**

  Its use is very limited as its uses entail very great problems of chemical engineering

## Source and nature of impurities of water

Water in the form of vapour in clouds is said to be pure. Yet when it condenses as rain and flows on the ground it takes many impurities from atmosphere and ground. The major situations in which water gets impure are as followed:

- **Dissolved gases:-** during raining water absorbs much of the gases like oxygen, carbon dioxide, hydrogen sulphide etc. from atmosphere. The resultant water will be slightly acidic and on high concentrations of impurities it may result into acid rain.
- **Soluble crystalloids:-** water when flow over the surface of the land (like rivers, streams.) dissolves soluble minerals. The most of the soluble minerals include chlorides,sulphates and bicarbonates of sodium, calcium, magnesium and iron.
    - Where as in seawater 3.5% of dissolved salts are seen in which 2.5% include sodium chloride.
- **Organic matter:-** This is derived from the decomposition of plants and small particles of sand and rock in suspension.

## Characteristics imparted by impurities of water

As such pure water is odurless, colourless, tasteless, etc., but the presence of impurities imparts various physical and chemical changes to water nature which are as followed.

1. **Colour:-** The metallic substances like humus, tannins, peat, algae, weeds, protozoa, industrial effluents and salts of iron, manganese in the colloidal form imparts color to water.

   For example yellowish tinge is due to the presence of chromium or appreciable amount of organic matter, yellowish - red colour due to the presence of iron, while reddish brown is due to the presence of peat. (The intensity of the colour indicates the severity of toxic nature of water).

2. **Turbidity:-** The colloidal, extremely fine suspension particles such as clay, silt, finely divided matter, micro-organisms etc. increases the turbidity of the water. The turbid water is not fit for either consumption or industrial purpose.

3. **Taste:-** Usually this property is linked to odour. Yet under certain conditions taste is not accompanied by odour. For example,

   - Bitter taste can be due to the presence of iron, aluminum, manganese, sulphate or excess of lime.
   - Soapy taste can be due to the presence of large amount of sodium bicarbonate.
   - Brackish taste is due to the presence of unusual amount of salts.
   - Palatable taste is due to the presence of dissolved gases $(CO_2)$ and minerals like nitrates.

4. **Odour:-** The odour may be due to the presence of living organisms, decaying vegetation. The common disagreeable odour is due to the presence of sulphides. The odour of sewage water is due to the presence of organic compounds of N, S and P along with the putrefaction of proteins and the industrial effluents like alcohols, aldehydes, phenols, esters, ketones etc. Besides these,

   - The presence of algae in waterimpart strong grassy odour.
   - Growth of iron and sulphur bacteria produces offensive odour.
   - Sand in finely divided state imparts faint earthy odour.
   - When water pases through iron pipes, it gives tarry odour.
   - The faint odour when the water passes through galvanized iron pipes is due to the impure hydrogen.

5. **Chemical impurities in Water:-** Chemical impurities in Water includes

   - Inorganic and organic chemicals released from dyes, paints, varnishes, drugs, insecticides, pesticides, detergents and textiles, industries, etc,. All these pollute the water bodies.
   - Acid discharged in water by DDT, high explosives, battery, industries, etc. The use of this type of contaminated water causes harmful effects on health of human-beings

6. **Boilogical impurities:-** Biological impurities are algae, pathogenic bacteria, fungi, viruses, pathogens, etc. The source of these contamination is discharged of domestic and sewage wastes, excreta (from man, animals and birds), etc.

### 2.2.2 Hardness of water

Hardness in water is the character, which "prevents the lathering of soap". This is due to the presence of bicarbonates, chlorides and sulphates of calcium, magnesium and other heavy metals like strontium and iron etc.

**For example:-** Insoluble carbonates of $Ca, Mg$ and $Fe$ readily transform into soluble bicarbonates in the presence of carbon dioxide.

$$\underset{\text{Insoluble}}{CaCO_3 + CO_2 + H_2O} \rightarrow \underset{\text{Soluble}}{Ca(HCO_3)_2}$$

$$\underset{\text{Insoluble}}{MgCO_3 + CO_2 + H_2O} \rightarrow \underset{\text{Soluble}}{Mg(HCO_3)_2}$$

Many of the mineral constituents of rocks like $NaCl, CaSO_4.H_2O$ readily dissolve in water and collects in it.

$$\underset{\text{Anhydrite}}{CaSO_4 + 2H_2O} \rightarrow \underset{\text{Gypsum}}{CaSO_4.H_2O}$$

If a sample of water is treated with soap ($Na/K$ salt of higher fatty acids like oleic, palmitic/stearic) like sodium sterate and if the water does not produces lather, then the water is said to be hard water, else soft water.

In the hard water the soap produces precipitate or white scum, which is due to the formation of insoluble soap of calcium & magnesium. For example a typical soap (Sodium Sterate) reaction with salts like calcium chloride & magnesium sulphate are depicted as followed.

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca \downarrow + 2NaCl$$

Sodium Sterate Hardness Insoluble PPT

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg \downarrow + Na_2SO_4$$

Sodium Sterate Hardness Insoluble PPT

## Types of Hardness

Hardness of water is of two types

1. Temporary or Carbonate Hardness
2. Permanent or Non - Carbonate Hardness

### 1. Temporary or Carbonate Hardness:-

Temporary hardness of water is due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals or carbonate of iron. It is easily destroyed by mere boiling of water. When the water is boiled, the bicarbonates are decomposed yielding insoluble carbonates or hydroxides which are deposited as a crust or scales at the bottom of the vessel, while carbon dioxide escapes out.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 \downarrow + H_2O + CO_2$$

Soluble Insoluble

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 \downarrow + 2CO_2$$

Soluble Insoluble

### 2. Permanent or Non - Carbonate Hardness:-

Permanent hardness is due to the presence of chlorides, sulphates of calcium, magnesium, iron and other heavy metals. It cannot be removed by boiling; it is removed by using softeners or chemical treatment.

## Disadvantages of Hard water

### 1. Domestic:-

- **Washing & Bathing:-** Hard water does not form lather easily with soap. As a result, a large amount of soap is wasted.

- **Drinking:-** Hard water causes bad effects on our digestive system. Sometimes, stone formation takes place in kidneys.
- **Cooking:-** The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking.

2. **Industrial:-**

- **Textile industry:-** Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
- **Paper industry:-** Calcium and magnesium salts in water may affect the quality of paper.
- **Sugar industry:-** Water containing sulphates, carbonates, nitrates affects the crystallization of sugar.
- **Dyeing industry:-** The salts of calcium and magnesium in hard water react with dyes and spoil the desired shade.
- **Pharmaceutical industry:-** Hard water may form some undesirable products while preparation of pharmaceutical products.
- **Concrete making:-** Chloride and sulphates present in hard water will affect the hydration of cement and the final strength of the hardened concrete.

Finally in industries where steam is employed, if hard water is used in steam production, the troubles like corrosion, scale & sludge formation, priming & foaming & caustic embrittlement are seen.

## Expression of Concentration of Hardness

The concentration of hardness as well as non - hardness constituting ions is expressed in terms of an equivalent amount of $CaCO_3$. The equivalence of $CaCO_3$ is used because it permits the addition & subtraction of concentration, when required. The choice of $CaCO_3$ in particular is due to its molecular weight is 100 (equivalent wt. is 50). Not only that, it is the most insoluble salt that can be precipitated in the water treatment easily. The equivalents of $CaCO_3$ can be defined as: The equivalents of $CaCO_3$

$$= \frac{[\text{Mass of hardness producing substance}] \times [\text{Chemical equivalent of } CaCO_3]}{\text{Chemical equivalent of hardness producing substance}}$$

$$= \frac{\text{Mass of hardness Producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}} \text{ in } mg/L$$

## Units of Expression of Hardness of Water

Normally the hardness of water is represented in ppm. ie. Parts per million or mg/L.

$$1\ \text{mg/L} = 1\ \text{ppm}.$$

1. **Parts per million(ppm):-** It is the number of parts by weight of $CaCO_3$ equivalent hardness present per million ($10^6$) parts by water

   i.e. 1 ppm = 1 part of $CaCO_3$ equivalent hardness in $10^6$ parts of water.

2. **Milligram/Litre(mg/L):-** It is the number of milligrams of calcium carbonate equivalent present per liter of water.

   i.e. 1 mg/L = 1 mg of $CaCO_3$ equivalent hardness per liter of water.

   But, it is known that 1 lit = 1 kg = 1000 g = 1000 × 1000 mg = $10^6$ mg.

   $\Rightarrow$ $1mg/L = 1mg$ of $CaCO_3$ equivalent hardness per $10^6$ mg of water.

   = 1 part of $CaCO_3$ equivalent hardness per $10^6$ mg of water.

   = 1 ppm.

   Hardness is also expressed in the following ways

3. **Degree clark(°Cl):-**

   $°Cl = 1$ part of $CaCO_3$ equivalent hardness per 70,000 parts of water

   i.e. $1\ ppm = 0.07°Cl$

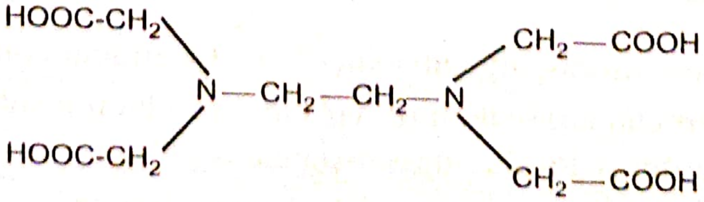
4. **Degree French(°Fr):-**

   $°Fr = 1$ part of $CaCO_3$ equivalent hardness per $10^5$ parts of water

   i.e. $1ppm = 0.1°Fr$

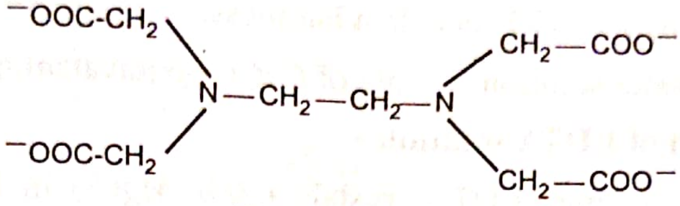
## Determination of Hardness of water EDTA method

EDTA is Ethylene diamaine tetra acetic acid whose structural formulae is



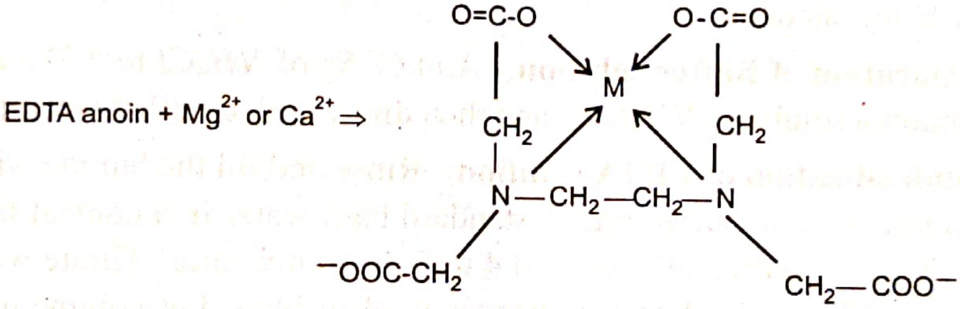
Structure of EDTA

In the form of its sodium salt yields the anion;



EDTA anion

Which forms complex ions with $Ca^{+2}$ and $Mg^{+2}$



Where $M = Ca$ or $Mg$. It may be pointed the EDTA is used as its disodium salt,

## Principle

In this complex metric Titration, the water sample is titrated with standard solution of di sodium salt of EDTA using EBT indicator.

## Reactions Involved

In order to determine the equivalent point, indicator Eriochrome black $-T$ (EBT) is used. When EBT is added to hard water at a pH of about 10, using Ammonical buffer solution $(NH_4OH + NH_4Cl)$, a wine red unstable complex with $Ca^{2+}$ or $Mg^{2+}$ ions is formed. When this solution is titrated with EDTA, at the endpoint wine red colour changes to deep blue colour solution i.e. the EDTA has formed stable complexes.

$$M^{2+} + EBT \longrightarrow M - EBT + EDTA \longrightarrow M - EDTA + EBT$$

Unstable wine Red Stable deep blue

Thus, change of **wine-red** colour to distinct **blue** marks the end-point of titration.

Various steps involved in this method are...

1. **Preparation of standard hard water:-**

   Dissolve 1g of pure, dry $CaCO_3$ in minimum quantity of dil. HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each ml of this solution thus contains 1 mg of $CaCO_3$ equalent hardness.

1 mL hard water solution $= 1$ mg of $CaCO_3$ equivalent hardness.

2. **Preparation of EDTA solution:-**

   Dissolve 4 g of pure EDTA crystals + 0.1g $MgCl_2$ in 1 Litre of distilled water.

3. **Preparation of Indicator (EBT):-** Dissolve 0.5 g of Eriochrome Black-T in 100 mL alcohol.

4. **Preparation of Buffer solution:-** Add 67.5g of $NH_4Cl$ to 570 mL of Con. Ammonia solution ($NH_4OH$) and then dilute with distilled water to 1 Litre.

5. **Standardization of EDTA solution:-** Rinse and fill the burette with EDTA solution. Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by $V_1$ mL.

6. **Titration of Unknown Hard water:** Titrate 50 mL of water sample just in Step-5. Let volume used be $V_2$ mL.

7. **Titration of Permanent hardness:-** Take 250 mL of the water sample in a large beaker. Boil it. Till the volume is reduced to about 50 mL, filter it, wash the precipitate with distilled water, collecting filtrate and washing in a 250 mL measuring flask. Finally make up the volume to 250 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in Step (5). Let volume used by $V_3$ mL.

## Calculations:

$$\text{Molarity of standard hard water} = \frac{\text{Weight of } CaCO_3}{\text{Molecular weight of } CaCO_3} = \frac{1}{100} = 0.01M$$

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$$

Where, $M_1 =$ Molarity of standard hard water $= 0.01M$

$V_1 =$ Volume of standard hard water $= 50$ml

$n_1 =$ number of moles of $Ca^{+2} = 1$

$M_2 =$ Molarity of EDTA

$V_2 =$ Volume of EDTA $= x$ ml

$n_2 =$ number of moles of EDTA $= 1$

$$\therefore\ M_2 = \frac{M_1\,V_1}{V_2} = \frac{0.01 \times 50}{x}$$

Total hardness is calculated by

$$\frac{M_2\,V_2}{n_2} = \frac{M_3\,V_3}{n_3};n_2 = n_3 = 1$$

Where, $M_2$ = Molarity of EDTA
$V_2$ = Volume of EDTA = yml
$M_3$ = Molarity of hard water
$V_3$ = Volume of hard water = 50ml

$$\therefore\ M_3 = \frac{M_2\,V_2}{V_3} = \frac{0.01 \times y}{50}$$

Total hardness of water = $M_3 \times 100 \times 1000$ mg/L (or) ppm Permanent hardness is calculated by

$$\frac{M_2\,V_2}{n_2} = \frac{M_4\,V_4}{n_4};n_2 = n_4 = 1$$

Where, $M_2$ = Molarity of EDTA
$V_2$ = Volume of EDTA = $z$ ml
$M_4$ = Molarity of boiled water
$V_4$ = Volume of boiled water = 50ml

$$\therefore\ M_4 = \frac{M_2\,V_2}{V_4} = \frac{0.01 \times z}{50}$$

Permanent hardness of water = $M_4 \times 100 \times 1000$ mg/L (or) ppm
Temporary hardness = Total Hardness − Permanent Hardness
= $M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000$ mg/L (or) ppm

### Advantages of EDTA method

This method is definitely preferable to the other methods, because of the,

i. Greater accuracy
ii. Convenience, and
iii. More rapid procedure.

## 2.2.3 Alkalinity of Water and Its Determination

The alkalinity may be defined as a measure of the capacity of water to neutralize acids. The total of all of the alkaline species found in a water sample contribute to the alkalinity of the water sample. However, for the sake of simplicity, the alkalinity of water samples is expressed in terms of mg of $CaCO_3/dm^3$.

Alkalinity refers to the presence of bases ($OH^-, CO_3^{2-}, HCO_3^-$) in a solution that can be converted to uncharged species by a strong acid. Alkalinity can be measured by titrating a sample with a standard acid using phenolphthalein and methyl orange indicators. The following reactions take place during the addition of acid to the water sample solution:

$$OH^- + H^+ \rightarrow H_2O \quad \text{(i)}$$

$$CO_3^{2-} + H+ \rightarrow HCO_3^- \quad \text{(ii)}$$

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \quad \text{(iii)}$$

The titration of the water sample with a standard acid up to the phenolphthalein end point marks the completion of reactions (i) and (ii) only. The amount of acid consumed corresponds to hydroxide plus one half of the carbonate present. The titration of the water sample with a standard acid to methyl orange end point marks the completion of all the reactions above. Hence, the amount of the total acid consumed corresponds to the total alkalinity and the amount of acid used after the phenolphthalein end point corresponds to the one half of carbonate plus all the bicarbonates.

The alkalinity in water can be due to $OH^-$ only or carbonate only or bicarbonate only or due to their combinations. But $OH^-$ and bicarbonate can't exist together because they combine instantaneously to form carbonate ions.

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$$

On the basis of same reasoning all the three OH$^-$, carbonate and bicarbonate cannot exist together.

### Types of Alkalinity:

There are two types of alkalinity present in water:

- P-Alkalinity also called Phenolphthalein Alkalinity because Phenolphthalein indicator used for analysis.
- M-Alkalinity also called Methyl orange Alkalinity because Methyl orange indicator used for analysis.

### Sources of alkalinity:

The main sources for natural alkalinity are soil and rocks which contain carbonate, bicarbonate, and hydroxide compounds. Borates, silicates, and phosphates may also contribute to alkalinity.

### Determination of alkalinity

- Pipette out 100 mL of the water sample into a clean conical flask.
- Add 2-3 drops of phenolphthalein indicator to the sample and stir.
- Titrate with sulphuric acid solution from the burette to the contents of the flask until the pink colour disappears.
- Note down the titre value.
- Then add 2-3 drops of methyl orange indicator to same solution and titrate further with standard acid solution till pink colour reappears.
- Again note down the titre value.

### Calculations:

Volume of water sample taken = 100 ml

Concentration of sulphuric acid solution $= XN$.

Volume of acid consumed for phenolphthalein end point $= V_1$ ml.

Volume of acid consumed for methyl orange end point $= V_2$ ml.

Phenolphthalein alkalinity in terms of $CaCO_3$ equivalents

$$= P = \frac{V_1 \times X \times 50 \times 1000}{\text{Volume of sample in } mL}\ mg/L$$

$$= P = \frac{V_1 \times X \times 50 \times 1000}{100}\ mg/L \text{ (or) ppm}$$

Methyl orange alkalinity in terms of $CaCO_3$ equivalents

$$= M = \frac{(V_2 - V_1) \times X \times 50 \times 1000}{100}\ mg/L \text{ (or) ppm}$$

Total alkalinity in terms of $CaCO_3$ equivalents

$$= T = P + M\ mg/L \text{ (or) ppm}$$

Then the calculation of $OH^-, CO_3^{2-}, HCO_3^-$ can be calculated as follows:

1. When $P=0$, both $OH^-, CO_3^{2-}$ are absent and alkalinity is due to bicarbonate only.
2. When $P=1/2M$, only $CO_3^{2-}$ is present since half of carbonate neutralization reaction takes place with phenolphthalein indicator while complete neutralization takes place when methyl orange indicator is used. Therefore, alkalinity due to $CO_3^{2-}=2P$.
3. When $P=M$ only $OH^-$ is present. Thus alkalinity due to $OH^-=P=M$.
4. When $P>1/2M$ both $OH^-, CO_3^{2-}$ are present. Now half of $CO_3^{2-}=M-P$, therefore, alkalinity due to $CO_3^{2-}=2(M-P)$ and alkalinity due to $OH^-=M-2(M-P)=2P-M$.
5. When $P<1/2M$ carbonates and bicarbonates are present. Now alkalinity due to carbonates $=2P$. Therefore alkalinity due to bicarbonate $=M-2P$.

### 2.2.4 Softening of water

#### Definition

The process of removing hardness-causing salts from water is known as "Softening of water".

#### Internal treatment

The internal treatment consists of adding chemicals directly to the water in the boilers for removing scales and sludges.

1. **Colloidal conditioning:-** organic substances like kerosene and agar-agar are added to water which prevent the scales.
2. **Phosphate conditioning:-** Phosphates react with water and a loose sludge is formed which can be easily removed by blow-down operation.

$$3CaSO_4+2Na_3PO_4 \rightarrow Ca_3(PO_4)_2+3Na_2SO_4$$

3. **Carbonate conditioning:-** In low pressure boilers, scale formation can be avoided by adding sodium carbonate to the boiler water.

$$CaSO_4+Na_2CO_3 \Longleftrightarrow CaCO_3+Na_2SO_4$$

4. **Calgon conditioning:-** Sodium hexa meta phosphate (calgon) is added to boiler water to prevent scale formation by formation of soluble complex.

$$2CaSO_4+Na_2(Na_4(PO_3)_6) \rightarrow Na_2(Ca_2(PO_3)_6)+2Na_2SO_4$$

5. **Sodium aluminate conditioning:-** Sodium aluminate gets hydrolysed yielding NaOH and aluminium hydroxide precipitate. The sodium hydroxide reacts with magnesium salts to magnesium hydroxide. These hydroxides entrap finely divided particles and neutralize the charge on colloidal particles, and the loose precipitate can be removed by the blow-down operation.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3 \downarrow$$

## Softening of Water by Ion exchange process (External treatment)

Softening of water means the removal of calcium, magnesium, iron salts and similar other metallic ions, which would form insoluble metallic soaps.

Ion exchange resins are insoluble, cross-linked, long chain organic polymers with a micro porous structure and the functional groups are attached to the chains which are responsible for the ion exchange properties.

In the Ion Exchange process the cations are exchanged with $H^+$ and anions are exchanged with $OH^-$ ions. For this two types of ion-exchangers are commonly employed, which are insoluble, cross-linked long chain organic polymers with microscopic structure.

i. Cation exchange resins

ii. Anion exchange resins

i. **Cation exchange resins:-**

Cation exchange resins ($RH^+$) are phenol-sulfonic acid-formaldehyde resin, styrene-divinyl benzene copolymers which exchange their $H^+$ ions with the cations present in the water i.e., $Ca^{2+}$ and $Mg^{2+}$

ii. **Anion exchange resins:-**

Anion exchange resins ($ROH^-$) are the styrene divinyl benzene or amine formaldehyde copolymers contain quaternary ammonium tertiary sulphonium or amino group in the resin. The resin on treatment with $NaOH$ solution is capable of exchanging the $OH^-$ with different anions of water. i.e., $Cl^-, SO_4^{2-}$ etc.

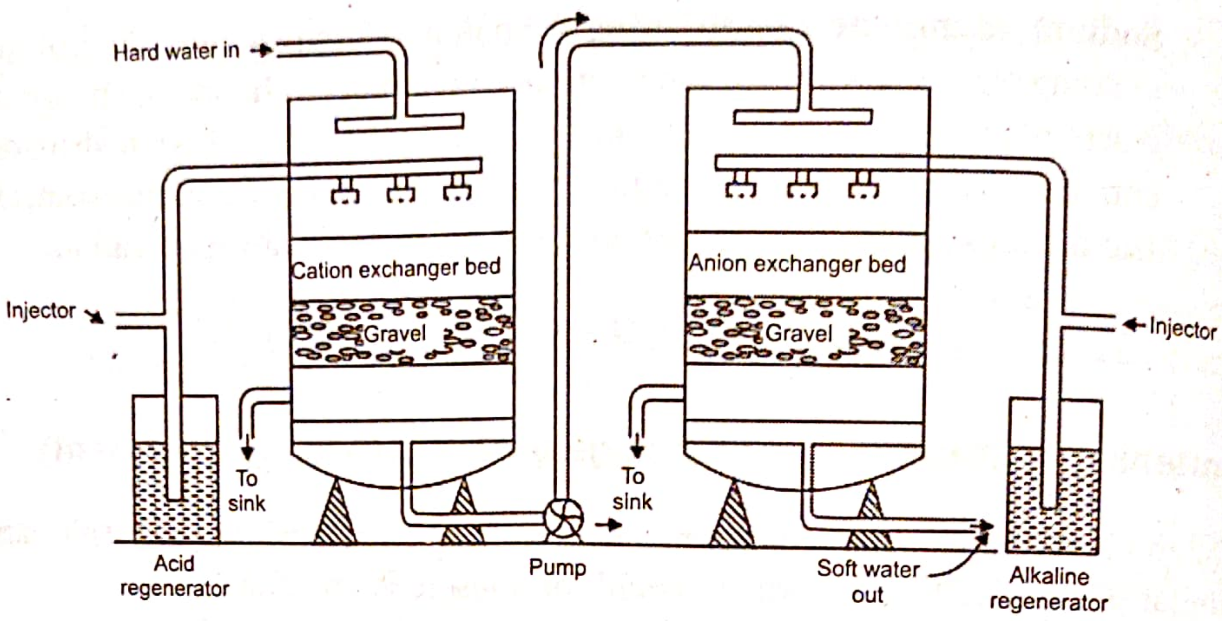


Figure. 2.7 Demineralization of water

## Method

The hard water is passed first through cation exchange resin similar to the permutit process whereby the cations like $Ca^{2+}$, $Mg^{2+}$ are removed from the hard water and exchanged with $H^+$ as follows,

$$2RH + Ca(HCO_3)_2 \rightarrow R_2Ca + 2H_2CO_3$$
$$2RH + Mg(HCO_3)_2 \rightarrow R_2Mg + 2H_2CO_3$$
$$2RH + CaCl_2 \rightarrow R_2Ca + 2HCl$$
$$2RH + MgCl_2 \rightarrow R_2Mg + 2HCl$$
$$2RH + CaSO_4 \rightarrow R_2Ca + H_2SO_4$$
$$2RH + MgSO_4 \rightarrow R_2Mg + H_2SO_4$$
$$2RH + Ca(NO_3)_2 \rightarrow R_2Ca + 2HNO_3$$
$$2RH + Mg(NO_3)_2 \rightarrow R_2Mg + 2HNO_3$$

The $Ca^{2+}$ and $Mg^{2+}$ are retained by the cation exchangers as Ca-R and Mg-R releasing $H^+$ into water. Thus the water coming out of the resin is highly acidic because the $H^+$ released by the exchange combines with anion of the dissolved salt to produce the corresponding acids.

After this the hard water is again passed through anion exchange column, which exchanges all the anions like $SO_4^{2-}$, $Cl^-$ etc. present in the water with $OH^-$. The $H^+$ and $OH^-$ released from exchangers get combined and produce $H_2O$.

$$R^{|}OH + HCl \rightarrow R^{|}Cl + H_2O$$

$$2R^{|}OH + H_2SO_4 \rightarrow R^{|}_2SO_4 + 2H_2O$$

$$R^{|}OH + H_2CO_3 \rightarrow R^{|}HCO_3 + H_2O$$

$$R^{|}OH + HNO_3 \rightarrow R^{|}NO_3 + H_2O$$

Thus the water coming out finally from the two exchangers is ion free and called deioinized or de-mineralized water.

When water sample is completely deionised, it has the tendency to absorb gases like $CO_2, O_2$ etc,from atmosphere which cause boiler corrosion. Hence deionization must be followed by degasification.

## Regeneration

After the deionization of certain amount of raw water the cation and anion exchangers will be exhausted. Regeneration of cation exchanger is carried out by passing dil. HCl or $H_2SO_4$ solution into the bed. The $H^+$ ions of the acid are exchanged with the cations ($Ca^{2+}$ and $Mg^{2+}$) present in the cation exchanger regenerating it the following way.

$$R_2Ca + 2HCl \rightarrow 2RH + CaCl_2$$

$$R_2Mg + H_2SO_4 \rightarrow 2RH + MgSO_4$$

The washings containing $CaCl_2$ and $MgSO_4$ etc., were passed to sink or drain. Similarly the exhausted anion exchanger is treated with dil. NaOH solution. The regeneration can be represented as;

$$R^{|}_2SO_4 + 2NaOH \rightarrow 2R^{|}OH + \underset{\text{(Washings)}}{Na_2SO_4}$$

$$R^{|}Cl + NaOH \rightarrow R^{|}OH + \underset{\text{(Washings)}}{NaCl}$$

$$R^{|}HCO_3 + NaOH \rightarrow R^{|}OH + \underset{\text{(Washings)}}{NaHCO_3}$$

$$R^{|}NO_3 + NaOH \rightarrow R^{|}OH + \underset{\text{(Washings)}}{NaNO_3}$$

The washings are discarded into sink. The regenerated ion-exchangers are used for softening. Thus deionization and regeneration are the alternate process.

### Advantages

1. Highly acidic or alkaline water samples can be purified by this process.
2. The hardness possessed by the de-ionised water is 2 ppm.
3. The de-ionised water is most suitable for high pressure boilers.

### Disadvantages

1. The ion exchanging resins are expensive; hence the cost of purification is high.
2. Raw water should contain turbidity below 10 ppm. Otherwise pores in the resin will be blocked and output of the process is reduced.

### Reverse Osmosis

**Principle:-** When two solutions of unequal concentrations are separated by a semi-permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverse, i.e. solvent is forced to move from concentrated side to dilute side across the membrane. This is the ***principle of reverse osmosis***. Thus in reverse osmosis methods, pure solvent (water) is separated from its contaminates,rather than removing contaminants from the water. This membrane filtration is sometimes also called "***Super-filtration***" or "***Hyper-filtration***".

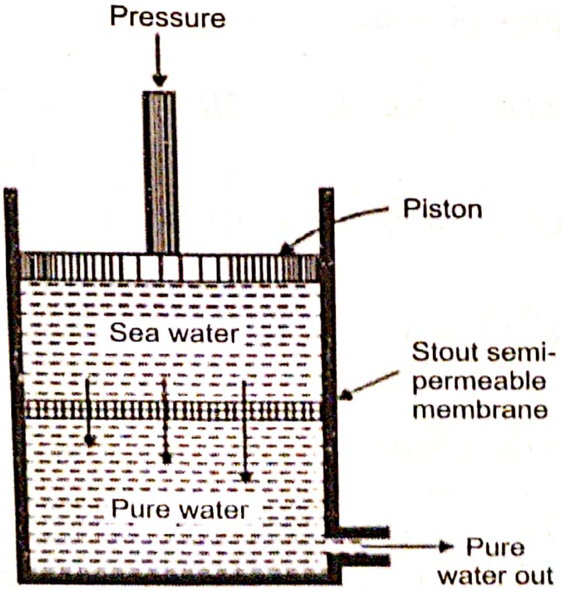


**Figure. 2.8 Reverse osmosis**

**Method:-** In this process, pressure (of the order 15 to 40 $Kg/Cm^2$) is applied to the Sea water/impure water to force its pure water out through the semi-permeable membrane, leaving behind the dissolved salts (both ionic as well as non ionic). The principle of reverse osmosis, as applied for treating saline/Sea water, is illustrated in figure. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of poly methacrylate and poly amides have come in to use.

## Advantages

1. Reverse osmosis process a distinct advantage of remaining ionic as well as non ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by de mineralization.
3. The maintenance cost is almost entirely on the replacement of the semi-permeable membrane.
4. The life time of membrane is quite high, about 2 years.
5. The membrane can be replaced within a few minutes, thereby provided nearly uninterrupted water supply.
6. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

## Potable water (or) Drinking water (or) Municipal water

Municipalities have to supply potable water; *Water which is safe to drink is known as Potable water.*

Potable water fit for human consumption, should satisfy the following essential requirements:

1. It should be sparking clear and odourless.
2. It should be pleasant in taste.
3. It should be perfectly cool.
4. Its turbidity should not exceed 10 ppm.
5. It should be free from,objectionable dissolved gases like hydrogen sulphide.
6. It should be free from objectionable minerals such as Pb, As, Cr and Manganese salts.
7. Its alkalinity should not be high. Its pH should be 8.0.

8. It should be reasonably soft.
9. Its total dissolved solids should be less than 500 ppm.
10. It should be free from disease-producing micro-organisms.

### 2.2.5 Purification of water for domestic use (or) Treatment of water for municipal supply

Natural water from the rivers, canals, etc., does not confirm to all the required specifications of drinking water. For removing various types of impurities, the following methods are employed;

1. Removal of Suspended impurities
2. Sterilisation or Disinfection

#### Removal of Suspended impurities

Various impurities of water are removed in the following stages

- **Screening:-** The process of removing floating matter from the water is known as screening. In this process, water is passed through a screen, which arrests all the floating matter.
- **Aeration:-** The water is subjected to aeration, which helps in
  - Exchange of gases,
  - Increased oxygen content and
  - By removing the impurities like Fe & Mn by precipitating as their hydroxides.
- **Sedimentation:-** It is a process of removing suspended impurities by allowing the water to stand un disturbed for 2-6 hours in a big tanks about 5 m deep, when most of the suspended particles settle down at the bottom, due to the force of gravity.

  **Sedimentation by coagulation:-** This is the process of removal of suspended colloidal impurities by using coagulants like

  - Alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$)
  - Ferrous Sulphate ($FeSO_4$)
  - Sodium Aluminate ($NaAlO_2$)

When a coagulant is added to water, floc formation takes place due to hydroxide [$Al(OH)_3$] formation which can gather tiny particles together to form bigger particles and settle down quickly.

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4$$
$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$

- **Filtration:-** This process helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually the water is passed through filters or suitable porus material so as to remove the suspended impurities and some microorganisms. Normally filters made of three layers like sand, gravel and charcoal is employed. Yet the Indian Cotton sariee four fold will work as ultra filter. (Proved by the NASA testing, reported in News papers).

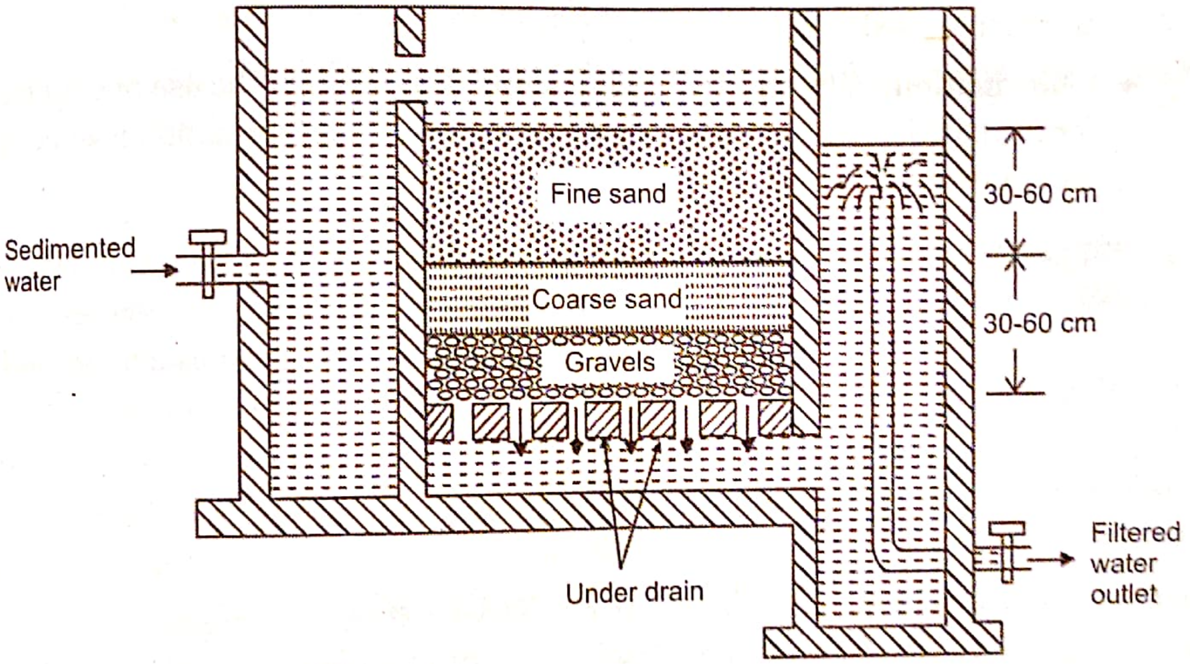


Figure. 2.9

## Sterilisation or Disinfection

The process of killing pathogens or other microorganisms in the water is known as Sterilisation or Disinfection. The water which is free from microorganisms or other pathogens is known as potable water.

Sterilisation is done in the following ways:

- **Boiling:-** Boiling water for 15 - 20 minutes, will kill the bacteria in water. Yet this method is not suitable for municipal supply of water. This is adopted for domestic purpose.
- **Aeration or UV treatment:-** Exposing water to UV rays or pumping water through nozzles into air in broad day light will kill the germs and microorganisms in water.
- **Ozonisation:-** Ozone passed into water acts as disinfectant. Ozone is an unstable isotope of oxygen, produces nascent oxygen which is a powerful disinfectant.

  $$O_3 \rightarrow O_2 + [O]$$

  Nascent oxygen

  This treatment is expensive and ozone cannot be stored for longtime due to its instability.
- **Chemicals:-** Chemicals like chlorine tablets and bleaching powder are more commonly used.
- **Chlorination:-** Chlorine is also a powerful disinfectant. The use of chlorine for disinfecting water is known as chlorination. The chlorination is done in the following ways:
  - **By adding Bleaching power:-** Bleaching power contains 80% chlorine When it is used as disinfectant, it is called hypo - chlorination because the disinfection is due to the formation of Hypochlorous acid formed during the process.

    $$CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$$

    Bleaching powder

    $$Cl_2 + H_2O \rightarrow HOCl + HCl$$

    Disinfectant

    $$HOCl \rightarrow [O] + HCl$$
  - **By passing Chloramines:-** Chlorine mixed with ammonia in the ratio of 2:1 by volume will produce a stable chloramine. This is a very powerful disinfectant. This is normally employed in swimming pools.

    $$Cl_2 + NH_3 \rightarrow NH_2Cl + HCl$$

    $$NH_2Cl + H_2O \rightarrow HOCl + NH_3$$

- **Passing chlorine:-** Directly administering the chlorine gas along with water in a chlorinator will be an effective process. The passed chlorine reacts with water and generates hypochlorous acid, which acts as disinfectant.

$$Cl_2 + H_2O \rightarrow \underset{\text{Hypochlorus acid}}{HOCl} + HCl$$

Chlorine is a powerful disinfectant than chloramines and bleaching powder. Calculated amount must be added to water because in excess will be toxic and tastes bad. The amount of chlorine required to kill bacteria and to remove organic matter is called break point of chlorination.

## Break point Chlorination

- The process of applying calculated amounts of chlorine to water in order to kill the pathogenic bacteria is called chlorination.
- Chlorine also reacts with water and generates hypochlorous acid, which kills bacteria.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

- Chlorine is a powerful disinfectant than chloramine and bleaching powder. Calculated amount of chlorine must be added to water because chlorine after reaction with bacteria and organic impurities or ammonia, remains in water as residual chlorine which gives bad taste, odour and toxic to human beings.
- The amount of chlorine required to kill bacteria and to remove organic matter is called **break point chlorination.**
- The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted as a graph as shown below which gives the break point chlorination.

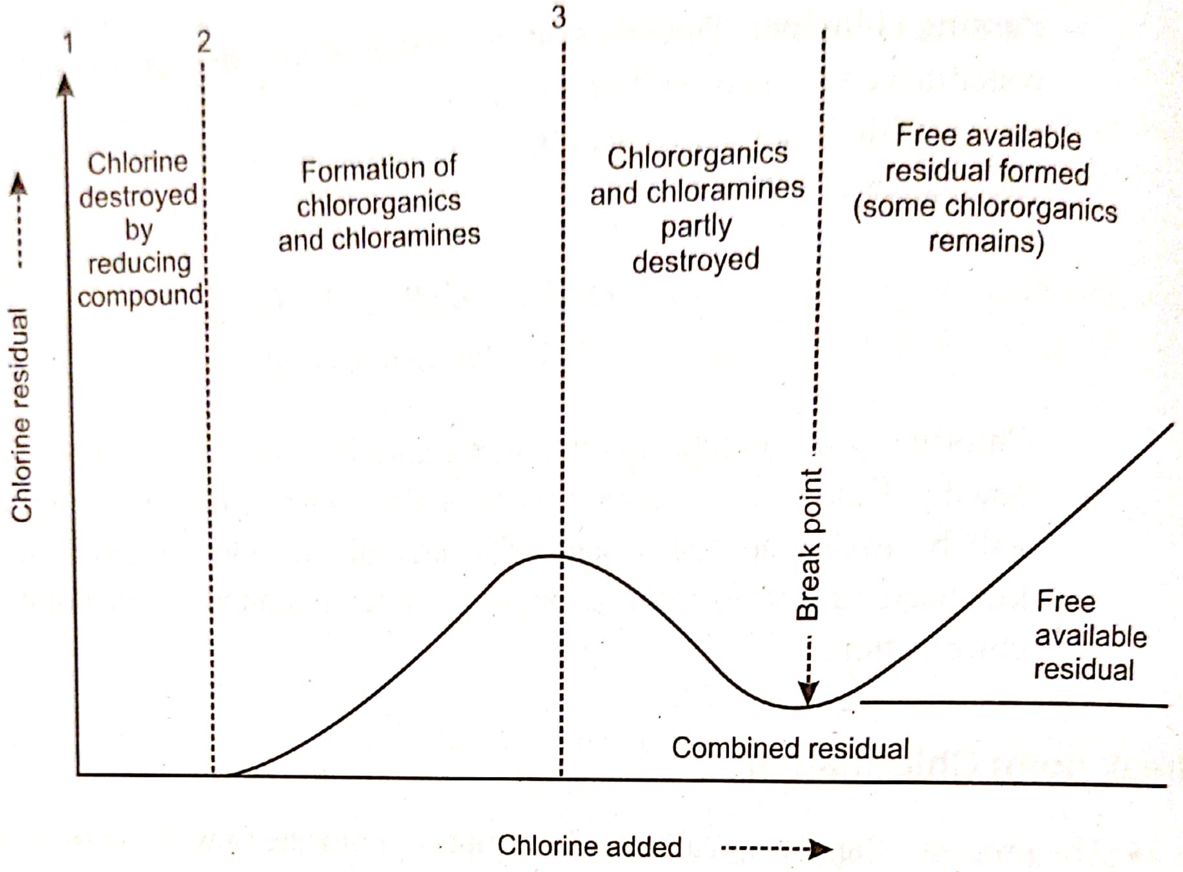


**Figure. 2.10 A break point chlorination graph**

From the graph it is clear that the area under represents,

1-2: chlorine added oxidises reducing impurities of water.

2-3: chlorine added forms chloramine and chloro compounds.

3-4: chlorine added causes destruction of bacteria.

After 4: chlorine is residual chlorine.

So, 4 is the break point for the addition of chlorine to water.This is called break point chlorination.

## Advantages of break point chlorination

1. It removes taste, colour, oxidise completely organic compounds, ammonia and other reducing impurities.
2. It destroys completely (100%) all disease producing bacteria.
3. It prevents growth of any weeds in water.
4. **De-chlorination:** The over chlorination is removed by passing the water through a bed of granular carbon and also by addition of $SO_2$ and sodium thiosulphate.

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + S + 2HCl$$