Unit-4
Chapter-1- Water Chemistry

1.1 INTRODUCTION

Water is the most important compound for the existence of human beings, animals and plants. Besides these, water has great applications in industries. Water is mainly used in power generation industry for the production of electric current through steam generation. Water is also used as a coolant in atomic reactors as well as chemical plants. It is also largely used in irrigation for agricultural purposes.

The main sources of water are (a) rain, (b) rivers and lakes (surface water), (c) wells and springs (ground water), and (d) sea water.

From the point of view of industrial applications, it is not usually feasible to use rainwater and seawater. Rainwater is irregular in supply and generally expensive to collect. Sea water is too saline for most industrial uses except cooling.

So, surface and ground water is normally used for industrial and domestic purposes. Each industry has its own specifications for water and so the treatment of water depends on the purpose for which it is to be used. A few examples are given in Table 1.1.

From the requisites of water for various industries, it is thus seen that water is to be treated to remove all the undesirable substances to suit a particular industry. The process of removing all types of impurities from water and making it fit for domestic or industrial purposes is called *water treatment*. Before treating water one must know the nature as well as the amount of impurities.

TABLE 1.1 Different uses of water

Purpose	Specification	Remark
Beverages	Should not be alkaline	Alkalinity in water tends to neutralize the fruit acids and destroy the taste.
Laundries	Soft, free from colour, Fe and Mn salts	Hardness increases the consumption of soaps and detergents. Salts of Fe and Mn give a grey or yellow shade to the fabric.
Power stations		
(a) Cooling systems	Non-corrosive, non-scale forming, must not promote the growth of algae	
(b) Boiler feed	Zero hardness	Scale formed on using untreated water prevents efficient heat transfer.
Paper	Free from	
	(a) hardness and alkalinity	Consumption of alum by the alkaline water increases the cost of production.
	(b) SiO_2	Produces cracks on the paper.
Textiles	Free from turbidity, colour, Fe and Mn	Causes uneven dyeing, leaves stains on fabric.

1.2 IMPURITIES IN WATER

The impurities present in water may be broadly classified as follows.

1. **Dissolved impurities:** The dissolved impurities are mainly the carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron, sodium and potassium. The presence of these salts imparts hardness to water. The dissolved impurities also include dissolved gases like oxygen and carbon dioxide.

2. **Suspended impurities:** The following are the types of suspended impurities:
   (a) Inorganic: Clay and sand
   (b) Organic: Oil globules, vegetable and animal matter
   The above suspended impurities impart turbidity, colour and odour to water.

3. **Colloidal impurities:** They are finely-divided silica and clay, organic waste products, complex protein aminoacids, etc.

4. **Microorganisms:** They are algae, fungi and bacteria.

1.2.1 Sources of Impurities in Water

The sources of impurities in water are the following:

1. Water collects impurities from the ground, rocks or soil with which it comes in contact.
2. Water becomes impure when it comes in contact with sewage or industrial wastes.

3. Organic impurities in water are generally introduced by the decomposition of plant and animal remains.

4. Gases like oxygen and carbon dioxide are picked up by rainwater from the atmosphere.

1.3   HARD WATER

A sample of water which produces lather readily with soap is called *soft water*. If it does not produce lather readily with soap, it is said to be *hard water*.
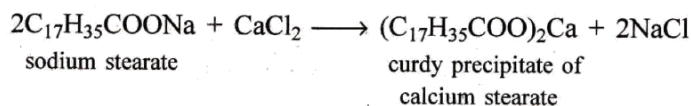
1.3.1   Disadvantages of Hard Water

The following are the disadvantages of hard water:

1. Hard water is not useful for various domestic purposes, viz. washing, bathing and drinking. The hardness producing ions convert soluble soaps to insoluble precipitates. This results in wastage of soaps in washing and bathing.

2. Hard water is not useful for many industries such as textile, sugar and paper. Dissolved salts like Ca, Mg, Fe and Mn affect the following properties.

   (a) Giving a smooth and glossy finish to paper in paper industry.
   (b) Producing good lather in laundry.
   (c) Producing good shades and colour to fabrics in textile industry.

3. Hard water is also not suitable for steam raising in boilers, since they produce scales on inner plates. Corrosion, priming, foaming and caustic embrittlement are the other problems caused by hard water.

4. Hard water is not suitable for laboratory analysis, because the hardness producing ions interfere in various reactions.

1.3.2   Hardness of Water

Hardness was originally defined as the soap consuming capacity of a water sample. Soap is the sodium salt of higher fatty acids, e.g. sodium stearate. The sodium salt is soluble in water, but the corresponding calcium and magnesium ions are insoluble in water. When soap is added to soft water, it dissolves and lathers readily. On adding soap solution to a sample of hard water which contains calcium or magnesium ions, soap is precipitated as insoluble salts which prevent the formation of lather. This reaction causes the loss of soap. No lather is obtained until all the ions are removed. So, large amount of soap is consumed unnecessarily before lather is formed.

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

　　sodium stearate　　　　　　　　　　curdy precipitate of
　　　　　　　　　　　　　　　　　　　calcium stearate

Hardness of water due to the presence of bicarbonates of Ca and Mg is called *temporary hardness*. It is also called *carbonate hardness* (CH). Temporary hardness can be removed by boiling, which converts the bicarbonates into insoluble carbonates:

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

Permanent hardness is due to the presence of chlorides and sulphates of Ca and Mg and cannot be removed by boiling. It is also called *non-carbonate hardness* (NCH). CH and NCH thus constitute the total hardness.

Units of hardness

The following are the common units used in hardness measurements.

1. **Parts per million (ppm):** It is defined as the number of parts by weight of $CaCO_3$ present in million parts by weight of water.

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

2. **Milligram per litre:** It is defined as the number of milligrams of $CaCO_3$ present in one litre of water.

   1 mg/l = 1 mg of $CaCO_3$ equivalent hardness in one litre of water

   Since weight of 1 litre of water = 1 kg

   $$= 1000 \text{ g}$$
   $$= 1000 \times 1000$$
   $$= 10^6 \text{ mg}$$

   1 mg/l = 1 mg of $CaCO_3$ per 10^6 mg of water

   $$= 1 \text{ part of } CaCO_3 \text{ per } 10^6 \text{ parts of water}$$
   $$= 1 \text{ ppm}$$

   Thus, mathematically both units are equal.

   Hardness is usually expressed in terms of equivalent of $CaCO_3$ in order to simplify calculations in water analysis. Hence, all the hardness causing impurities are first converted in terms of their respective weights equivalent to $CaCO_3$ by using the relation

   $$\frac{\text{weight of the hardness producing salt}}{\text{molecular weight of the salt}} \times \text{molecular weight of } CaCO_3$$
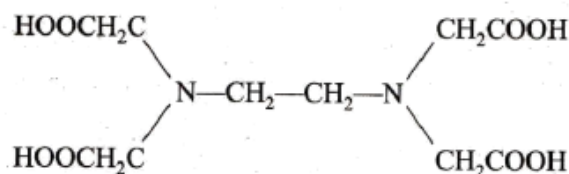
   or

   $$\frac{\text{weight of the hardness producing salt}}{\text{equivalent weight of the salt}} \times \text{equivalent weight of } CaCO_3$$

$$1 \text{ ppm} = 1 \text{ mg/ltr} = 0.1 \,^0 \text{French} = 0.07 \,^0 \text{Clark}$$

Estimation of hardness
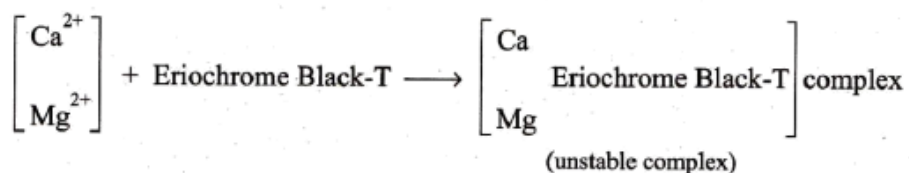
Hardness is usually determined by the EDTA method.

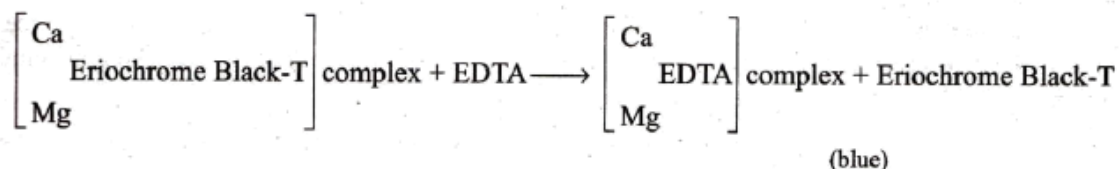**EDTA method:** EDTA is ethylenediaminetetraaceticacid. The structure of EDTA is

$$\text{HOOCH}_2\text{C} \diagdown \atop \text{HOOCH}_2\text{C} \diagup \text{N—CH}_2\text{—CH}_2\text{—N} {\diagup \text{CH}_2\text{COOH} \atop \diagdown \text{CH}_2\text{COOH}}$$

Since EDTA is insoluble in water, its disodium salt is used as a complexing reagent.

Principle: Estimation of hardness by EDTA method is based on the principle that EDTA forms metal complexes with hardness producing metal ions in water. These complexes are stable when the pH is maintained between 8 and 10. In order to maintain the pH, buffer solution (NH_4Cl and NH_4OH mixture) is added. The completion of the complexation reaction is indicated by Eriochrome Black-T indicator. When this indicator is added to the sample water it forms indicator–metal complexes of purple red colour.

$$\begin{bmatrix} Ca^{2+} \\ Mg^{2+} \end{bmatrix} + \text{Eriochrome Black-T} \longrightarrow \begin{bmatrix} Ca \\ \quad \text{Eriochrome Black-T} \\ Mg \end{bmatrix} \text{complex}$$

(unstable complex)

When this solution is titrated against EDTA, EDTA replaces the indicator from the indicator complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free and the end point is the sharp change in colour from purple red to blue. The total hardness is thus determined.

$$\begin{bmatrix} Ca \\ \quad \text{Eriochrome Black-T} \\ Mg \end{bmatrix} \text{complex} + \text{EDTA} \longrightarrow \begin{bmatrix} Ca \\ \quad \text{EDTA} \\ Mg \end{bmatrix} \text{complex} + \text{Eriochrome Black-T}$$

(blue)

The temporary hardness is removed by boiling and after the removal of precipitate by filtration, the permanent hardness in the filtrate is determined by titration with EDTA as before. Therefore,

total hardness – permanent hardness = temporary hardness

Experimental procedure: A known volume of the sample of hard water (V ml) is treated with about 10 ml of a buffer solution and 5 drops of Eriochrome Black-T indicator. This solution is then titrated against the standard EDTA reagent (standardized such that 1 ml of the reagent corresponds to 1 mg of $CaCO_3$). The end point is the colour change from purple red to blue.

Let the volume of EDTA consumed be V_1 ml.

$$1 \text{ ml of EDTA} = 1 \text{ mg of CaCO}_3$$

$$V_1 \text{ ml of EDTA} = V_1 \text{ mg of CaCO}_3$$

This hardness is present in V ml of hard water.

$$\text{Total hardness of the sample} = \frac{V_1 \times 1000}{V} \text{ ppm of CaCO}_3 \text{ equivalent}$$

A known volume (V ml) of sample water is taken in a beaker and boiled for 15 minutes. After cooling the mixture, it is filtered and thoroughly washed. The filtrate is collected and made up to a known volume (V ml). This solution is titrated against EDTA as before. The volume of EDTA consumed is V_2 ml. Then,

$$\text{Permanent hardness of the sample} = \frac{V_2 \times 1000}{V} \text{ ppm of CaCO}_3 \text{ equivalent}$$

Hence, (total hardness) – (permanent hardness) gives the temporary hardness. From the volume of EDTA it is equated to $CaCO_3$ equivalent as follows:

$$1000 \text{ ml of 1M EDTA} = 100 \text{ g of CaCO}_3$$

$$1000 \text{ ml of 0.01M EDTA} = 1 \text{ g of CaCO}_3$$

$$1 \text{ ml of 0.01M EDTA} = 1 \text{ mg of CaCO}_3$$

$$1 \text{ ml of 0.02N EDTA} = 1 \text{ mg of CaCO}_3$$

1.4 ALKALINITY

The alkalinity of water is due to the presence of a wide variety of salts of weak acids such as carbonates, bicarbonates, phosphates, etc., and also due to the presence of weak and strong bases (due to contamination with industrial wastes). The major portion of alkalinity in natural water is caused by the presence of bicarbonates that are formed when water containing free carbon dioxide percolates through soils containing calcium carbonate and magnesium carbonate.

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

The alkalinity of natural water may be taken as an indication of the concentration of hydroxides, carbonates and bicarbonates.

The type and extent of alkalinity present in a water sample may be determined by titrating the water with a standard acid to phenolphthalein end point (P) and continuing the titration to methyl orange end point (M). The reactions taking place are as follows:

$$OH^- + H^+ \longrightarrow H_2O \tag{1}$$

$$CO_3^{2-} + H^+ \longrightarrow HCO_3^- \tag{2}$$

$$HCO_3^- + H^+ \longrightarrow H_2O + CO_2 \tag{3}$$
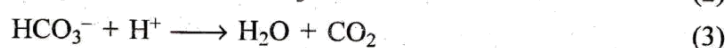
The volume of the acid used up to phenolphthalein end point P corresponds to the completion of equations (1) and (2), while the volume of the acid used after P corresponds to the completion of equation (3). The total amount of the acid used from beginning of the experiment corresponds to the total alkalinity present which represents the completion of equations (1) to (3).

The results are summarized in Table 1.3 from which the amount of hydroxides, carbonates and bicarbonates present in the water sample can be calculated.

TABLE 1.3 Calculation of hydroxides, carbonates and bicarbonates

Alkalinity	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^- (ppm)
P = 0	0	0	M
P = ½ M	0	2P	0
P < ½ M	0	2P	(M − 2P)
P > ½ M	(2P − M)	2(M − P)	0
P = M	M	0	0

(P = Phenolphthalein alkalinity; M = Methyl orange alkalinity)

Highly alkaline water may lead to caustic embrittlement and also may cause deposition of precipitates and sludges in boiler tubes and pipes.

The determination of alkalinity is used in the following ways:

1. In calculating the amounts of lime and soda needed for water softening
2. In corrosion control
3. In internal conditioning of boiler-feed water

1.4.1 Experimental Determination of Alkalinity

About 20 ml of the given water sample is pipetted out into a clean conical flask. A drop of phenolphthalein indicator is added. Now the water sample becomes pink colour and this solution is titrated against standard sulphuric acid taken in the burette. The end point is the colour change from pink to colourless. The volume of acid consumed is taken as V_1 ml. To the same water sample, a drop of methyl orange indicator is added and the sample is again titrated against sulphuric acid taken in the burette. The end point is the colour change from yellow to light pink. The additional volume of acid consumed is taken as V_1 ml.

Calculation

Volume of acid used up to phenolphthalein end point = V_1 ml

Normality of acid = N_1

Phenolphthalein alkalinity (P) in terms of calcium carbonate equivalent

$$= \frac{V_1 \times N_1}{20} \times 50 \times 1000 \text{ mg/litre}$$

Additional volume of acid used up to methyl orange end point = V_2 ml

Normality of acid = N_1

Methyl orange alkalinity (M) in terms of calcium carbonate equivalent

$$= \frac{(V_1 + V_2) \times N_1}{20} \times 50 \times 1000 \text{ mg/litre}$$

Then the calculation of hydroxides, carbonates and bicarbonates is made with the help of Table 1.3.

1.5 BOILER FEED WATER

In industry, one of the chief uses of water is generation of steam by boilers. Water fed to a boiler for the generation of steam is called *boiler feed water*.

1.5.1 Essential Requirements of Boiler Feed Water

Boiler feed water should be free from the following:

1. Turbidity, oil and non-scaling dissolved salts to reduce the tendency for priming and foaming.
2. Hardness-causing and scale-forming constituents like Ca and Mg salts as the formation of scales would result in wastage of fuel, loss in output and overheating of the boiler tubes leading to explosion.
3. Dissolved oxygen and CO_2 in order to prevent corrosion in the boiler.
4. Caustic alkali to remove caustic embrittlement.

If the hard water obtained from natural sources is fed directly to the boilers, there arise many troubles such as priming, foaming, sludge and scale formation and caustic embrittlement.

1.5.2 Priming

During the production of steam in the boiler, due to rapid boiling some particles of liquid water are carried along with steam. Steam containing droplets of water is called wet steam. This process of wet steam formation is called priming.

Priming causes the following harmful effects.

1. Wet steam carries dissolved salts of water with it to the super-heater where they are deposited after the evaporation of water. The deposited salts hinder the flow of steam and hence reduce the efficiency.
2. Water and dissolved salts may enter the parts of the machinery thereby decreasing the life of the machinery.

Priming may be caused by (a) a very high water level, (b) presence of foam on the surface and (c) high steam velocity.

Priming can be prevented by maintaining a low water level in the boiler and by removing oily materials present in water.

1.5.3 Foaming

The formation of stable bubbles above the surface of water is called *foaming*. These bubbles are carried over by steam leading to excessive priming. It is caused by the presence of soluble impurities like alkali metal salts and oil which form a soap. Foaming can be controlled by the action of anti-foaming agents like synthetic polyamides.

1.5.4 Sludge and Scale Formation in Boilers

In a boiler, water is continuously converted into steam. Due to this continuous evaporation of water, the concentration of soluble matters increases progressively. Then the salts start separating out from the solution in the order of their solubility, the least soluble one separating out first. Some of the salts like $MgCl_2$, $CaCl_2$ and $MgSO_4$ separate in the body of the liquid in the form of soft deposits which can be flushed out easily (Figure 1.1a). Such soft and non-adherent deposits are known as *sludges*.

Some salts like $CaSO_4$ and $Mg(OH)_2$ form hard adherent deposits on the inner walls of the boiler. They are called scales (Figure 1.1b). Scales are so hard and adherent that they are difficult to remove even with the help of hammer and chisel.
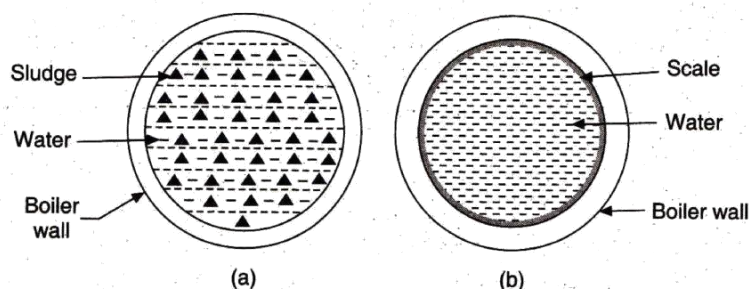
FIGURE 1.1   (a) Sludge in boiler and (b) scale in boiler.

Table 1.4 shows the differences between sludges and scales.

TABLE 1.4   Differences between sludges and scales

Sludges	*Scales*
1. Sludges are soft and non-adherent deposits.	1. Scales are hard deposits which stick very firmly to the inner surface of the boiler.
2. Sludges can be removed easily.	2. Scales are very difficult to remove.
3. Sludges can transfer heat to some extent and are less dangerous.	3. Scales are bad conductors of heat and are more dangerous.
4. Sludges are formed by substances like $MgCl_2$ and $CaCl_2$.	4. Scales are formed by substances like $CaSO_4$ and $Mg(OH)_2$.

Disadvantages of scale formation

The following are the disadvantages of scale formation:

1. Scale is a poor conductor of heat and thus it decreases the evaporative capacity of the boiler. So, the consumption of fuel is much more than usual.

2. Since the scale acts as a heat insulator, the boiler metal is overheated. Due to overheating, the metal expands until the scale on it cracks. When thick scales crack, the water suddenly comes in contact with overheated boiler metal. This causes the formation of a large amount of steam suddenly. This results in the development of high pressure inside the boiler which may lead to a dangerous explosion.

3. Due to scale formation, heat available to water is reduced and hence more heat is required to produce steam. This causes overheating of boiler plates and tubes and thus their life is reduced.

1.5.5　Caustic Embrittlement

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances.

It is a very dangerous form of stress corrosion occurring in mild steel boiler metals exposed to alkaline solution at high temperatures, resulting in the failure of the metal. Stressed parts like bends, joints and rivets are severely affected.

Boiler water usually contains a small proportion of Na_2CO_3. In high pressure boilers, this breaks up to give NaOH and makes the boiler water more alkaline:

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

This very dilute alkaline boiler water flows into the minute hair cracks and crevices by capillary action. There the water evaporates and the concentration of caustic soda increases progressively. The concentrated alkali dissolves iron as sodium ferroate in crevices, cracks, etc. where the metal is stressed. This causes brittlement of boiler parts particularly stressed parts like bends, joints and rivets causing even failure of the boiler.

Caustic embrittlement can be avoided (a) by using sodium phosphate as softening reagent instead of Na_2CO_3 and (b) by adding tannin or lignin to boiler water which blocks the hair cracks.

1.6　BOILER CORROSION

Boiler corrosion is the decay of boiler material due to chemical or electrochemical attack of its environment. The corrosion in boilers is due to dissolved oxygen, dissolved CO_2 and acids produced by the hydrolysis of dissolved salts. Therefore, removal of these prevents the corrosion of boilers.

1.6.1　Removal of Dissolved O_2

Dissolved oxygen in water is mainly responsible for the corrosion of a boiler. The dissolved oxygen in water attacks the boiler material at high temperatures.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2$$
$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3 \cdot 3H_2O]$$
$$\text{(rust)}$$
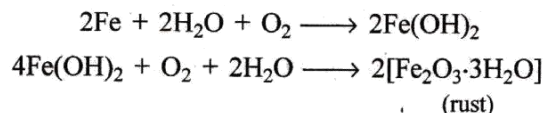
Dissolved oxygen can be removed from water by chemical and mechanical means. Sodium sulphite, hydrazine, etc. are some of the chemicals used for removing oxygen.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$
$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$
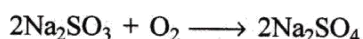
Hydrazine is found to be an ideal compound for removing dissolved oxygen since the products are water and inert N_2 gas. It removes oxygen without increasing the concentration of dissolved salts.

Dissolved O_2 can also be removed from water by mechanical deaeration (Figure 1.2). In this process, water is allowed to spray slowly by the perforated plates fitted inside the tower. Vacuum is applied to this tower and the sides of the tower are also heated. High temperature and low pressure reduce the quantity of dissolved O_2 in water.
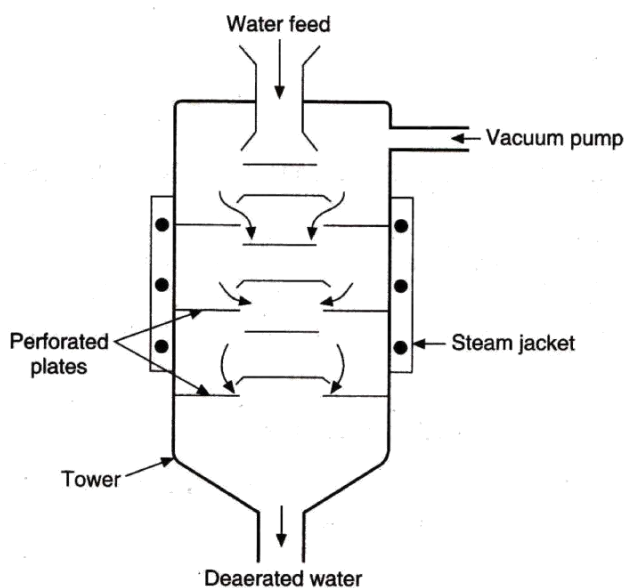
FIGURE 1.2 Mechanical deaeration of water.

1.6.2 Removal of Dissolved CO_2

Dissolved CO_2 in water produces carbonic acid which is corrosive in nature:

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
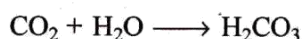
CO_2 can be removed from water by chemical or mechanical means. In the chemical method CO_2 is removed from water by the addition of a calculated quantity of NH_4OH:

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$
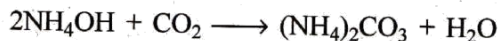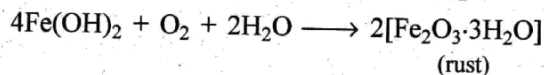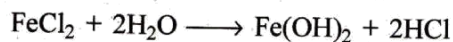
Dissolved CO_2 along with oxygen can be removed by mechanical deaeration.

1.6.3 Removal of Acids

Acids produced from salts dissolved in water are also mainly responsible for corrosion of boilers. Certain salts like $MgCl_2$ and $CaCl_2$ on hydrolysis at higher temperatures produce hydrochloric acid which corrodes the boiler.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
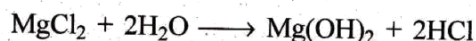
The liberated acid can produce rust in the following way.

$$Fe + 2HCl \longrightarrow FeCl_2 + H_2$$
$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCl$$
$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3 \cdot 3H_2O]$$
$$\text{(rust)}$$

Hence, even a very small amount of $MgCl_2$ can cause considerable corrosion of the boiler metal. Corrosion by acids can be avoided by the addition of alkali to the boiler water from outside.

1.7 PREVENTION OF SCALE FORMATION OR SOFTENING OF WATER

Water used for industrial purposes should be pure, i.e. it should be free from hardness, scale forming substances and corrosive agents like dissolved oxygen. The process of removing hardness producing salts from water is known as *softening of water*.

Softening of water can be done in two ways (a) external treatment and (b) internal treatment.

1.7.1 External Treatment or External Conditioning

The external treatment of water is carried out before its entry into the boiler. The external treatment can be done by the following methods.

1. Zeolite process
2. Ion exchange or deionization or demineralization process

Zeolite process or permutit process

Zeolites are naturally occurring hydrated sodium aluminosilicate minerals. The chemical formula is

$$Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$$
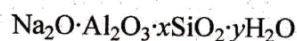
The synthetic form of this zeolite is called *permutit* and is represented by Na_2Ze. In this process the hard water is allowed to percolate through sodium zeolite. The sodium ions which are loosely held in this compound are replaced by Ca^{2+} and Mg^{2+} ions.

When zeolite comes in contact with hard water, it exchanges its sodium ions with calcium and magnesium ions of hard water to form calcium and magnesium zeolites:

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$
$$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$$
$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$
$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

As sodium ions do not give any hardness to water, the effluent water will be soft. The exhausted zeolite is again regenerated by treating with 5–10% of sodium chloride solution.

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$
$$MgZe + 2NaCl \longrightarrow Na_2Ze + MgCl_2$$

A simple zeolite softener is shown in Figure 1.3.
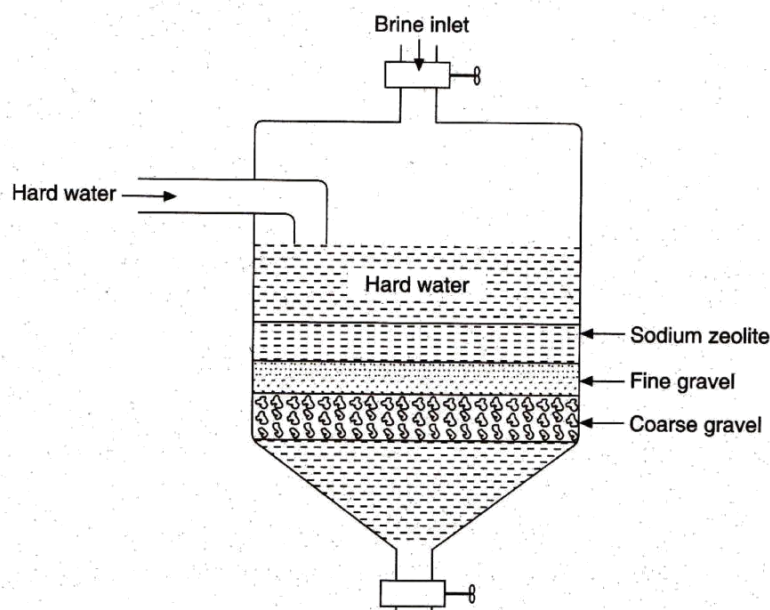
FIGURE 1.3   Zeolite softener.

Advantages: The following are the advantages of the zeolite process:

1. Water of nearly zero hardness is obtained.
2. This method is very cheap because the regenerated permutit is again used.
3. No sludge is formed during this process.
4. The equipment used is compact and occupies a small space.
5. Its operation is also easy.
6. The process can be made automatic and continuous.

Disadvantages: The following are the disadvantages of the zeolite process:

1. The zeolite process cannot be used for turbid and acidic water as they will destroy the zeolite bed.

2. This treatment replaces only the cations leaving all the anions like HCO_3^- and CO_3^{2-} in the soft water.

   When such water is boiled in boilers CO_2 is liberated. Free CO_2 is weakly acidic in nature and extremely corrosive to boiler metal.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$
$$NaHCO_3 \longrightarrow NaOH + CO_2$$
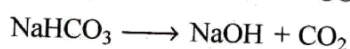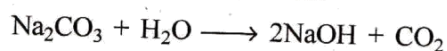
   Due to the formation of sodium hydroxide, the water becomes alkaline and can cause caustic embrittlement.

3. The zeolite process cannot be used for softening brackish water because brackish water also contains Na^+ ions. So, the ion exchange reaction will not take place.

Ion exchange or deionization or demineralization process

In ion exchange process, cations like Ca^{2+} and Mg^{2+}, and anions like Cl^- and SO_4^{2-} which are responsible for hardness are removed respectively by cation exchange resins and anion exchange resins.

Ion exchange resins are insoluble, crosslinked, long chain organic polymers with a microporous structure. The functional groups attached to the chains are responsible for the ion exchanging properties. Resins containing acidic groups ($-COOH$, $-SO_3H$) are capable of exchanging their H^+ ions cations of hard water. Resins containing basic groups ($-NH_2$, $-OH$) are capable of exchanging their anions with the anions of hard water.

Process: Water is passed through a tank having a cation exchanger which adsorbs all the cations present in water.

$$RH_2 + CaCl_2 \longrightarrow RCa + 2HCl$$
$$RH_2 + MgSO_4 \longrightarrow RMg + H_2SO_4$$
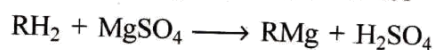
The cation-free water is now passed through another tank having an anion exchanger which adsorbs all the anions present in water.

$$R'(OH)_2 + 2HCl \longrightarrow R'Cl_2 + 2H_2O$$
$$R'(OH)_2 + H_2SO_4 \longrightarrow R'SO_4 + 2H_2O$$
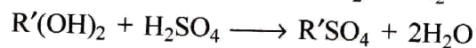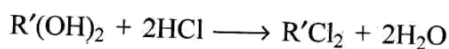
The water coming out of the anion exchanger is completely free from cations and anions responsible for hardness. It is known as deionized water or demineralized water. It is as pure as distilled water.

Regeneration: Cation exchange resins are regenerated by passing a dilute solution of hydrochloric acid through them.

$$RCa + 2HCl \longrightarrow RH_2 + CaCl_2$$
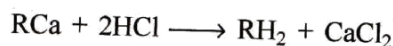
Similarly, the anion exchange resins are regenerated by passing a dilute solution of sodium hydroxide through them.

$$R'Cl_2 + 2NaOH \longrightarrow R'(OH)_2 + 2NaCl$$
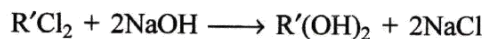
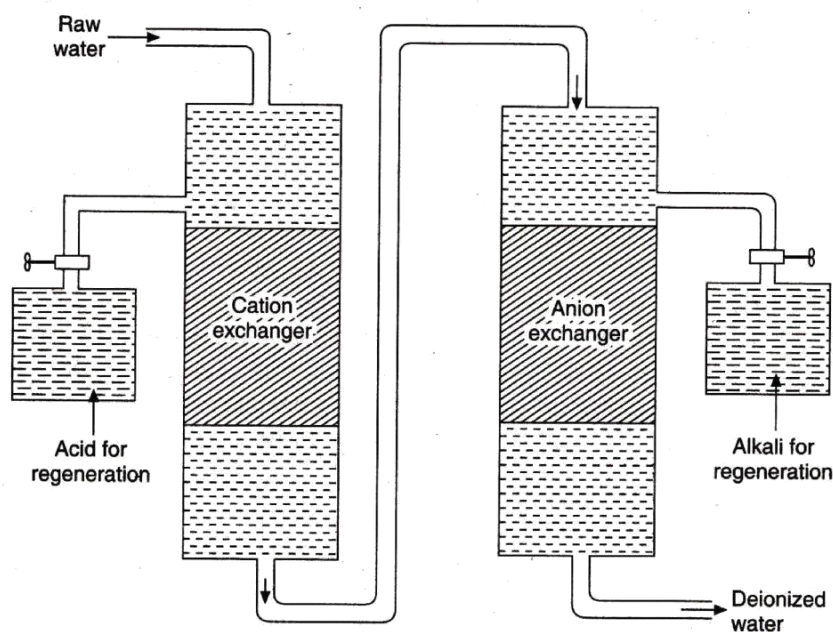A typical deionizer is shown in Figure 1.4.

FIGURE 1.4 Deionizer.

Advantages: The following are the advantages of the ion exchange process:

1. Highly acidic or alkaline water can be treated by this process.
2. This produces water of very low hardness (nearly 2 ppm).

Disadvantages: The disadvantages of the ion exchange process are as follows:

1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, then the output of the process is reduced.

Table 1.5 lists the difference between zeolite and demineralization processes.

TABLE 1.5 Differences between zeolite and demineralization processes

Zeolite process	*Demineralization process*
1. Exchanges only cations.	1. Exchanges cations as well as anions.
2. Acidic water cannot be treated because acid decomposes the zeolite.	2. Acidic water can be treated.
3. Dissolved salt concentration of treated water is higher than that of untreated water. Hence the treated gives rise to priming and foaming in boilers.	3. Dissolved salt concentration of the water is nil or less. Hence there is no priming and foaming.

Softening Methods

The process of removal of hardness producing ions/salts from water is known as softening of water. We will discuss here some important methods for water softening.

Lime–soda process

In lime–soda (LS) process, the dissolved hardness-causing salts are converted into insoluble carbonates and hydroxides by the adding a calculated quantity of lime $[Ca(OH)_2]$ and soda (Na_2CO_3). The insoluble compounds so precipitated are then filtered off. The LS process can again be applied either at the room temperature or at an elevated temperature.

1. **Cold LS process**

   Principle: In this process, calculated quantity of lime and soda are mixed with water at room temperature. The insoluble carbonates and hydroxides so formed are very fine and cannot be filtered easily. To facilitate filtration, a small amount of coagulant such as alum, aluminum sulfate, sodium aluminate, or ferrous sulfate is added. The coagulant hydrolyses to aluminum hydroxide which entraps the fine particles, thus
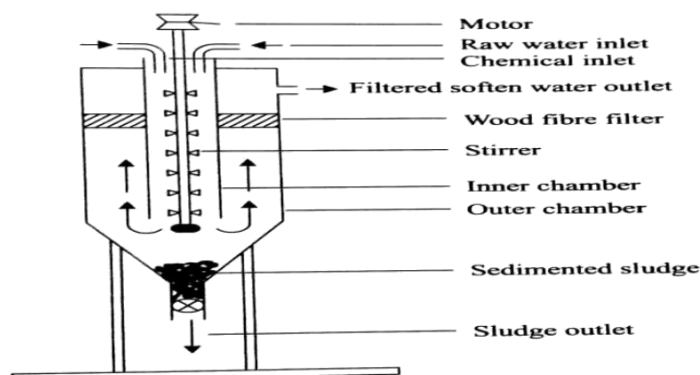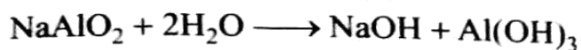

Fig. 13.1 Cold lime–soda softener

facilitating the easy filtering of the sludge. This process produces water containing residual hardness of ~50 ppm.

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

Method: Raw water and calculated quantities of lime, soda, and coagulant are introduced from the top into the inner cylindrical chamber fitted with a vertical rotating shaft attached with paddles as shown in Fig. 13.1. As the water comes down, it gets softened which then flows into the outer coaxial chamber and rises in the upward direction. Sludge or floc with relatively higher specific gravity settles down. The softened water is then allowed to pass through a filtering medium made of wood fibers to confirm the complete removal of the sludge. Finally, the soft water comes out through the outlet at the top, while the sludge is removed from the bottom periodically.

2. **Hot LS method**

The softening process is carried out at a temperature close to the boiling point of water. Here all the reactions are boosted up, increasing the softening process to manyfold. In the process, the sludge quickly settles down without the help of coagulant. The dissolved gases such as carbon dioxide and air are driven out easily. The filtration becomes much easier due to lower viscosity of the water. This process produces water containing residual hardness of ~15 ppm. In this process, the raw water mixed with chemicals is sprayed into superheated steam in a reaction tank as shown in Fig. 13.2. Here the plant consists of three parts:

(i)   A reaction tank in which raw water, chemicals, and steam are thoroughly mixed.

(ii) A sedimentation tank where sludge settles down.

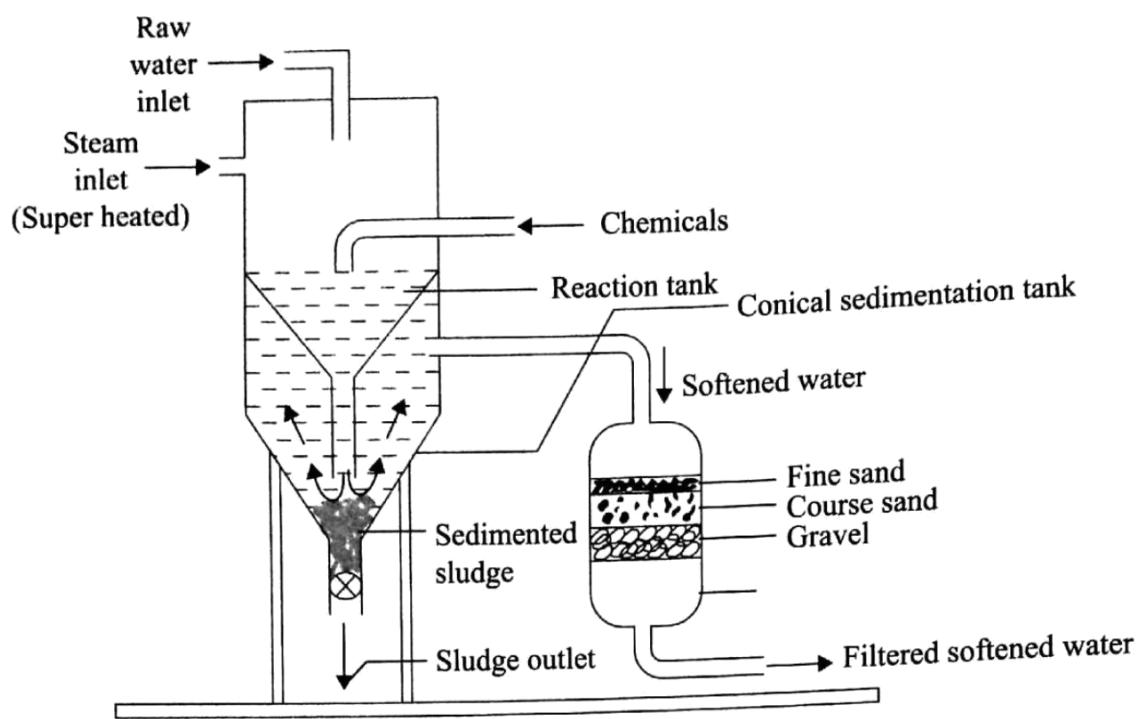(iii) A sand filter which ensures the complete removal of sludge.

Fig. 13.2 Hot lime-soda softener

1. **Differences between cold and hot LS processes**

Cold LS process	Hot LS process
Achieved at room temperature	Achieved at an elevated temperature of ~100°C.
It is a slow process	It is a rapid process
Coagulant is required	Coagulant is not required
Chemical requirement is relatively high	Chemical requirement is relatively less
Filtration is difficult	Filtration is rather easy due to decrease in viscosity at elevated temperature
Residual hardness ~50 ppm (relatively high)	Residual hardness ~15 ppm (relatively small)
Dissolved gases are not removed	Dissolved gases are removed

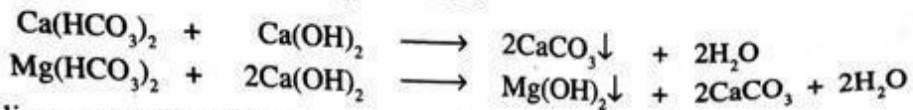2. **Advantages of LS process**

    - It is economical.

    - Pathogenic bacteria are considerably reduced owing to its alkaline nature.

    - Iron and manganese are also removed to some extent.

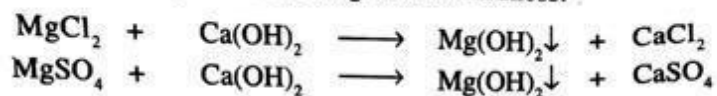3. **Disadvantages of LS process**

    - It needs careful operation and skilled supervision.

    - Disposal of sludge is a problem.

    - Softened water still contains a lot of soluble salts such as sodium sulfate which cannot be used in high pressure boilers.

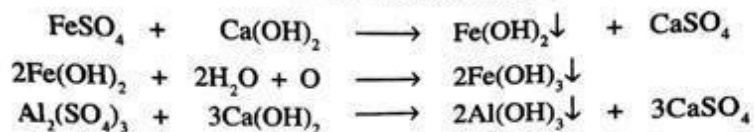**Reaction of lime and soda with different salts present in water**

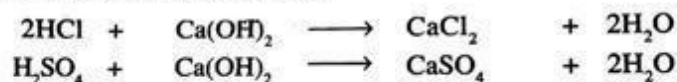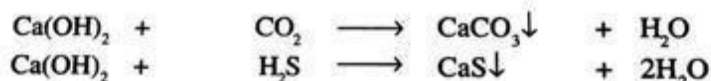(i) lime removes the temporary hardness:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3 + 2H_2O$$

(ii) lime removes the permanent magnesium hardness:

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$$

(iii) lime removes dissolved iron and aluminium salts:

$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2\downarrow + CaSO_4$$

$$2Fe(OH)_2 + 2H_2O + O \longrightarrow 2Fe(OH)_3\downarrow$$

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3\downarrow + 3CaSO_4$$

(iv) lime removes free mineral acids:

$$2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$$

$$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O$$

(v) lime removes dissolved CO_2 and H_2S

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

$$Ca(OH)_2 + H_2S \longrightarrow CaS\downarrow + 2H_2O$$

(vi) Soda removes all the soluble calcium permanent hardness (*i.e.,* that which is originally present as well as that which is introduced during the removal of Mg^{2+}, Fe^{2+}, Al^{3+}, HCl, H_2SO_4 etc., by lime).

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

❖
   Equation for calculating required lime & soda

(A) $\left.\begin{array}{l}\text{Lime required}\\\text{for softening}\end{array}\right\} = \dfrac{74}{100} \times \left\{\begin{array}{l}\text{Temporary calcium hardness}+(2\times\text{Temporary magnesium}\\ \text{hardness})+\text{Perm. Mg harndess}+CO_2+HCl+H_2SO_4\\ +HCO_3^-+\text{salts of }Fe^{2+},Al^{3+}\text{ etc.,}-Na\,AlO_2\,;\text{all expressed}\\ \text{in terms of their }CaCO_3\text{ equivalents.}\end{array}\right\}$

(B) $\begin{aligned}\left.\begin{array}{l}\textbf{Soda required}\\\textbf{for softening}\end{array}\right\}\end{aligned} = \dfrac{106}{100} \times \left\{\begin{array}{l}\text{Permanent Ca}-\text{hardness}+\text{permanent Mg hardness}+\text{Salts}\\\text{of Fe}^{2+}, \text{Al}^{3+}, \text{etc.}, + HCl + H_2SO_4 - HCO_3^- - Na\,AlO_2;\\\text{all expressed in terms of their CaCO}_3 \text{ equivalents}\end{array}\right\}$

(C) If the analytical report shows the quantities of Ca^{2+} and Mg^{2+}, then; 1 eq. of soda is required for Ca^{2+}; whereas one eq. of lime and 1 eq. of soda is required for Mg^{2+}.

5. If the lime and soda used are impure and if the % purity given, then the actual requirements of the chemicals should be calculated accordingly. Thus, if lime is 90% pure, then the value obtained under 4-A above should be multiplied by $\dfrac{100}{90}$ to get the actual requirement of lime.

Similarly, if soda is 95% pure, then the value obtained under 4-B above should be multiplied by $\dfrac{100}{95}$ to get the actual soda requirement.

Lime requirement for sofening (mg/l)

$$= \dfrac{74}{100}\left[\text{Temp.}\left\{Ca^{2+}+2\times Mg^{2+}\right\}+\text{Perm.}\left\{Mg^{2+}+Fe^{2+}\,Al^{3+}\right\}+CO_2+H^++HCO_3^- - NaAlO_2\\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{all in tems of CaCO}_3\text{ equivalents}\right]$$

Soda requirement for sofening (mg/l)

$$= \dfrac{106}{100}\left[\text{Perm.}\left\{Ca^{2+}+Mg^{2+}+Fe^{2+}+Al^{3+}\right\}+H^+ - HCO_3^-\\ \qquad\qquad\qquad \text{all in tems of CaCO}_3\text{ equivalents}\right]$$

1.8 POTABLE WATER (WATER FOR DOMESTIC SUPPLY)

Municipalities have to supply potable water, i.e. water which is safe to drink.

Characteristics of potable water

The following are the characteristics of potable water:

1. Potable water should be colourless and odourless.
2. It should have a good taste.
3. Potable water should be clear from suspended impurities.
4. It should be free from objectionable gases like CO_2, NH_3 and H_2S.
5. Potable water should be free from harmful bacteria.
6. It should not have more than 0.1–0.2 ppm of free chlorine.

Rivers, lakes and wells are the most common sources of water used by municipalities. The actual treatment methods depend directly on the impurities present. For removing various types of impurities (see Table 1.7), the following treatment processes are employed.

TABLE 1.7 Types of impurities and their removal processes

Impurity	*Process used for removal*
1. Floating matter such as leaves and wood pieces	1. Screening
2. Suspended impurities such as clay and sand	2. Sedimentation
3. Fine suspended matter (silt)	3. Coagulation
4. Microorganisms and colloidal matter	4. Filtration
5. Pathogenic bacteria	5. Disinfection (Sterilization)

1.8.1 Treatment Processes for Removal of Impurities

Screening

Screening is the process of removing floating materials like wood pieces and leaves from water. Raw water is allowed to pass through a screen having a large number of holes which removes the small and large floating matter.

Sedimentation

Sedimentation is the process of removing suspended impurities by allowing the water to stand undisturbed for 2–6 hours in big tanks. Due to force of gravity, most of the suspended particles settled down at the bottom and they are removed. Sedimentation removes only 70–75% of the suspended matter.

Coagulation

Finely-divided silica, clay, etc. do not settle down easily and hence cannot be removed by sedimentation. Most of these are in colloidal form and are negatively charged and hence do not coalesce because of mutual repulsion. Such impurities are removed by coagulation method. Here, certain chemicals like alum and $Al_2(SO_4)_3$ are added to water. When $Al_2(SO_4)_3$ is added to water, it hydrolyzes to form a gelatinous precipitate of $Al(OH)_3$. The gelatinous precipitate of $Al(OH)_3$ entraps finely divided and colloidal impurities, settles to the bottom and can be removed easily.

Filtration

For removing bacteria, colour, taste, odour, fine suspended particles, etc. and to produce clear water, filtration is used. In this process, water is passed through beds of fine sand, coarse sand and other granular material. The porous material used is the filtering medium and the equipment used for filtration is known as filter, e.g. slow sand filter.

A typical slow sand filter is shown in Figure 1.5.

It consists of a tank containing thick beds of fine sand (at the top), coarse sand, fine gravel and coarse gravel (at the bottom). When the water passes through the filtering medium, it flows through the various beds slowly due to gravity. The rate of filtration slowly decreases due to the clogging of impurities in the pores of the sand bed. When the rate of flow becomes
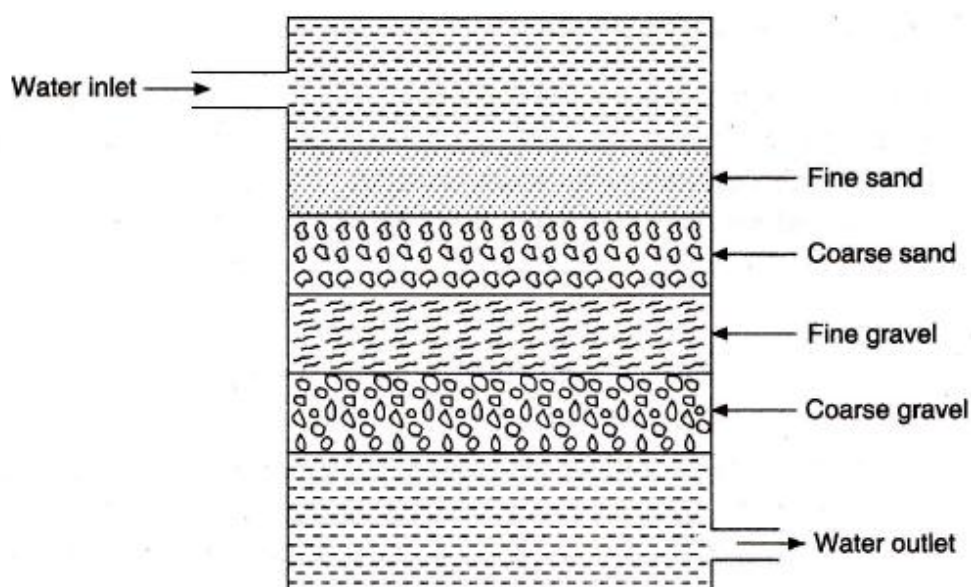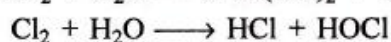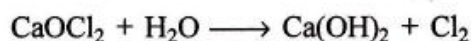

FIGURE 1.5 Slow sand filter.

very slow, filtration is stopped and the bed is cleaned by scraping of a smaller layer of the sand bed (top layer) and replacing it with the clean sand. Bacterias are partly removed by this filtration process.

Sterilization

The complete removal of harmful bacteria is known as *sterilization*. The following sterilizers are generally used for sterilizing water.

1. **Sterilization by chlorine or bleaching powder:** Chlorine is the most common sterilizing agent in water treatment. Chlorine may be added in the form of bleaching powder or directly as a gas or in the form of concentrated solution in water.

   When bleaching powder is added to water, HOCl which acts as a powerful germicide is produced. It is believed that HOCl reacts with bacteria and inactivate the enzymes present in the cells of bacteria. These enzymes are responsible for the metabolic activities of microorganisms. Since these enzymes are inactivated, microorganisms become dead.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$
$$HOCl + Bacteria \longrightarrow Bacteria \text{ are killed}$$

2. **Sterilization by ultraviolet radiations:** Ultraviolet radiations emanating from electric mercury vapour lamp is capable of sterilizing water. This process is particularly useful for sterilizing swimming pool water. This process is highly expensive.

3. **Sterilization by ozone:** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and decomposes to give nascent oxygen which is capable of destroying the bacteria.

$$O_3 \longrightarrow O_2 + [O]$$
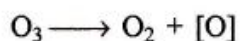
This process is relatively expensive.

1.10 DESALINATION

Depending upon the quantity of dissolved solids water is graded as follows:

1. Fresh water: <1000 ppm of dissolved solids
2. Brackish water: >1000 ppm but <35,000 ppm of dissolved solids
3. Sea water: >35,000 ppm of dissolved solids

Water containing dissolved salts with a peculiar salty or brackish taste is called *brackish water*. It is totally unfit for drinking purposes. Sea water and brackish water can be made available as drinking water through desalination process. The removal of dissolved solids (NaCl) from water is known as *desalination process*. The need for such a method arises due to the non-availability of fresh water. Desalination is carried out by the following methods:

1. Electrodialysis
2. Reverse osmosis

1.10.1 Electrodialysis

Electrodialysis is based on the fact that the ions present in saline water migrate towards oppositely charged electrodes under the influence of an applied emf. The movement of ions takes place through ion-selective membranes.

An electrodialysis cell consists of alternate cation- and anion-permeable membranes (Figure 1.7). The cathode is placed near the cation-permeable membrane (C) and the anode is placed near the anion-permeable membrane (A). Under the influence of an emf applied across the electrodes, the anions (Cl^-) move towards the anode and the cations (Na^+) move towards the cathode. The net result is the depletion of ions in the even-numbered compartments and concentration of ions in the odd-numbered compartments. Now the compartments with even-number are filled with pure water and the compartments with odd-number are with concentrated brine solution. Thus the salinity is removed from salt water.
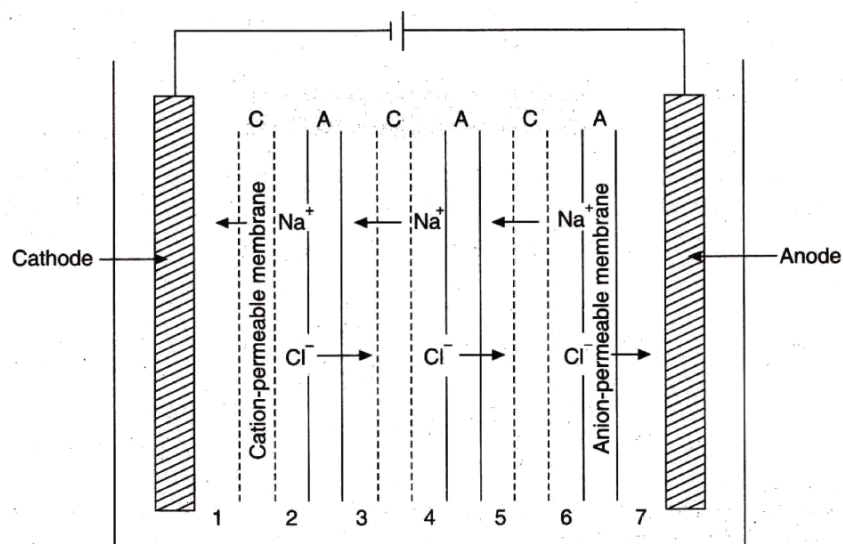

FIGURE 1.7   Desalination by electrodialysis.

1.10.2 Reverse Osmosis

When two solutions of different concentrations are separated by a semi-permeable membrane, flow of solvent takes from a region of low concentration to high concentration until the concentration is equal on both the sides. This process is called *osmosis*. The driving force in this phenomenon is called *osmotic pressure*. If a hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration side, the solvent flow reverses, i.e. solvent is forced to move from higher concentration to lower concentration (Figure 1.8). This is the principle of reverse osmosis. Thus in the reverse osmosis method pure water is separated from its dissolved solids.
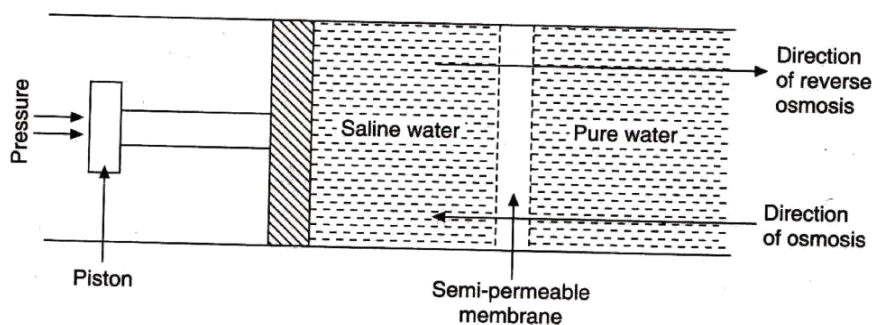
FIGURE 1.8 Reverse osmosis.

Using this method pure water is separated from sea water. This process is also called *super-filtration*. The membranes used are cellulose acetate, cellulose butyrate, etc.

SOLVED EXAMPLES

Example 1.1: Calculate the temporary and permanent hardness of a water sample having the following data: $Mg(HCO_3)_2$: 73 mg/l, $Ca(HCO_3)_2$: 162 mg/l, $CaSO_4$: 136 mg/l, $MgCl_2$: 95 mg/l, $CaCl_2$: 111 mg/l.

Solution:

Salt	CaCO₃ equivalent
$Mg(HCO_3)_2$	$\dfrac{73}{146} \times 100 = 50$ mg/l
$Ca(HCO_3)_2$	$\dfrac{162}{162} \times 100 = 100$ mg/l
$CaSO_4$	$\dfrac{136}{136} \times 100 = 100$ mg/l
$MgCl_2$	$\dfrac{95}{95} \times 100 = 100$ mg/l
$CaCl_2$	$\dfrac{111}{111} \times 100 = 100$ mg/l

Temporary hardness due to the presence of bicarbonates of Ca and Mg = 50 + 100

$$= 150 \text{ mg/l or ppm of CaCO}_3 \text{ equivalent}$$

Permanent hardness due to the presence of $CaSO_4$, $MgCl_2$ and $CaCl_2$ = 100 + 100 + 100

$$= 300 \text{ mg/l or ppm of CaCO}_3 \text{ equivalent}$$

Example 1.2: Calculate the carbonate and non-carbonate hardness of a sample of water containing dissolved solids (mg/l) given as follows: $Mg(HCO_3)_2$: 7.3, $Ca(HCO_3)_2$: 40.5, $CaSO_4$: 13.6, $MgCl_2$: 21.75 and NaCl: 60.

Solution:

Salt	$CaCO_3$ *equivalent*
$Mg(HCO_3)_2$	$\dfrac{7.3}{146} \times 100 = 5 \text{ mg/l}$
$Ca(HCO_3)_2$	$\dfrac{40.5}{162} \times 100 = 25 \text{ mg/l}$
$CaSO_4$	$\dfrac{13.6}{136} \times 100 = 10 \text{ mg/l}$
$MgCl_2$	$\dfrac{21.75}{95} \times 100 = 22.9 \text{ mg/l}$

Sodium chloride does not contribute any hardness to water.

Carbonate hardness due to the presence of bicarbonates of Ca and Mg = 25 + 5

$$= 30 \text{ mg/l or ppm of CaCO}_3 \text{ equivalent}$$

Non-carbonate hardness due to the presence of $CaSO_4$ and $MgCl_2$ = 10 + 22.9

$$= 32.9 \text{ mg/l or ppm of CaCO}_3 \text{ equivalent}$$

Example 1.3: 100 ml of a sample of water has a hardness equivalent to 12.5 ml of 0.08N $MgSO_4$. What is the hardness of water?

Solution:

100 ml of sample of water = 12.5 ml of 0.08N $MgSO_4$

$$N_{hardness} = \frac{12.5 \times 0.08}{100}$$

$$\text{Hardness in terms of CaCO}_3 \text{ equivalent} = \frac{12.5 \times 0.08}{100} \times 50 \times 1000$$

$$= 500 \text{ mg/l or ppm of CaCO}_3 \text{ equivalent}$$

Example 1.4: 50 ml of a hard water required 15 ml of EDTA solution for titration (1 ml of EDTA = 1 mg of $CaCO_3$). Calculate the hardness of the sample of water.

Solution:

$$1 \text{ ml of EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$
$$15 \text{ ml of EDTA} = 15 \text{ mg of } CaCO_3 \text{ equivalent}$$

This amount of hardness is present in 50 ml of hard water.
So

$$\text{hardness present in 1 litre} = \frac{15}{50} \times 1000$$

$$= 300 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Example 1.5: 250 ml of a sample of water on EDTA titration with Eriochrome Black-T as indicator consumed 13 ml of 0.022M EDTA till end point is reached. Calculate the hardness of water.

Solution:

$$1 \text{ ml of 0.01M EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$

$$13 \text{ ml of 0.022M EDTA} = \frac{1 \times 13 \times 0.022}{1 \times 0.01}$$

$$= 28.6 \text{ mg of } CaCO_3$$

This amount of hardness is present in 250 ml of the water sample.
So

$$\text{hardness present in 1 litre} = \frac{28.6}{250} \times 1000$$

$$= 114.4 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Example 1.6: 100 ml of a sample of water required 20 ml of 0.01M EDTA for the titration with Eriochrome Black-T indicator. 100 ml of the same sample after boiling and filtering required 10 ml of 0.01M EDTA. Calculate the total, carbonate (temporary) and non-carbonate (permanent) hardness of the sample.

Solution:

Total hardness

$$1 \text{ ml of 0.01M EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$
$$20 \text{ ml of 0.01M EDTA} = 20 \text{ mg of } CaCO_3 \text{ equivalent}$$

This amount of hardness is present in 100 ml of the sample water.
So

$$\text{total hardness present in 1 litre} = \frac{20}{100} \times 1000$$

$$= 200 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Permanent or non-carbonate hardness

$$1 \text{ ml of } 0.01M \text{ EDTA} = 1 \text{ mg of } CaCO_3 \text{ equivalent}$$

$$10 \text{ ml of } 0.01M \text{ EDTA} = 10 \text{ mg of } CaCO_3 \text{ equivalent}$$

This amount of hardness is present in 100 ml of the water sample.
So

$$\text{permanent hardness present in 1 litre} = \frac{10}{100} \times 1000$$

$$= 100 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Carbonate or temporary hardness

$$\text{carbonate hardness} = \text{total hardness} - \text{non-carbonate hardness}$$

$$= 200 - 100$$

$$= 100 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Example 1.7: 0.5 g of $CaCO_3$ was dissolved in dil.HCl and diluted to 500 ml. 50 ml of this solution required 48 ml of EDTA solution for titration. 50 ml of a hard water sample required 5 ml of the same EDTA solution for titration. Calculate the total hardness of water.

Solution:

$$500 \text{ ml of } CaCl_2 \text{ solution} = 0.5 \text{ g of } CaCO_3$$

$$= 0.5 \times 1000 \text{ mg of } CaCO_3$$

$$= 500 \text{ mg of } CaCO_3$$

Standardization of EDTA

$$1 \text{ ml of } CaCl_2 \text{ solution} = 1 \text{ mg of } CaCO_3$$

$$50 \text{ ml of } CaCl_2 \text{ solution} = 50 \text{ mg of } CaCO_3$$

$$48 \text{ ml of EDTA solution} = 50 \text{ mg of } CaCO_3$$

$$1 \text{ ml of EDTA solution} = \frac{50}{48} \times 1$$

$$= 1.04 \text{ mg of } CaCO_3$$

Total hardness

$$1 \text{ ml of EDTA solution} = 1.04 \text{ mg of } CaCO_3$$

$$15 \text{ ml of EDTA solution} = 1.04 \times 15$$

$$= 15.6 \text{ mg of } CaCO_3$$

This amount of hardness is present in 50 ml of the water sample.

So

$$\text{total hardness present in 1 litre} = \frac{15.6}{50} \times 1000$$

$$= 312 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Example 1.8: 0.25 g of $CaCO_3$ was dissolved in dil. HCl and diluted to 250 ml. 100 ml of this solution required 20 ml of EDTA solution for titration. 100 ml of a hard water sample required 30 ml of the same EDTA solution for titration. 100 ml of the same water sample on boiling, filtering required 10 ml of EDTA. Calculate the total, permanent and temporary hardness.

Solution:

$$250 \text{ ml of } CaCl_2 \text{ solution} = 0.25 \text{ g of } CaCO_3$$
$$= 0.25 \times 1000 \text{ mg of } CaCO_3$$
$$= 250 \text{ mg of } CaCO_3$$
$$1 \text{ ml of } CaCl_2 \text{ solution} = 1 \text{ mg of } CaCO_3$$

Standardization of EDTA

$$100 \text{ ml of } CaCl_2 \text{ solution} = 100 \text{ mg of } CaCO_3$$
$$20 \text{ ml of EDTA solution} = 100 \text{ mg of } CaCO_3$$
$$1 \text{ ml of EDTA solution} = \frac{100}{20} \times 1$$
$$= 5 \text{ mg of } CaCO_3$$

Total hardness

$$30 \text{ ml of EDTA solution} = 30 \times 5$$
$$= 150 \text{ mg of } CaCO_3$$

This amount of hardness is present in 100 ml of the hard water. So

$$\text{total hardness present in 1 litre} = \frac{150}{100} \times 1000$$
$$= 1500 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Permanent hardness

$$10 \text{ ml of EDTA solution} = 5 \times 10$$
$$= 50 \text{ mg of } CaCO_3$$

This is present in 100 ml of hard water. So

$$\text{permanent hardness present in 1 litre} = \frac{50}{100} \times 1000$$
$$= 500 \text{ ppm of } CaCO_3 \text{ equivalent}$$
$$\text{temporary hardness} = \text{total hardness} - \text{permanent hardness}$$
$$= 1500 - 500$$
$$= 1000 \text{ ppm of } CaCO_3 \text{ equivalent}$$

Example 1. Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20,000 litres of water whose analysis is as follows:

$$Ca(HCO_3)_2 \quad - \quad 40.5 \text{ ppm}$$
$$Mg(HCO_3)_2 \quad - \quad 36.5 \text{ ppm}$$
$$MgSO_4 \quad - \quad 30.0 \text{ ppm}$$
$$CaSO_4 \quad - \quad 34.0 \text{ ppm}$$
$$CaCl_2 \quad - \quad 27.75 \text{ ppm}$$
$$NaCl \quad - \quad 10.0 \text{ ppm}$$

Also, calculate the temporary and permanent hardness of the water sample.

Solution.

Salt		$CaCO_3$ equivalent
$Ca(HCO_3)_2$	—	$40.5 \times \dfrac{100}{162} = 25$ ppm or mg/l
$Mg(HCO_3)_2$	—	$36.5 \times \dfrac{100}{146} = 25$ ppm or mg/l
$MgSO_4$	—	$30.0 \times \dfrac{100}{120} = 25$ ppm or mg/l
$CaSO_4$	—	$34.0 \times \dfrac{100}{136} = 25$ ppm or mg/l
$CaCl_2$	—	$27.75 \times \dfrac{100}{111} = 25$ ppm or mg/l
$NaCl$	—	Ignored as it does not contribute to hardness.

Temporary hardness $= [Ca(HCO_3)_2] + [Mg(HCO_3)_2] = 25 + 25 = 50$ ppm

Permanent hardness $= [MgSO_4] + [CaSO_4] + [CaCl_2] = 25 + 25 + 25 = 75$ ppm

Lime is required for $Ca(HCO_3)_2$, $Mg(HCO_3)_2$ and $MgSO_4$. Soda is required for $CaSO_4$, $CaCl_2$ and the $CaSO_4$ generated as a result of reaction of lime with $MgSO_4$.

Hence, 84% pure lime required for treating 20,000 litres of water

$$= \frac{74}{100} \underset{\substack{Ca(HCO_3)_2}}{[25} + \underset{\substack{Mg(HCO_3)_2}}{(2 \times 25)} + \underset{\substack{MgSO_4}}{25]} \times \underset{\substack{\text{Purity} \\ \text{factor}}}{\frac{100}{84}} \times \underset{\substack{\text{grams for} \\ \text{2,000 litres}}}{\frac{20,000}{1,000}}$$

$= 1761.905$ g

$= \mathbf{1.7619}$ **kg**

92% pure soda required for softening 20,000 litres of the water sample

$$= \frac{106}{100} \underset{\substack{CaSO_4}}{[25} + \underset{\substack{CaCl_2}}{25} + \underset{\substack{MgSO_4}}{25]} \times \underset{\substack{\text{Purity} \\ \text{factor}}}{\frac{100}{92}} \times \underset{\substack{\text{grams for} \\ \text{2,000 litres}}}{\frac{20,000}{1,000}}$$

$= 1728.26$ g $= \mathbf{1.72826}$ **kg**

Example 2. *A water sample has the analytical report as under:*

$$\begin{array}{lcl}
MgCO_3 & - & 84 \ mg/l \\
CaCO_3 & - & 40 \ mg/l \\
CaCl_2 & - & 55.5 \ mg/l \\
Mg(NO_3)_2 & - & 37 \ mg/l \\
KCl & - & 20 \ mg/l
\end{array}$$

Calculate the amount of lime (86% pure) and soda (83% pure) needed for the treatment of 80,000 litres of water.

Solution.

$CaCO_3$ and $MgCO_3$ should be regarded as being present in the form of their bicarbonates and only their weights have been expressed in terms of $CaCO_3$ and $MgCO_3$. KCl does not react with lime or soda and also it does not contribute to hardness.

On converting the weights of each constituent in terms of their $CaCO_3$ equivalent, we get the following:

Salt		$CaCO_3$ equivalent
$MgCO_3$	—	$84 \times \dfrac{100}{84} = 100 \ mg/l$
$CaCO_3$	—	$40 \times \dfrac{100}{100} = 40 \ mg/l$
$CaCl_2$	—	$55.5 \times \dfrac{100}{111} = 50 \ mg/l$
$Mg(NO_3)_2$	—	$37 \times \dfrac{100}{148} = 25 \ mg/l$
KCl	—	Ignored

86% pure lime required for softening 80,000 litres of the water

$$= \underset{}{\frac{74}{100}} \ [\underset{MgCO_3}{(2 \times 100)} + \underset{CaCO_3}{40} + \underset{Mg(NO_3)_2}{25}] \times \underset{\substack{Purity \\ factor}}{\frac{100}{86}} \times \underset{\substack{grams \ for \\ 80,000 \ litres}}{\frac{80,000}{1,000}}$$

$= 18241.86 \ g. = \textbf{18.24186 kg}$

83% pure soda required for softening 80,000 litres of the water

$$= \frac{106}{100} \ [\underset{CaCl_2}{50} + \underset{\substack{Ca(NO_3)_2 \\ generated \\ from \ reaction \\ of \ lime \ with \\ Mg(NO_3)_2}}{25}] \times \underset{\substack{Purity \\ factor}}{\frac{100}{83}} \times \underset{\substack{grams \ for \\ 80,000 \\ litres}}{\frac{80,000}{1,000}}$$

$= 7662.65 \ g. = \textbf{7.6625 kg.}$

Example 3.

Calculate the amount of lime and soda needed for softening 50000 l of water containing following salts per liter: $Ca(HCO_3)_2 = 10$ mg, $Mg(HCO_3)_2 = 15$ mg, $MgSO_4 = 20$ mg, $CaSO_4 = 18$ mg, $CaCl_2 = 8$ mg, and $NaCl = 4$ mg.

Solution

Lime requirement for sofening

$$= \frac{74}{100} [\text{Temp.} \{Ca^{2+} + 2 \times Mg^{2+}\} + \text{Perm.} (Mg^{2+})] \times \text{Volume of water}$$

$$= \frac{74}{100} \left[10 \times \frac{50}{81} + 2 \times 15 \times \frac{50}{73} + 20 \times \frac{50}{60} \right] \times 50000 \text{ mg}$$

$$= 1605430 \text{ mg} = 1.605 \text{ kg}$$

Soda requirement for sofening $= \dfrac{106}{100} [\text{Temp.} \{Ca^{2+} + Mg^{2+}\} \times H^+)] \times \text{Volume of water}$

$$= \frac{106}{100} \left[20 \times \frac{50}{60} + 18 \times \frac{50}{68} + 8 \times \frac{50}{55.5} \right] \times 50,000 \text{ mg}$$

$$= 1967360 \text{ mg} = 1.967 \text{ kg}$$

Numerical of Alkalinity

1. **About 50 ml of a water sample required 10 ml of N/50 sulfuric acid using methyl orange as indicator but failed to develop any color with phenolphthalein. What is the type of alkalinity present?**

Solution :

As P=0, only HCO_3^- ions ar present.

$N_1V_1 = N_2V_2$

$$N_2 = \frac{\frac{1}{50} \times 10}{50} = \frac{1}{250}$$

Strength in terms of calcium carbonate equivalent = N_2 X Equivalent weight of $CaCO_3$

$$= \frac{1 X 50 X 1000}{50} = 200 \text{ ppm}$$

Thus ,alkalinity due to bicarbonate 200 ppm.

2. **100 ml water sample on titration with N/50 sulfuric acid consumed 20 ml up to phenolphthalein end point. On continuous titration in present of methyl orange 40 ml of acid is consumed. Find the alkalinity of water sample in terms of $CaCO_3$. Also comment on the type of alkalinity.**

Solution

Here P=20 ml & M=40 ml
Hence, P=1/2 [M] , So Only carbonates are present in water sample.
Therefore , V_1 = 2[P]
= 2[20]
= 40 ml

Acid   Water

$N_1V_1 = N_2V_2$

$N_2 = \dfrac{1/50 \; X \; 40}{100}$

= 0.008 N

Strength in terms of calcium carbonate equivalent = N_2 X Equivalent weight of $CaCO_3$

= 0.008 X 50 X 1000

= 400 ppm

So, Carbonate alkalinity is 400 ppm .

Unit-4

Chapter 2-Corrosion

Corrosion: Corrosion can be defined as an unwanted destruction of a metallic substance due to chemical or electrochemical or environmental factors.
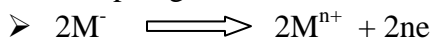
Types of Corrosion: [A] Dry Corrosion and [B] Wet Corrosion
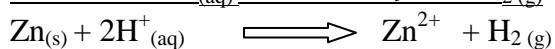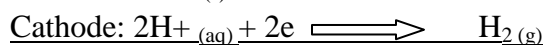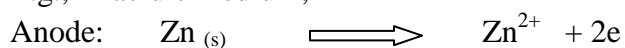
[A] Dry Corrosion:

> The corrosion which takes place in the absence of moisture or water is called Dry corrosion. It is uniform corrosion. This happens due to the direct interaction of atmospheric components such as O_2, X_2, SO_2, NO_2, H_2S, etc with the metallic materials in the absence of moisture. This can be discussed under basic three categories.

(1) Corrosion due to oxygen

> ➢ Alkali and alkaline earth metals react with oxygen at room temperature. Other metals except Ag, Au, Pt react with oxygen at elevated temperature.
> ➢ $2M^- \implies 2M^{n+} + 2ne$

$(n/2) O_2 + 2ne \implies nO^{2-}$

$2M + (n/2) O_2 \implies M^{n+} + nO^{2-} \implies$ MO (Metal Oxide film)
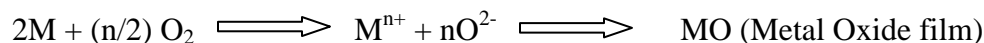
Corrosion product

> ➢ Further interaction depends on the nature of the oxide film formed.
> ➢ **Stable film:** If the oxide film is stable , it remains adhered to the surface strongly. This prevents further penetration of oxygen to the base metal. Egg. In case of oxides of Al, Pb, Cu etc.
> ➢ **Unstable film:** If the oxide formed is unstable, it dissociates back to metal and oxygen. Therefore corrosion does not take place. E.g., Oxides of Ag, Au, Pt.
> ➢ **Volatile:** If the oxide film is volatile, it gets volatized to expose new surface to interact with oxygen. Here corrosion continues to eat the whole metallic structure. Therefore corrosion is rapid and continuous, e.g., oxide of molybdenum.
> ➢ **Porous:** Here the oxide film has pores or channels through which oxygen slowly diffuses to interact with the base metal. Therefore in this case corrosion is slow but continuous. E.g., Oxide of iron

(2) **Corrosion due to other corrosive gases:**

➢ The extent of corrosion depends on the chemical affinity between the base metal and the atmospheric components.

➢ $Fe + H_2S \Longrightarrow FeS + H_2$
   Porous

➢ $2Ag + Cl_2 \Longrightarrow AgCl$ (Stable)
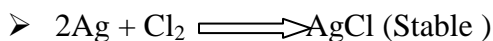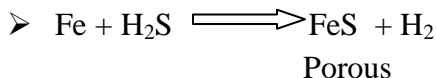
(3) Liquid metal corrosion

➢ This type of corrosion occurs when a molten liquid is passed continuously on a solid metal/alloy surface. The corrosion is attributed to either dissolution of the molten liquid into the solid metal phase.

[B] Wet corrosion

➢ The corrosion which takes place in the presence of moisture or water is called Wet corrosion. It is nonuniform corrosion.
➢ This type of corrosion occurs due to the setup of an electrochemical cell. Here anode is always destroyed or corroded while cathode is protected.
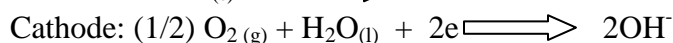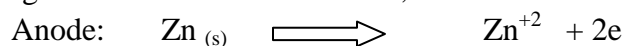
Types of wet corrosion

(1) Galvanic cell corrosion

➢ When two dissimilar metals remain in contact in the presence of conducting liquid then the more electropositive metal acts as anode and gets corroded. Such corrosion is known as Galvanic cell corrosion.
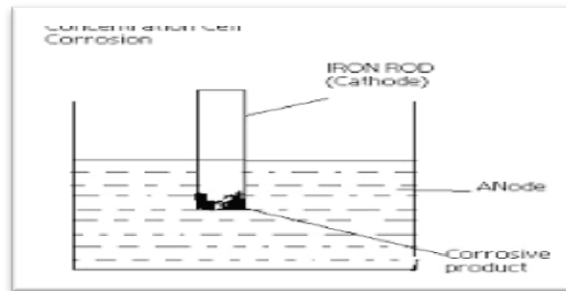➢ E.g., In acidic medium,
   Anode: $Zn_{(s)} \Longrightarrow Zn^{2+} + 2e$
   Cathode: $2H+_{(aq)} + 2e \Longrightarrow H_{2 (g)}$
   $Zn_{(s)} + 2H^+_{(aq)} \Longrightarrow Zn^{2+} + H_{2 (g)}$
➢ E.g. In neutral or basic medium;
    Anode: $Zn_{(s)} \Longrightarrow Zn^{+2} + 2e$
    Cathode: $(1/2) O_{2 (g)} + H_2O_{(l)} + 2e \Longrightarrow 2OH^-$
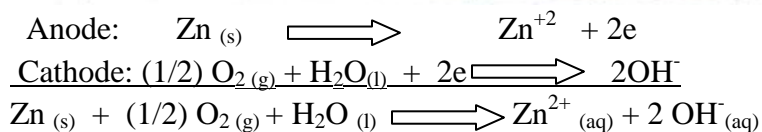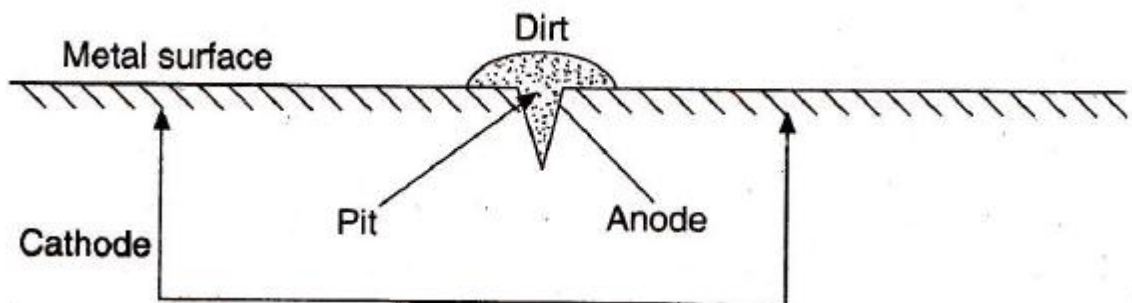 $Zn_{(s)} + (1/2) O_{2 (g)} + H_2O_{(l)} \Longrightarrow Zn^{2+}_{(aq)} + 2 OH^-_{(aq)}$
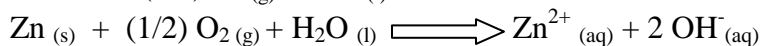
(2) Concentration cell corrosion

> If two portions of a metal have different access to oxygen then the portion which has limited access to oxygen behave anodic with respect to the portion which has more access to oxygen. This can be included in concentration cell corrosion. It is also known as oxygen concentration cell corrosion or differential aeration corrosion
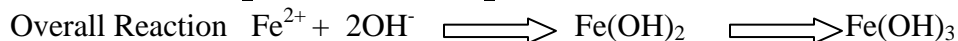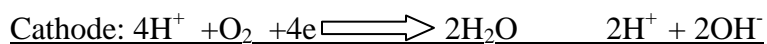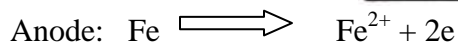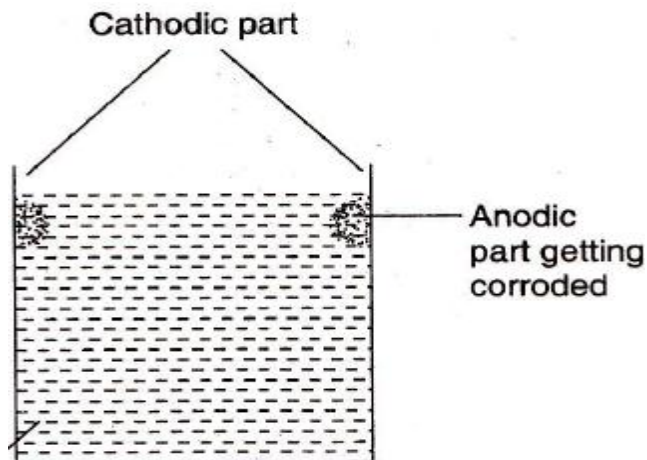
(3) Pitting corrosion

> The metal surface having pits or cavities undergoes corrosion due to development of separate anodic and cathodic areas. Here pits act as anode with respect to the normal portion. A typical pitting corrosion cell in iron surface is given below. Here corrosion is due to oxygen concentration cell.

Anode: $Zn_{(s)} \Longrightarrow Zn^{+2} + 2e$

Cathode: $(1/2) O_{2(g)} + H_2O_{(l)} + 2e \Longrightarrow 2OH^-$

$Zn_{(s)} + (1/2) O_{2(g)} + H_2O_{(l)} \Longrightarrow Zn^{2+}_{(aq)} + 2 OH^-_{(aq)}$

(4) Water-line corrosion

> When water is stored in a steel tank, corrosion take place along a line just below the level of water meniscus. In this case, the area above the water line having more access to oxygen acts as cathode, whereas the area below the water line having relatively less access to oxygen acts as anode.
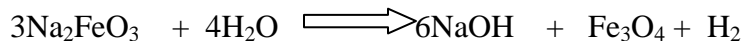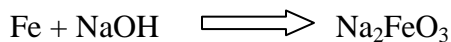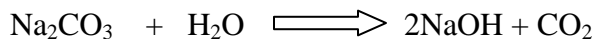
Anode: $Fe \implies Fe^{2+} + 2e$

Cathode: $4H^+ + O_2 + 4e \implies 2H_2O$ $2H^+ + 2OH^-$

Overall Reaction $Fe^{2+} + 2OH^- \implies Fe(OH)_2 \implies Fe(OH)_3$

(5) Soil or underground corrosion

➢ Metal or alloys that remains in contact with soil often suffer corrosion which known as soil corrosion. The presence of moisture, electrolytes, soil acidity, etc., is responsible for soil corrosion which is further promoted by differential aeration. The type of corrosion depends on the metal and the nature of the soil environment.

(6) Stress corrosion

➢ Metallic materials under strain due to mechanical operations like welding, bending, pressing, hammering, etc. During corrosion the stressed portion acts as anode with respect to the normal portion leading to highly localized corrosion.

➢ For example, caustic embrittlement, which occurs in mild steel exposed to alkaline solution as stressed areas such as joints and bent portion s at high temperature.

$Na_2CO_3 + H_2O \implies 2NaOH + CO_2$

$Fe + NaOH \implies Na_2FeO_3$

$3Na_2FeO_3 + 4H_2O \implies 6NaOH + Fe_3O_4 + H_2$

❏ Factor influencing corrosion

➢ The rate and extent of corrosion depends mainly on **(a) the nature of the metal (b) the nature of the environment.**

➢ **(a) Nature of the metal**

1. **Position in the galvanic series:** The extent of corrosion depends upon the position of the metal in the galvanic series. Greater the oxidation potential, the greater is the rate of corrosion. When two metals are in electrical contact, the metal higher up in the galvanic series becomes anodic and suffers corrosion. Further, the rate and severity of corrosion depend upon the difference in their positions in the galvanic series. The greater is the difference, the faster is the corrosion of anodic metal.

2. **Relative areas of the anode and cathode:** The rate of corrosion is more when the area of the cathode is larger. When the cathodic area is larger, the demand for electrons will be more, and this results in increased rate of dissolution of metals at anodic regions.

3. **Purity of the metal:** The impurities present in a metal creates heterogeneity and thus galvanic cells are set up with distinct anodic and cathodic areas in the metal. The higher the percentage of impurity present in a metal, the faster is the rate of corrosion

of the anodic metal. For instance, impurities such as Pb and Fe in zinc lead to the formation of tiny electrochemical cells at the exposed part of the impurity and the corrosion of zinc around the impurity takes place due to local action. The effect of even traces of impurities on the rate of corrosion of zinc can be seen from the following data.

Metal	Percentage of purity	Corrosion rate
Zinc	99.999	1
Zinc	99.99	2650
Zinc	99.95	5000

It is evident that the corrosion resistance of a metal may be improved by increasing its purity.

4. **Physical state of the metal:** Metal components subjected to unevenly distributed stresses are easily corroded. Even in a pure metal, the areas under stress tend to be anodic and suffer corrosion. Caustic embrittlement takes place in stressed parts such as bends, joints and rivets in boilers.

5. **Nature of the oxide film:** Metals such as Mg, Ca and Ba form oxides whose volume is less than the volume of the metal. Hence, the oxide film formed will be porous, through which oxygen can diffuse and bring about further corrosion. On the other hand, metals like Al, Cr and Ni form oxides whose volume is greater than that of the metal and the non-porous oxide film so formed will protect the metal from further corrosion.

6. **Solubilities of the products of corrosion:** Solubility of the corrosion product formed is an important factor in corrosion. If the corrosion product is soluble in the corroding medium, the corrosion of the metal will proceed faster. On the other hand, if the corrosion product is insoluble, then the protective film formed tends to suppress corrosion.

❖ **(b) Nature of the environment**

1. **Temperature:** The rate of chemical reactions and the rate of diffusion of ions increase with temperature. Hence, corrosion increases with temperature. A passive metal may become active at a higher temperature.

2. **Humidity:** Atmospheric corrosion of iron is slow in dry air but increases rapidly in the presence of moisture. This is due to the fact that moisture acts as the solvent for the oxygen in the air to furnish the electrolyte essential for setting up a corrosion cell. Rusting of iron increases when the relative humidity of air reaches from 60 to 80%.

3. **Effect of pH:** The possibility of corrosion with respect to pH of the solution and the electrode potential of the metal can be correlated with the help of a Pourbaix diagram. The Pourbaix diagram for iron in water is shown in Figure 11.3.

The diagram shows clearly the zones of corrosion, immunity and passivity. In the diagram x is a point where pH is 7 and the electrode potential is -0.4 V. It is present in the corrosion zone. This shows that iron rusts in water under those conditions. This is noticed to be true in actual practice also.
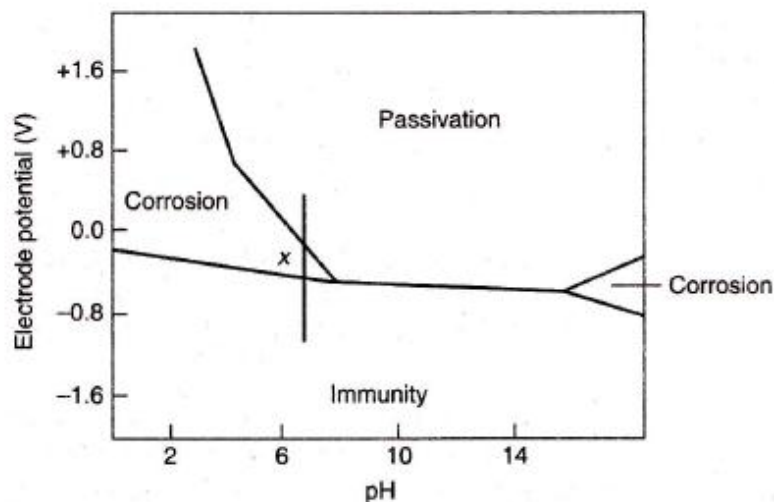
FIGURE 11.3   Pourbaix diagram.

From Figure 11.3, it is seen that the rate of corrosion can be altered by shifting the point x into immunity or passivity regions. The iron would be immune to corrosion if the potential is changed to about -0.8 V and this can be achieved by applying external current. On the other hand, the corrosion rate of iron can also be reduced by moving into the passivity region by applying positive potential. The diagram clearly indicates that the corrosion rate can also be reduced by increasing the pH of the solution by the addition of alkali without disturbing the potential.

4. **Nature of the electrolyte:**   The nature of the electrolyte also influences the rate of corrosion. If the electrolyte consists of silicate ions, they form insoluble silicates and prevent further corrosion. On the other hand, if chloride ions are present, they destroy the protective film and the surface is exposed for further corrosion. If the conductance of electrolyte is more, the corrosion current is easily conducted and hence the rate of corrosion is increased.

5. **Concentration of oxygen and formation of oxygen concentration cells:**   The rate of corrosion increases with increasing supply of oxygen. The region where oxygen concentration is lesser becomes anodic and suffers corrosion.

   Corrosion often takes place under metal washers where oxygen cannot diffuse readily. Similarly, buried pipelines and cables passing from one type of soil to another suffer corrosion due to differential aeration, e.g. lead pipeline passing through clay and then through sand. Lead pipeline passing through clay get corroded because it is less aerated than sand.

❐ Corrosion control

Corrosion can be controlled by the following ways:

1. **By selection of the material:**   Selection of the right type of the material is the main factor for corrosion control. Thus, noble metals are used for surgical instruments and ornaments as they are most immune to corrosion.

2. **By using pure metals:**   Pure metals have higher corrosion resistance. Even minute amount of impurities may lead to severe corrosion, e.g. 0.02% iron in aluminium decreases its corrosion resistance.

3. **By alloying:**   Both corrosion resistance and strength of many metals can be improved by alloying, e.g. stainless steels containing chromium produce a coherent oxide film which protects the steel from further attack.

4. **By annealing:**   Heat treatment like annealing helps to reduce internal stresses and reduces corrosion.

5. **By eliminating galvanic action:**   If two metals have to be in contact, they should be so selected that their oxidation potentials are as near as possible. Further, the area of the cathode metal should be smaller than that of the anode, e.g. copper nuts and bolts on large steel plate. The corrosion can also be reduced by inserting an insulating material between the two metals.

6. **By proper design:**   The corrosion of metals depends on the design of the equipment and structures which are always in contact with any corrosive medium. The design of a structure should be such that retention of moisture should be as low as possible because corrosion occurs in the presence of moisture. For example, electrical boxes exposed to the atmosphere should be so designed that water does not collect at the top. Tanks and other containers are designed such that the whole of the liquid should be drained off completely.

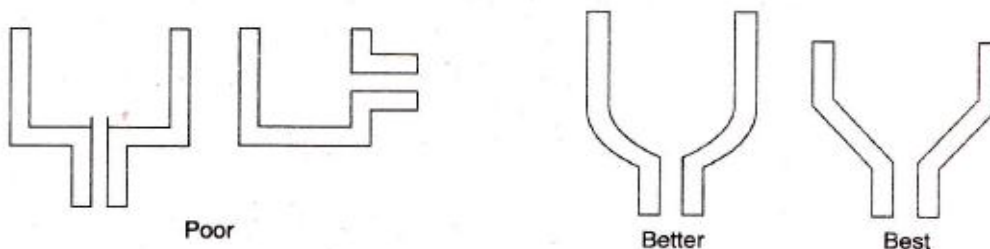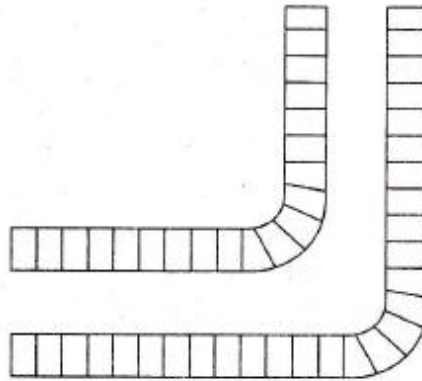On the basis of these general guidelines, some poor and good engineering designs are given in Figure 11.7.

Poor   Better   Best

FIGURE 11.7   Control of corrosion by design.

Erosion corrosion can be avoided by using smooth and curved pipe bends (Figure 11.8).

**FIGURE 11.8**   Corrosion prevention using curved pipelines.

Riveted joints should be avoided. In that place welded joints are used. Crevice corrosion and caustic embrittlement can be prevented in this way (Figure 11.9).

FIGURE 11.9   Welding reduces corrosion.

7. **By cathodic protection:**   The principle involved in cathodic protection is to force the metal behave like a cathode. Since there will not be any anodic area on the metal, corrosion does not occur. There are two types of cathodic protection.
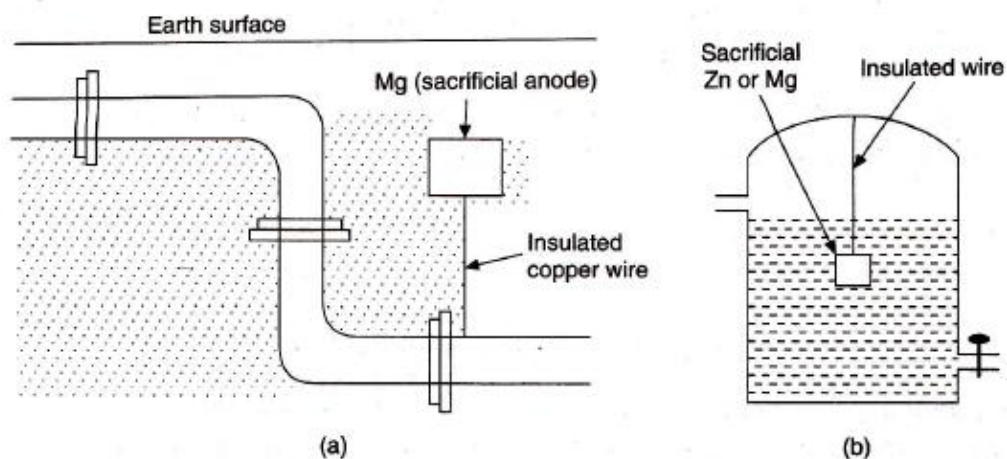
    (a) Sacrificial anodic protection.
    (b) Impressed current cathodic protection.

    (a) *Sacrificial anodic protection:*   In this technique, a more active metal is connected to the metal structure to be protected so that all the corrosion is concentrated at the more active metal and thus saving the metal structure from corrosion. This method is used for the protection of sea going vessels such as ships and boats. Sheets of zinc or magnesium are hung around the hull of the ship. Zinc and magnesium being anodic to iron get corroded. Since they are sacrificed in the process of saving iron (anode), they are called *sacrificial anodes*. The corroded sacrificial anode is replaced by a fresh one, when consumed completely (Figure 11.10).
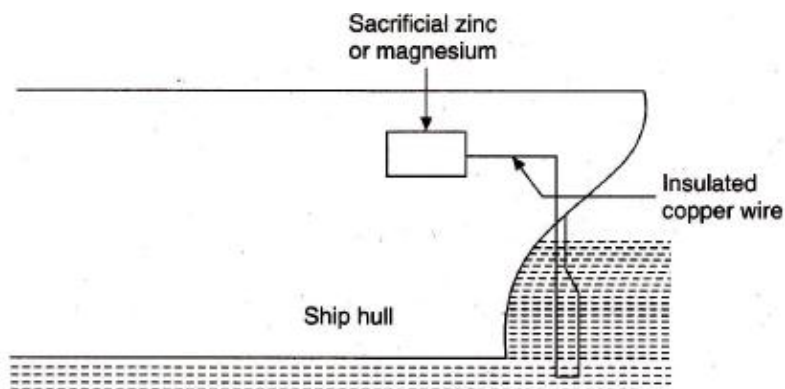
FIGURE 11.10   Sacrificial anodic protection.

Important applications of sacrificial anodic protection are as follows:

(i) Protection from soil corrosion of underground cables and pipelines (Figure 11.11a).

(ii) Magnesium sheets are inserted into domestic water boilers to prevent the formation of rust water (Figure 11.11b).

FIGURE 11.11   Sacrificial anodic protection (applications).

(b) *Impressed current cathodic protection:* In this method, an impressed current is applied in an opposite direction to nullify the corrosion current and converting the corroding metal from anode to cathode. This can be accomplished by applying sufficient amount of direct current from a battery to an anode buried in the soil and connected to the corroding metal structure which is to be protected. The anode is in a backfill (composed of gypsum) so as to increase the electrical contact with the soil. Since in this method current from an external source is impressed on the system, this is called impressed current method (Figure 11.12).
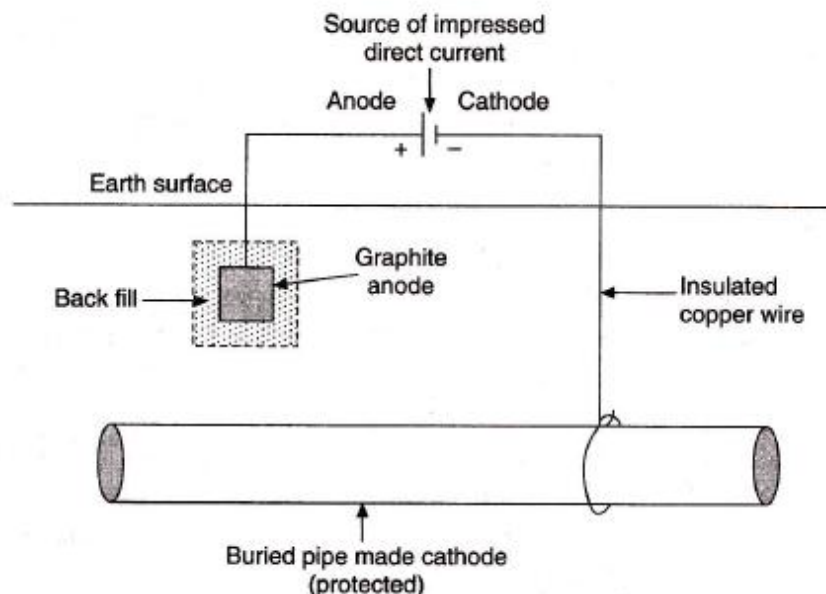

FIGURE 11.12 Impressed current cathodic protection.

8. **By applying protective coating:** The surface of engineering material can be protected from corrosion by covering it by a protective coating. This coating may be of organic or inorganic material.

9. **By modifying the environment:** The corrosion rate can be reduced by modifying the environment. The environment can be modified by the following:

    (a) *Deaeration:* The presence of increased amounts of oxygen is harmful since it increases the corrosion rate. Deaeration aims at the removal of dissolved oxygen. Dissolved oxygen can be removed by deaeration or by adding some chemical substances like Na_2SO_3.

    (b) *Dehumidification:* In this method, moisture from air is removed by lowering the relative humidity of surrounding air. This can be achieved by adding silica gel which can adsorb moisture preferentially on its surface.

    (c) *Inhibitors:* In this method, some chemical substances known as *inhibitors* are added to the corrosive environment in small quantities. These inhibitors substantially reduce the rate of corrosion.

(i) Anodic inhibitors: Anodic inhibitors include alkalis, molybdates, phosphates, chromates, etc. When these inhibitors are added, they react with the ions of the anode and produce insoluble precipitates. The so formed precipitate is adsorbed on the anode metal forming a protective film thereby reducing corrosion.

(ii) Cathodic inhibitors: In an electrochemical corrosion, the cathodic reactions are of two types depending on the environment.

In acidic solution, the cathodic reaction is

$$2H^+ + 2e^- \longrightarrow H_2$$
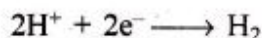
In acidic solution, the corrosion can be controlled by slowing down the diffusion of H^+ ions through the cathode. This can be done by adding organic inhibitors like amines and pyridine. They adsorb over the cathodic metal surface and act as a protective layer.

In neutral solution, the cathodic reaction is

$$H_2O + \tfrac{1}{2}O_2 + 2e^- \longrightarrow 2OH^-$$
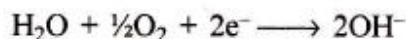
The formation of OH^- ions is only due to the presence of oxygen. By eliminating the oxygen from the medium, the corrosion rate can be reduced. Oxygen can be removed by adding some reducing agents (Na_2SO_3) or by deaeration.

(iii) Vapour phase inhibitors: Vapour phase inhibitors (VPIs) are organic inhibitors which readily sublime and form a protective layer on the metal surface, e.g. dicyclohexylammoniumnitrite. They are used in the protection of machinery, sophisticated equipment, etc. which are sent by ships. The condensed inhibitor can be easily wiped off from the metal surface.

10. **By passivation:** Passivation is a phenomenon of converting an active surface of a metal into passive i.e. more corrosion resistant by forming a thin, non-porous and highly protective film over the surface.

When the metals like aluminium and tin are exposed to the atmosphere or to the oxidizing environment, their surfaces rapidly get converted into oxides. The non-porous nature of these oxide layers prevent further corrosion. In other words, the metals are passivated.

Similarly, metals which are susceptible to corrosion are made passive by alloying with one or more metals which are passive or resist corrosion. For example, iron is rendered passive by alloying it with any of the transition metals such as chromium, nickel and molybdenum.