

1

UNIT

WATER TECHNOLOGY

Characteristics – alkalinity – types of alkalinity and determination – hardness – types and estimation by EDTA method (problems); Domestic water treatment – disinfection methods (Chlorination, ozonation, UV treatment) – Boiler feed water – requirements – disadvantages of using hard water in boilers – internal conditioning (phosphate, calgon and carbonate conditioning methods) – external conditioning – demineralization process – desalination and reverse osmosis.

**1.1 INTRODUCTION**

Water is the important compound for the existence of humanbeings, animals and plants. Water is used for agricultural, industrial and domestic purposes. About 80 % of the earth's surface is occupied by water. The minerals present in the top soil are dissolved by rain water, this water enters into waterbodies and get polluted. This is because almost all the compounds are dissolved in water. The important physical properties of water are summarised in Table 1.1.

S.No.	Properties	Specification
1.	Molecular Formula	H ₂ O
2.	Molar Mass	18.0153 g/mol
3.	Density	0.998 g/ml
4.	Melting Point	0°C
5.	Boiling Point	100°C
6.	Specific Heat Capacity	4.184 J/g.K

1.1.1 Sources of Water

The two main sources of water are as follows:

a) Surface Water

- i) **Rain Water** is the purest form of water. It is obtained by the evaporation of surface water. But, when it reaches earth's surface through atmosphere, it dissolves considerable amount of industrial gases (like CO₂, SO₂, NO₂, etc.) and suspended solid particles.
- ii) **River Water** consists of rain and springs water. Water from these sources flow over the surface of land and dissolves the soluble minerals present in the soil. River water contains the minerals of soil (such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron) and some organic matters.
- iii) **Lake Water** contains less amount of dissolved minerals, but the quantity of organic matter is very high.

- iv) **Sea Water** is the highest impure form of water. Major source of sea water is river water which consists of dissolved and suspended impurities. Due to continuous evaporation, the sea water becomes more saline.

b) Underground Water

Underground water is clear in appearance due to filtering action of the soil. A part of rain water percolates into the earth and dissolves the soluble salts present in the soil. So, the underground water contains higher dissolved salts.

Examples : Spring water and well water.

We know that, surface and underground water is used for domestic and industrial purposes. So, the water should be free from unwanted impurities and harmful bacteria.

The process of removing all types of impurities from water and making it fit for domestic and industrial purpose is called water treatment.

Before studying the water treatment, we should know the nature as well as the amount of impurities present in the water.

1.1.2 Types of impurities in water

The impurities present in the water are broadly classified into three types which are as follows:

i. Physical Impurities

Physical impurities are classified into two types:

- a) **Suspended Impurities:** They are sand, oil droplets, vegetable and animal matters which cause turbidity in water.

- b) **Colloidal Impurities** : They are finely divided silica, clay and organic waste products which imparts colours, odour and taste to water.

ii. Chemical Impurities

Chemical impurities are classified into two types.

- a) **Dissolved Salts** : They are bicarbonates, sulphates and chlorides of Ca and Mg, carbonates and bicarbonates of Na and K.

Dissolved magnesium and calcium salts in water cause 'hardness' whereas alkali salts (bicarbonate and carbonates of potassium and sodium, bicarbonate of calcium and magnesium) makes the water "alkaline".

- b) **Dissolved Gases** : They are O_2 , CO_2 , H_2S , SO_2 , NO_2 , CO, etc., which makes the water acidic. So, they accelerate the rate of corrosion.

iii. Biological Impurities

They are fungi, bacteria and other microorganisms which spread harmful diseases.



1.2 WATER QUALITY PARAMETERS

The water used for domestic and industrial purpose should be free from toxic substances and pathogenic bacteria. The specification of water for various industrial purposes are given in Table 1.2.

No.	Industry	Requirements	Remarks
1.	Textile and dyeing	(i) Free from colour, turbidity, organic matter, iron and manganese salts. (ii) Free from calcium and magnesium salts.	They produce coloured spots on fabrics. They precipitate basic dyes and decrease the solubility of acidic dyes. So, dyeing will not be uniform.
2.	Laundries	(i) Soft water. (ii) Free from colour, odour, turbidity, Fe and Mn Salts.	Hard water increases the consumption of soaps and detergents. Impart grey or yellow shades to the fabric.
3.	Sugar	Free from sulphates and alkali carbonates.	They causes difficulties in the crystallization of sugar from molasses.
4.	Beverages	Free from pathogens, Colour, odour, turbidity and alkaline salts.	They will neutralize the fruit acids and destroy the tastes.
5.	Paper and Pulp	(i) Free from Fe and Mn Salts. (ii) Free from harness and organic matter. (iii) Free from SiO_2 .	Affects colour and brightness of the paper. It increases the ash content of paper. Produces cracks in the paper.
6.	Power Station Cooling Systems	(i) It should be Non-Corrosive, Non-Scale forming, free from suspended impurities and should not promote algal growth.	Produces corrosion. Scale will act as insulator.
7.	Boiler Feed	(i) Zero hardness. (ii) Free from dissolved gases, disolved gases, silica suspended impurities.	Scale prevents efficient heat transfer. Lead to boiler corrosion.

The parameters used to determine the quality of water are given below:

Colour, Turbidity, Taste and odour, pH, Acidity, Alkalinity, Electrical conductivity, Chloride, Fluoride,

Sulphate, Nitrogen compound, Dissolved oxygen, Biological oxygen demand, Chemical oxygen demand and Hardness.

1.2.1 Alkalinity

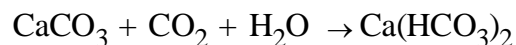
The ability of water to neutralize the acid is called alkalinity.

(or)

Alkalinity is the tendency of water to neutralize the H^+ ions by the supply of OH^- ions.

Alkalinity of water is due to the presence of carbonates (CO_3^{2-}), bicarbonates (HCO_3^-) and hydroxide (OH^-) ions.

The major portion of alkalinity in natural water is caused by the presence of bicarbonates. They are formed when water containing CO_2 is percolates through the soil having calcium carbonate and magnesium carbonate.



Depending upon the anion present in water, alkalinity is classified into three types.

1. Hydroxide alkalinity due to OH^- ions.
2. Carbonate alkalinity due to CO_3^{2-} ions.
3. Bicarbonate alkalinity due to HCO_3^- ions.

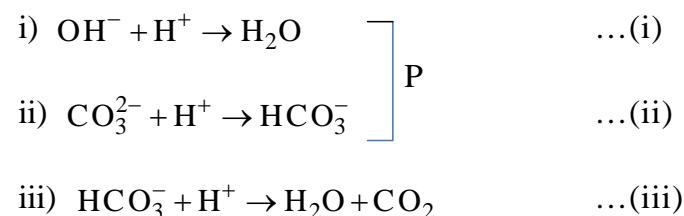
1.2.2 Determination of Alkalinity of given Water Sample

Principle

The alkalinity of a given water sample is determined by titrating water with standard acid. The titration is first carried out using phenolphthalein as indicator. The end point is the colour change from pink to colourless. The volume of acid ('P' ml) consumed upto this point corresponds to complete neutralization of hydroxide and converts all the carbonates into bicarbonates. The alkalinity measured upto this point is called phenolphthalein alkalinity.

Beyond the phenolphthalein alkalinity, the titration is continued using methyl orange as indicator. The end point is the colour change from yellow to pink. The total volume of acid ("M" ml) consumed by the water sample corresponds to the complete neutralization of all the bicarbonate, carbonates, and hydroxide ions.

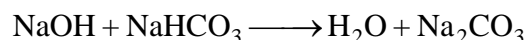
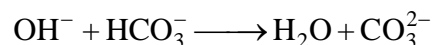
The total alkalinity of water can be calculated from the titre value 'M'. The individual alkalinity can be calculated based on the following theory:



Alkalinity of water sample is mainly due to the presence of

- i) Only hydroxide ion or
- ii) Only carbonate ions or
- iii) Only bicarbonate ions or
- iv) Combination of hydroxide and carbonate ions or
- v) Combination of hydroxide and bicarbonate ions.

It is noted that co-existence of hydroxide and bicarbonate ions in water are impossible because these two ions undergo reaction with each other to form carbonate ions.



Thus, the co-existence of OH^- and HCO_3^- ions are impossible in water. On the basis of same reason, the existence of all the three (OH^- , CO_3^{2-} and HCO_3^-) ions are also impossible in water.

Based on the above theory, the individual alkalinity can be calculated.

Procedure

Titration-I

100 ml of the given water sample is pipette out into a clean conical flask. A drop of phenolphthalein indicator is added. Now the water sample is titrated against the

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 'P' ml.

Titration-II

To the same water sample, 2–3 drops of methyl orange indicator is added and continue the titration against the standard sulphuric acid taken in the burette. The end point is the colour change from yellow to pink. The total volume of acid consumed is taken as 'M' ml.

The titration of water sample against the standard acid upto phenolphthalein end point marks the completion of reactions (i) and (ii) only. The amount of acid used corresponds to the hydroxide ions and one-half of the normal carbonate ions present in the water sample. On the otherhand, titration of the water sample against the standard acid to methyl orange end point marks the completion of all the three reactions (i), (ii), and (iii). Hence, the amount of acid used after the phenolphthalein end-point corresponds to one half of normal carbonate and all the bicarbonates which already present in the water sample originally. The total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions) of water sample.

Calculations:

Let, the volume of acid used upto phenolphthalein end point is 'P' ml and total volume of acid used upto methyl orange end-point is 'M' ml.

$$\text{OH}^- + \frac{1}{2}\text{CO}_3^{2-} = \text{P} \quad \dots(1)$$

$$\text{OH}^- + \text{CO}_3^{2-} + \text{HCO}_3^- = \text{M} \quad \dots(2)$$

$$\frac{1}{2}\text{CO}_3^{2-} + \text{HCO}_3^- = \text{M} - \text{P} \quad \dots(3)$$

- i. When $\text{P} = 0$, both OH^- and CO_3^{2-} ions are absent, then the alkalinity of water sample is only due to bicarbonate ions.
- ii. When $\text{P} = \frac{1}{2}\text{M}$, then only carbonate ions are present in the water. OH^- and HCO_3^- ions are absent. Hence, the alkalinity of water sample is only due to the presence of CO_3^{2-} ions.
- iii. When $\text{P} = \text{M}$, both CO_3^{2-} and HCO_3^- ions are absent. Alkalinity of water sample is only due to the presence of OH^- ions.
- iv. When $\text{P} > \frac{1}{2}\text{M}$, both CO_3^{2-} and OH^- ions are present in the water sample and HCO_3^- ions are absent.

So, alkalinity due to complete carbonate ions can be calculated as given below :

When HCO_3^- is absent, the equation (2) and (3) becomes (4) and (5) respectively.

$$\text{OH}^- + \text{CO}_3^{2-} = \text{M} \quad \dots(4)$$

$$\frac{1}{2}\text{CO}_3^{2-} = \text{M} - \text{P} \quad \dots(5)$$

Alkalinity due to half of carbonate is equal to ' $\text{M} - \text{P}$ ' then the alkalinity due to complete carbonate ions can be calculated by multiplying equation (5) by 2.

$$\text{CO}_3^{2-} = 2(\text{M} - \text{P}) \quad \dots(6)$$

From equation (6), complete alkalinity due to CO_3^{2-} ions can be calculated.

Calculation of OH^- alkalinity is done by substituting the equation (6) in (4).

$$\begin{aligned} \text{OH}^- + 2(\text{M} - \text{P}) &= \text{M} \\ \text{OH}^- &= \text{M} - 2(\text{M} - \text{P}) \\ &= \text{M} - 2\text{M} + 2\text{P} \\ \text{OH}^- &= 2\text{P} - \text{M} \end{aligned}$$

$$\text{Alkalinity due to } \text{OH}^- \text{ ions} = 2\text{P} - \text{M} \quad \dots (7)$$

From equation (7), alkalinity due to OH^- ions can be calculated.

- v. When $\text{P} < \frac{1}{2}\text{M}$, in this case, CO_3^{2-} and HCO_3^- ions are present and OH^- ions are absent. Hence, the equation (2) and (3) becomes (8) and (9) respectively.

$$\frac{1}{2}\text{CO}_3^{2-} = \text{P} \quad \dots(8)$$



$$\text{equation (8) } \times 2 \quad \text{CO}_3^{2-} = 2\text{P}$$

$$\therefore \text{Alkalinity due to } \text{CO}_3^{2-} = 2\text{P} \quad \dots(10)$$

Substitute the equation (10) in (9), we get

$$2\text{P} + \text{HCO}_3^- = \text{M}$$

$$\text{HCO}_3^- = \text{M} - 2\text{P} \quad \dots(11)$$

$$\therefore \text{Alkalinity due to } \text{CO}_3^{2-} = \text{M} - 2\text{P}$$

Alkalinity calculations with respect to OH^- , CO_3^{2-} and HCO_3^- ions are summarized in Table. 1.3.

Result of titration	Hydroxide alkalinity	Carbonate alkalinity	Bicarbonate alkalinity
$\text{P} = 0$	0	0	M
$\text{P} = \text{M}$	P or M	0	0
$\text{P} = \frac{\text{M}}{2}$	0	2P or M	0
$\text{P} > \frac{\text{M}}{2}$	$2\text{P} - \text{M}$	$2(\text{M} - \text{P})$	0
$\text{P} < \frac{\text{M}}{2}$	0	2P	$\text{M} - 2\text{P}$

From the above calculation, the individual alkalinity of water sample can be calculated by using the following formula:

Alkalinity of water sample for the specified ions

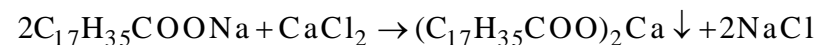
$$= \frac{\text{Volume of acid consumed} \times \text{normality of acid} \times 50 \times 1000}{\text{Volume of water sample}}$$

Or

$$= \text{Normality of water sample} \times 50 \times 1000 \text{ ppm.}$$

1.2.3 Hardness of Water (or) Hard Water and Soft Water

Water which does not produce lather readily with soap solution is called hard water. This is due to the presence of calcium, magnesium and other heavy metal ions in water.



Sodium	Hard	Calcium
Stearate	Water	Stearate
(Soluble)		(Insoluble)

We know that, soap is Na or K salt of higher fatty acids (like oleic, palmitic or stearic acid).

Water produces lather readily with soap solution is called soft water. This is due to the absence of Ca and Mg salts in water.

Hardness is *the characteristic property of water which prevents lather formation with soap solution.*

1.2.4 Types of Hardness

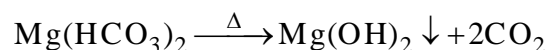
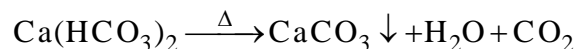
Based on the dissolved salts present in water, hardness can be classified into two types:

- (a) Temporary (or) Carbonate (or) Alkaline hardness.
- (b) Permanent (or) Non-carbonate hardness

a) Temporary Hardness (or) Carbonate Hardness (or) Alkaline Hardness

This is due to the presence of bicarbonates of Ca, Mg and other heavy metal ions. It can be removed by boiling the water.

The boiling process converts the bicarbonate into insoluble carbonate (or) hydroxides, which can be removed by filtration.



Hardness which can be easily removed by simple boiling process is called temporary hardness.

b) Permanent (or) Non-Carbonate Hardness (NCH) (or) Non-Alkaline Hardness

This is due to the presence of soluble salts like chlorides and sulphates of Ca and Mg ion. It cannot be removed by boiling the water because they are highly soluble in water.

Hardness which cannot be easily removed by simple boiling is called permanent hardness.

c) Total Hardness

The sum of temporary and permanent hardness is called total hardness of water sample.

Total Hardness = Temporary Hardness + Permanent Hardness

Difference between the temporary hardness and permanent hardness

S. No.	Carbonate hardness (or) Temporary hardness	Non-carbonate hardness (or) Permanent hardness
1.	It is due to bicarbonates of calcium and magnesium ions.	It is due to chlorides and sulphates of calcium and magnesium.
2.	It can be removed by boiling the water.	It cannot be removed by boiling the water.
3.	It is also called as alkaline hardness.	It is also called as non-alkaline hardness.

1.2.5 Units of Hardness

i) Parts per million (ppm)

The number of parts of CaCO_3 equivalent hardness per 10^6 parts of water is called ppm.

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

ii) Milligrams per litre (mg/l)

It is defined as the number of milligrams of CaCO_3 equivalent hardness present in one litre water.

Thus, 1 mg/l = 1 mg of CaCO_3 equivalent hardness present in one litre water

Relationship between ppm and mg/l

Weight of 1 litre water = 1 kg.

$$= 1000 \text{ gms} = 1000 \times 1000 = 10^6 \text{ mgs}$$

Therefore, 1 mg/l = 1 mg of CaCO_3 equivalent hardness in 10^6 mgs of water
= 1 ppm

Thus, 1 mg/l = 1 ppm.

OTHER UNITS:**iii) Clarke's degree ($^{\circ}\text{Cl}$)**

The number of parts of CaCO_3 equivalent hardness in 70,000 parts of water is called Clarke's degree.

1 $^{\circ}\text{Cl}$ = 1 part of CaCO_3 equivalent hardness in 70,000 parts of water.

1 $^{\circ}\text{Cl}$ = 14.3 ppm or 1 ppm = 0.07 degree Clarke's

iv) Degree French ($^{\circ}\text{Fr}$)

The number of parts of CaCO_3 equivalent hardness in 10^5 parts of water is called degree French.

1 $^{\circ}\text{Fr}$ = 1 part of CaCO_3 hardness equivalent in 10^5 parts of water.

1 ppm = 1 mg/l = 0.1 $^{\circ}\text{Fr}$ = 0.07 $^{\circ}\text{Cl}$

10 ppm = 10 mg/l = 1 $^{\circ}\text{Fr}$ = 0.7 $^{\circ}\text{Cl}$

1 $^{\circ}\text{Cl}$ = 1.43 $^{\circ}\text{Fr}$ = 14.3 ppm = 14.3 mg/l

v) Milliequivalent per litre (meq/l)

It is the number of milliequivalent of hardness present in one litre. Thus,

1 meq/l = 1 meq of CaCO_3 in one litre water

= $10^{-3} \times 50$ gm equivalent of CaCO_3 in one litre water

= 50 mg of CaCO_3 equivalent in one litre water

= 50 mg/l of CaCO_3 equivalent = 50 ppm

1.2.6 Expression for Hardness interms of CaCO_3 Equivalents

The concentration of hardness producing salts is expressed interms of CaCO_3 equivalent. CaCO_3 is used as a standard because of the following reasons:

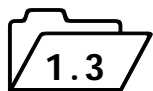
- Its molecular weight is 100 and equivalent weight is 50 which are whole number, so the calculations in water analysis can be simplified.
- It is the most insoluble salt, that can be precipitated in water treatment.

If the concentration of hardness producing salt is in mg/l, then

$$\text{Amount equivalent to CaCO}_3 = \frac{\text{Wt. of hardness producing salt} \times 100}{\text{Molecular wt. of hardness producing salt}}$$

$$\text{Amount equivalent to CaCO}_3 = \frac{\text{Wt. of hardness producing salt} \times 50}{\text{Eq. wt. of hardness producing salt}}$$

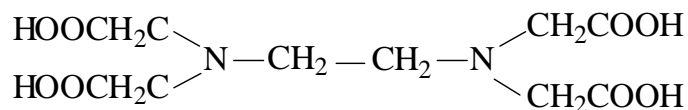
$$\left. \begin{array}{l} \text{If the weight of CaSO}_4 \text{ is 43 gm/l} \\ \text{then the amount equivalent to CaCO}_3 \end{array} \right\} = \frac{43 \times 100}{136} \text{ gm/l} \\ = 31.6176 \text{ gm/l}$$



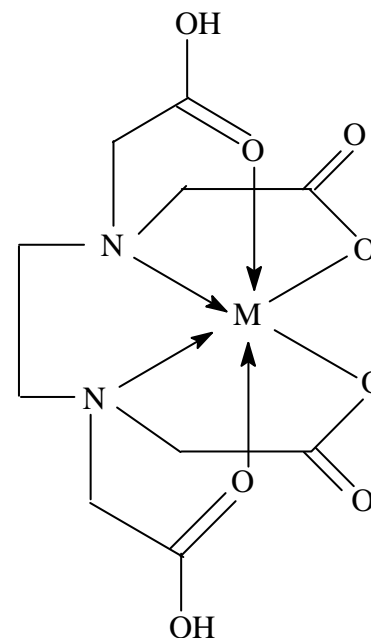
1.3 ESTIMATION OF HARDNESS BY EDTA METHOD

Amount of hardness present in the water can be estimated by the EDTA method. This is more accurate, easy and widely used.

EDTA → Ethylenediamine Tetraacetic Acid



EDTA is insoluble in water, so its disodium salt is used as complexing agent with Ca^{2+} and Mg^{2+} ions. The structure of the EDTA – metal complex is given below:

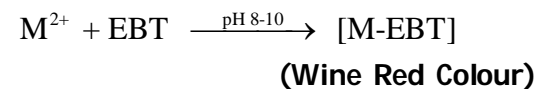


The Structure of Metal – EDTA Complex

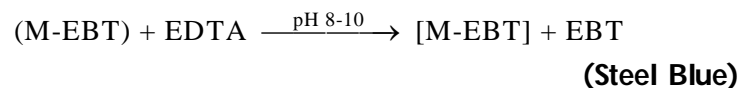
Principle

The amount of hardness causing ions (Ca^{2+} and Mg^{2+}) can be estimated by titrating the water sample with EDTA using Erichrome-Black-T (EBT) indicator at a pH 8-10. In order to maintain the pH, buffer solution ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$) is added. Only at this pH, complexation is possible.

When EBT indicator is added to the water sample, it forms wine red colour weak complex with Ca^{2+} and Mg^{2+} ions.



When this solution is titrated against EDTA, it replaces the indicator from the weak complex and form a stable, colourless and soluble EDTA complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free. The colour of the true indicator is steel blue. Thus, the end point is the colour changes from wine red to steel blue.



Various steps involved in this method are given below:

1) Preparation of standard hard water

1 gm of pure and dry $CaCO_3$ is dissolved in minimum amount of dilute HCl and made upto 1 litre solution using distilled water. Each 1 ml of this solution is equal to 1 mg of $CaCO_3$ equivalent hardness.

2) Preparation of EDTA solution

3.9 g of pure di-sodium salts of EDTA is dissolved in 1 litre distilled water.

3) Preparation of indicator

0.5 gm of Eriochrome Black-T indicator is dissolved in 100 ml of ethanol.

4) Preparation of buffer solution

67.5 gm NH_4Cl is dissolved in 570 ml of concentrated ammonia solution and then diluted upto 1 litre using distilled water.

Procedure

Titration-I

a) Standardisation of EDTA Solution

Rinse and fill the burette with EDTA solution. 50 ml of standard hard water is pipette out in a conical flask. Add 10–15 ml of buffer solution and 4 to 5 drops of EBT indicator. Titrate it with EDTA solution taken in the burette till the colour changes from wine red to steel blue. The volume of EDTA consumed by the standard hard water is taken as V_1 ml.

Titration-II

b) Estimation of Total Hardness

Pipette out 50 ml of given water sample in a conical flask. Add 10–15 ml of buffer solution and 4 to 5 drops of EBT indicator. Titrate it with EDTA solution taken in the burette till the colour changes from wine red to steel blue. The volume of EDTA consumed by the given water sample is taken as V_2 ml.

Titration-III

c) Estimation of Permanent Hardness (Titration-III)

250 ml of given water sample is taken in a 500 ml beaker. Boil it till the volume is reduced to about 50 ml. At the time of boiling, the soluble bicarbonates are converted into insoluble carbonates is removed. Cool and filter the solution and made upto 250 ml by using distilled water.

Then, pipette out 50 ml of boiled water sample in a conical flask. Add 10–15 ml of buffer solution and

4 to 5 drops of EBT indicator. Titrate it with EDTA solution till the colour changes from wine red to steel blue. The volume of EDTA consumed by boiled water sample is taken as V_3 ml.

Calculation:

Titration - I - Standardisation of EDTA Solution using Standard Hard Water

$$50 \text{ ml of standard hard water} = V_1 \text{ ml EDTA} \quad \dots(1)$$

We know that,

$$1 \text{ ml standard hard water} = 1 \text{ mg of CaCO}_3 \text{ equivalent.}$$

$$\text{Therefore, } 50 \text{ mg of CaCO}_3 \text{ equivalent} = V_1 \text{ ml of EDTA} \quad \dots(2)$$

Compare equation (1) and (2)

$$\begin{aligned} 50 \text{ ml of standard hard water} &= 50 \text{ mg of CaCO}_3 \text{ equivalent} \\ &= V_1 \text{ ml of EDTA} \quad \dots(3) \end{aligned}$$

\therefore The above equation can be written as

$$1 \text{ ml of EDTA} = \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent} \quad \dots (4)$$

Titration - II - Determination of Total Hardness

$$50 \text{ ml of water sample} = V_2 \text{ ml of EDTA} \quad \dots (5)$$

Using equation (4)

$$= V_2 \times \frac{50}{V_1} \text{ of CaCO}_3 \text{ equivalent}$$

$$\therefore 1 \text{ ml of water sample} = \frac{V_2}{50} \times \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\left[\begin{array}{l} \text{Total hardness of} \\ \text{1 ml of water sample} \end{array} \right] = \frac{V_2}{V_1} \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\left[\begin{array}{l} \text{Total hardness of} \\ \text{1000 ml of water sample} \end{array} \right] = \frac{V_2}{V_1} \times 1000 \text{ mg of CaCO}_3 \text{ equivalent}$$

Titration - III - Determination of Permanent Hardness

$$50 \text{ ml of boiled water sample} = V_3 \text{ ml of EDTA} \quad \dots (6)$$

Using equation (4)

$$= V_3 \times \frac{50}{V_1} \text{ of CaCO}_3 \text{ equivalent}$$

$$\left[\begin{array}{l} \text{Permanent hardness} \\ \text{of 1 ml of} \\ \text{boiled water sample} \end{array} \right] = \frac{V_3}{50} \times \frac{50}{V_1} \text{ mg of CaCO}_3 \text{ equivalent}$$

$$= \frac{V_3}{V_1} \text{ mg of CaCO}_3 \text{ equivalent}$$

$$\left[\begin{array}{l} \text{Permanent hardness} \\ \text{of 1000 ml of} \\ \text{boiled water sample} \end{array} \right] = \frac{V_3}{V_1} \times 1000 \text{ mg of CaCO}_3 \text{ equivalent} \quad \dots(7)$$

Determination of Temporary Hardness

Temporary hardness of water sample can be calculated from the total hardness and permanent hardness.

$$\text{Temporary Hardness} = \left(\begin{array}{c} \text{Total} \\ \text{hardness} \end{array} \right) - \left(\begin{array}{c} \text{Permanent} \\ \text{hardness} \end{array} \right)$$



BOILER FEED WATER (OR) BOILER TROUBLES

The water supplied into boiler for the production of steam is called boiler feed water. Boiler feed water should be free from turbidity, oil, dissolved gases, alkali and hardness causing substances.

If raw water is supplied directly to the boilers, the following troubles may arise:

- i) Scale and Sludge Formation
- ii) Priming and Foaming (Carry Over)
- iii) Caustic Embrittlement
- iv) Boiler Corrosion

1.5.1 Scale and Sludge formation in boilers

a) Sludge

When water is continuously converted into steam in boilers, the concentration of dissolved salts in water increases progressively. When the concentration of the salts reaches their saturation point, they are thrown out in the form of precipitate. The poor soluble substance gets precipitated first (Fig. 1.1a).

Sludge is a soft, loose and slimy precipitate formed within the boiler. It can be scrapped off with the wire brush. Sludges are formed by the substances which have greater solubilities in hot water than cold water (e.g., MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 , etc.).

Disadvantages of sludges

- ✱ Sludges are poor conductor of heat, so a portion of heat is wasted.
- ✱ Excessive sludge formation decreases the efficiency of the boiler.
- ✱ If the sludges are formed along with the scales, then the sludges get entrapped by the scales and both gets deposited as scales.

Prevention of sludges

- i) Sludge formation can be prevented by using softened water.
- ii) Sludge can be removed by blow down operation.

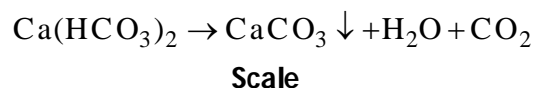
Blow down operation is the process of removing a portion of concentrated water by fresh water frequently from the boiler.

Fig.1.1 (a) Sludge in Boiler (b) Scale in Boiler

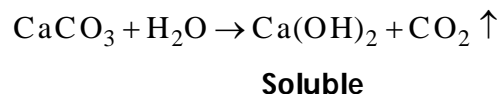
b) Scales

Scales are hard deposit which stick on the inner surface of the boiler.

Formation of scales may be due to following reasons:

i) Decomposition of calcium bicarbonate

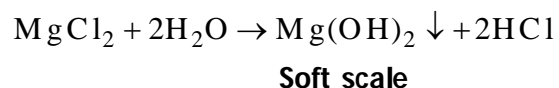
Scale formed due to $\text{Ca(HCO}_3)_2$ is soft, this scale is formed only in low pressure boilers. But in high pressure boilers, CaCO_3 is soluble,

**ii) Deposition of calcium sulphate**

CaSO_4 is soluble in cold water, but completely insoluble in superheated water. So, in high-pressure boilers more amount of scale is formed.

iii) Hydrolysis of magnesium salts

Dissolved magnesium salts undergo hydrolysis to give magnesium hydroxide precipitate which forms a soft scale.

**iv) Presence of silica**

Silica present in small quantities are deposited as calcium silicate or magnesium silicate (MgSiO_3). These deposits stick on the inner side of the boilers and it is very difficult to remove.

Disadvantages of scale formation

- * Decreases the efficiency of the boilers.
- * Lowering of boiler safety, any crack develops on the scale leads to explosion.
- * Scales are thermal insulator. In order to produce the steady supply of steam, more amount of heat (fuel) is required.

Removal of scales

- * If the scales are loosely adhering, it can be removed by using scrapper (wood or wire brush).
- * By giving thermal shocks (heating the boiler and then suddenly cooling the cold water).
- * If they are hard, it can be removed by dissolving it with the help of chemicals.
- * Calcium carbonate scales can be dissolved by using 5-10 % HCl and calcium sulphate scales can be dissolved by using EDTA.

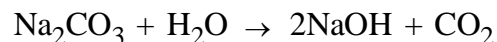
Table 1.4 : Difference between sludges and scales

No.	Sludges	Scales
1.	Sludges are soft deposits.	Scales are hard deposits
2.	They can be prevented by softened water.	It can be prevented by dissolving the scales with acids like HCl, H ₂ SO ₄ , etc.
3.	Sludges are loose precipitate. So, they are less dangerous.	Scales are stick on the walls of boiler and acts as bad conductor of heat. So, they are more dangerous.
4.	Sludges are formed by the substances like MgCl ₂ , CaCl ₂ , MgCO ₃ , MgSO ₄ , etc.	Scales are formed by substances like CaSO ₄ , Mg(OH) ₂ , MgSiO ₃ , etc.
5.	It can be removed by blowdown operation.	It can be removed by thermal shocks, scrapers, wire brush, etc.

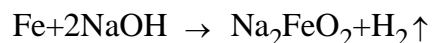
1.5.2 Caustic embrittlement

It means intercrystalline cracking of boiler metal.

It is due to the presence of highly alkaline water in the boiler. During softening process (lime soda process), a small amount of Na₂CO₃ is present in the soft water. When it is used in boiler, it decomposes to give sodium hydroxide and carbon dioxide.



This sodium hydroxide containing water flows into the minute hair cracks present in the inner side of the boilers by capillary action and dissolves the surrounding area of iron as sodium ferroate.



This causes brittleness of boiler especially in stressed parts like bends, joints, rivets, etc.

Prevention

It can be prevented by

- ✧ Using sodium phosphate instead of Na₂CO₃.
- ✧ Adding tannin, lignin and MgSO₄ to boiler water, which blocks the hair cracks thereby preventing infiltration of caustic soda.

1.5.3 Boiler corrosion

Boiler corrosion is the decay of boiler materials by chemical or electrochemical attack by its environment. It is due to the presence of dissolved oxygen, dissolved CO₂ and dissolved salts.

i) Dissolved oxygen

Water contains about 8 mg of dissolved oxygen per litre at room temperature. The dissolved oxygen in water attacks the boiler material at higher temperature.



Removal of dissolved oxygen

Dissolved oxygen can be removed by chemical and mechanical methods.

a) Chemical methods

Dissolved oxygen can be removed by adding calculated quantity of sodium sulphite (or) hydrazine (or) Sodium Sulphide.



Hydrazine is an ideal compound for removing dissolved oxygen in the water, since the products are water and N_2 gas.

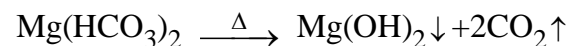
b) Mechanical deaeration

In this process (Fig.1.2), water is sprayed on the perforated plates fitted inside the tower. The sides of the tower are heated by steam. Vacuum pump is also attached to the sides of the tower. High temperature and low pressure reduce the dissolved oxygen contents in water.

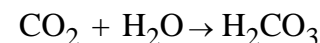
Fig. 1.2 Mechanical Deaeration

ii) Dissolved carbon dioxide

Water containing bicarbonate salts undergo decomposition to produce CO_2 gas.



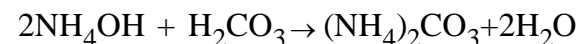
Dissolved CO_2 in water produces carbonic acid which is acidic and corrosive in nature.



Removal of Dissolved CO_2

CO_2 can be removed by

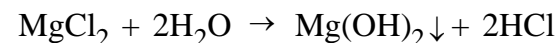
- a) Adding a calculated quantity of ammonium hydroxide in water.



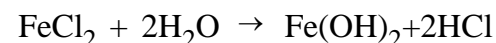
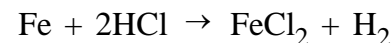
- b) Mechanical – deaeration process.

iii) Dissolved salts

The dissolved salts like MgCl_2 , CaCl_2 , etc., undergo hydrolysis at higher temperature to give HCl , which corrodes the boilers.

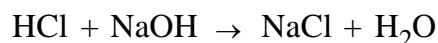


This liberated acid reacts with iron in chain-like reactions by producing HCl again and again.



Hence, presence of even a small amount of MgCl_2 will cause corrosion of iron to a large extent.

Corrosion by acids can be removed by the addition of calculated quantity of alkali to the boiler water.



1.5.4 Priming and Foaming

When boiler produces steam rapidly, some droplets of liquid water are carried along with the steam. Steam containing droplets of liquid water is called wet steam. These droplets carry some dissolved salts and suspended impurities. This phenomenon is called carry over. It occurs due to priming and foaming.

a) Priming : The process of wet steam formation is called priming.

Priming is caused by

- ✧ The presence of large amount of dissolved solids.
- ✧ High steam velocity.
- ✧ Sudden boiling.
- ✧ Improper boiler design.
- ✧ Sudden increase in steam production rate.

Priming can be controlled and prevented by

- ✧ Fitting mechanical steam purifier.
- ✧ Avoiding rapid change in steam production rate.

- ✧ Maintaining the water level lower in boilers.
- ✧ Using soft water.
- ✧ Controlling the velocity of steam.
- ✧ Good boiler design.

b) Foaming : The formation of stable bubbles over the surface of water in boiler is called foaming.

Foaming leads to excessive priming. It is caused by the presence of oil, grease and finely divided particles.

It can be prevented by

- i. Adding coagulants like sodium aluminate or aluminium hydroxide.
- ii. Adding antifoaming agents like castor oil or synthetic polyamides.



SOFTENING METHODS

The process of removing hardness producing salts from water is known as softening of water.

Softening of water can be done by two different types of treatment.

1. External Treatment or Conditioning
2. Internal Treatment or Conditioning

External Treatment or Conditioning

It involves the removal of hardness producing salts from the water before feeding into the boiler.

The external treatment can be done by Demineralisation or Ion-exchange process.



1.7 ION-EXCHANGE (OR) DE-IONISATION (OR) DEMINERALISATION PROCESS

It removes almost all the ions (both anion and cation) present in hard water. The soft water produced by lime soda and zeolite processes, do not contain hardness producing ions. But, this soft water contains other ions like, Na^+ , K^+ , CO_4^{2-} , Cl^- , etc. demineralised water does not contain both anions and cations. Hence, a soft water is not demineralised water. But, a demineralised water is soft water.

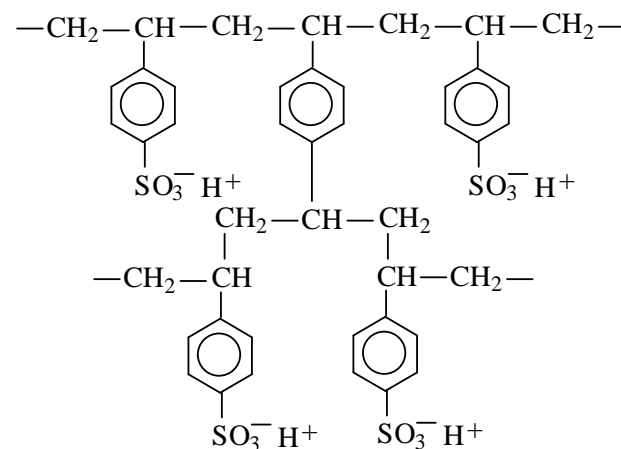
Demineralisation process is carried out by using ion exchange resins, which are long chain, cross-linked, insoluble organic polymers with a microporous structure. The functional groups attached to the chains which are responsible for the ion exchanging properties. In ion-exchange process, two types of exchange resins are used.

- (i) Cation exchange resin or Cation Exchanger
- (ii) Anion exchange resin or Anion Exchanger

i) Cation Exchange Resin (or) Cation Exchanger (RH):

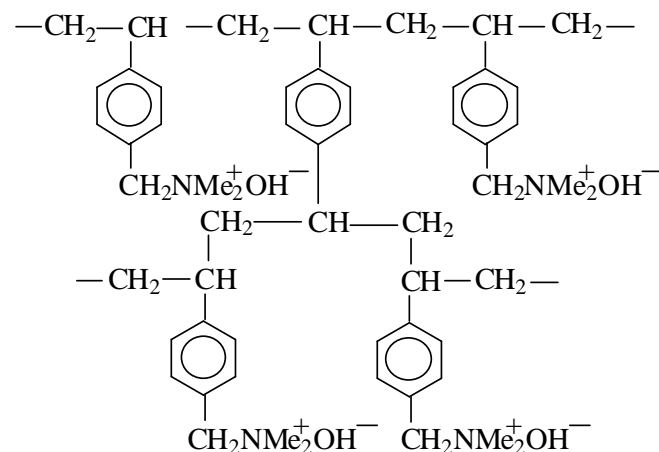
Resins containing acidic functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$) are capable of exchanging their H^+ ions with cations. They are represented as RH.

Examples : Sulphonated coals, sulphonated polystyrene, phenol-formaldehyde resins, etc.



Acidic or Cation Exchange Resin (Sulphonate Form)

ii) Anion-Exchange Resin or Anion Exchanger (ROH):



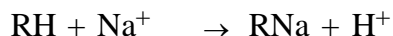
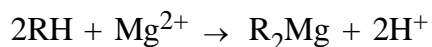
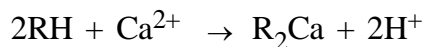
Basic (or) Anion Exchange Resin (Hydroxide Form)

Resins containing basic functional groups ($-\text{NH}_2$, $-\text{OH}$) are capable of exchanging their OH ions with other anions. They are represented as ROH.

Examples : Urea-formaldehyde, Melamine-formaldehyde, resins, crosslinked quaternary ammonium salts, etc.

Process

The hard water is passed through a cation exchanger column. It adsorbs all the cations like Ca^{2+} , Mg^{2+} , Na^+ , K^+ etc., present in hard water and releases an equivalent amount of H^+ ions from the resins.



The cation free water is passed through an anion exchanger column. It adsorbs all the anions like Cl^- , SO_4^{2-} , HCO_3^- , etc., present in water and releases an equivalent amount of OH^- ions from the resins.

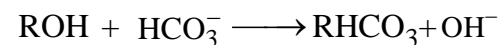
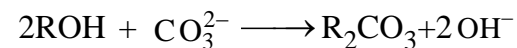
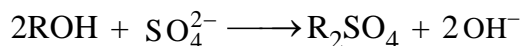
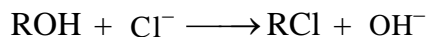
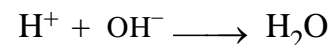


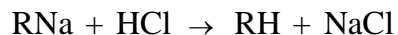
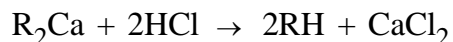
Fig. 1.3 Demineraliser (or) Deioniser

H^+ and OH^- ions (released from cation and anion exchanger) are combined to produce water molecules.

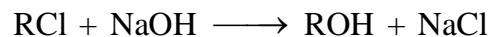
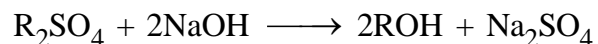


Thus, the water coming out from the exchanger is free from cations as well as anions. Ion free water is known as deionised or demineralised water.

Regeneration : When the cation exchange resin is exhausted, it can be regenerated by passing a solution of dil. HCl or dil. H_2SO_4 .



Similarly, when the anion exchange resin is exhausted, it can be regenerated by passing a solution of dil. NaOH.



Both the column are washed with deionised water and regenerated ion exchange resins are used again.

Advantages

- * It can be used to soften highly acidic or alkaline water.
- * It produces water with very low hardness (nearly 2 ppm).

Disadvantages

- * The turbid water cannot be treated by this method because turbidity blocks the surface of resins and reduces the output.
- * The equipment is costly and more expensive chemicals are needed.
- * Water containing Fe and Mn cannot be treated because they form stable compound with the resins.



INTERNAL TREATMENT (OR) INTERNAL CONDITIONING OR BOILER COMPOUNDS

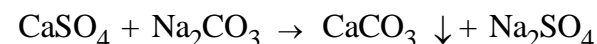
The removal of scale forming substance by adding chemicals directly into boiler is called internal treatment.

The chemicals used for this purpose is called boiler compounds. This boiler compounds convert the insoluble carbonates, hydroxides of calcium and magnesium salt into soluble compounds or loose precipitates.

After the internal treatment, blow-down operation is done in order to remove the precipitates (sludges) formed within the boilers. Various internal treatments are given below:

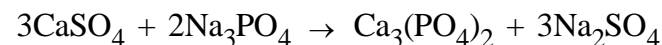
i) Carbonate Conditioning

In low pressure boilers, scale formation can be avoided by adding Na_2CO_3 to boiler water. The scale forming salt like $CaSO_4$ is converted into $CaCO_3$ which can be removed easily by blow-down operation.



ii) Phosphate Conditioning

In high pressure boilers, scale formation can be avoided by adding sodium phosphate to boiler water. The scale forming Ca^{2+} and Mg^{2+} salts react with phosphate to give soft sludges of calcium and magnesium phosphate which can be removed by blow-down operation.



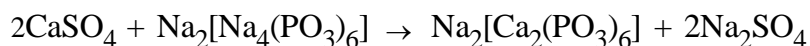
Generally 3 types of phosphates are used.

- i) Sodium dihydrogen phosphate (acidic) – used for alkaline water.

- ii) Disodium hydrogen phosphate (weakly alkaline) – used for weekly acidic water.
- iii) Trisodium phosphate (Too Alkaline) – used for too acidic water.

iii. Calgon Conditioning

Calgon is sodium hexametaphosphate $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$. It reacts with calcium ions and forms a highly soluble complex. Thus, it prevents the precipitation of scale forming salt.



Soluble Complex

It is better than phosphate conditioning because it converts scale forming substances into soluble complexes whereas phosphate conditioning produces sludges which requires blow down operation.

Table 1.5 : Differences between external treatment and internal treatment

No.	External treatment	Internal treatment
1.	External treatment of water is carried out before its entry into the boiler.	Internal treatment of water is carried out within the boiler itself.
2.	It includes soda - lime process, zeolite process and ion exchange process.	It includes colloidal conditioning, carbonate conditioning, phosphate conditioning, calgon conditioning, etc.
3.	High pressure boiler requires external treatment.	Low pressure boilers requires internal treatment.
4.	It is the preventive method.	It is the corrective method.



DESALINATION OF BRACKISH WATER

The process of removing common salt from water is known as desalination. Depending upon the quantity of dissolved solids, water is graded as below:

- (a) Fresh water - has < 1000 ppm of dissolved solids.
- (b) Brackish water - has > 1000 ppm; but < 35000 ppm of dissolved solids.
- (c) Sea water - has > 35,000 ppm of dissolved solids.

The water containing dissolved salts with peculiar salty or brackish taste is called brackish water. It is totally unfit for drinking purpose.

Sea water and brackish water can be converted into drinking water through reverse osmosis.

1.9.1 Reverse osmosis (R.O)

When two solutions of different concentration are separated by a semi-permeable membrane (which allows only solvent not solute), solvent (water) flows from lower concentration side to higher concentration side is due to osmosis. The driving force involved in this process is called osmotic pressure. *If the external pressure applied on the higher concentration side is greater than osmotic pressure, the solvent flow is reversed (i.e., solvent flows from higher concentration side to lower concentration side). This process is called reverse osmosis and it is also known as super-filtration* (Fig.1.4).

Fig.1.4 Reverse Osmosis Process

This method is used to separate the pure water from sea water.

In this process, pressure (15 to 40 Kg cm⁻²) is applied on the sea water side. So, the pure water flows through the semi-permeable membrane and leaves the dissolved solids (both ionic and non-ionic). The membrane is affixed to either side of a perforated plate.

Cellulose acetate, cellulose butyrate or polyamide polymers are used as membranes.

Advantages

- * This process removes ionic, non-ionic, colloidal and high molecular weight organic compounds (matters).
- * The life time of membrane is high and it can be easily replaced within few minutes.
- * Due to low capital cost, simplicity, low operating cost and high reliability, it is used to convert the sea water into drinking water.

- * Water obtained by this method is used as boiler feed water in very high pressure boilers.

1.10 REQUIREMENTS OF DRINKING WATER

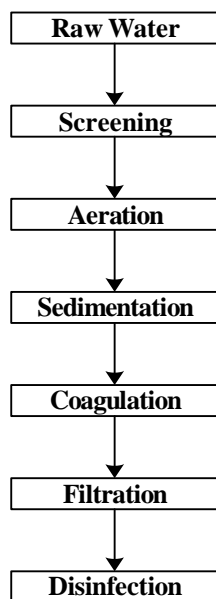
- 1) It should be colourless and odourless.
- 2) It should be pleasant taste.
- 3) It should not be turbid.
- 4) It should be free from dissolved gases like H₂S, CO₂ and NH₃.
- 5) It should be free from toxic substances like lead, arsenic, chromium and manganese salts.
- 6) Its total dissolved solids should be less than 500 ppm.
- 7) It should be free from harmful pathogenic bacteria and suspended impurities.
- 8) It should not have more than 0.1 – 0.2 ppm of free chlorine.
- 9) It should be less alkaline in nature.
- 10) It should have a pH of 7.0 – 8.0.

1.11 TREATMENT OF WATER FOR DOMESTIC SUPPLY (OR) POTABLE WATER

Water used for domestic purpose should be free from harmful contaminant.

The process of removal of suspended and colloidal impurities from raw water is called treatment of drinking water.

Treatment of water for domestic supply involves various steps like screening, sedimentation, coagulation, filtration and sterilization, which are given in the flow chart as below:



Flowchart of Drinking Water Treatment

1) Screening

The process of removal of floating matters from the water by using screen is called screening.

In this process, the raw water is allowed to pass through a screen, having large number of holes, which retains floating materials like leaves, wood pieces, insoluble organic matter, etc., and allows only the water.

2) Aeration

The process of mixing water with air is called aeration. It is used to remove the unwanted gases like CO_2 , H_2S and other volatile impurities causing bad taste and odour. The soluble ferrous and manganous salts are converted into insoluble ferric and manganic salts which can be removed easily.

3) Sedimentation

It is a process of removing suspended impurities by allowing the water to stand for 4–6 hours in a large settling tank. All the suspended particles settle down at the bottom due to forces of gravity. They are easily removed by filtration. Sedimentation removes 70 to 75% of the suspended matter in the water.

4) Coagulation

Impurities like finely divided silica, clay and organic matter cannot be removed by simple sedimentation process. They can be removed by coagulation process. Generally, the finely divided colloidal impurities are exist as negatively charged species.

In this method, certain chemicals are added to water during the sedimentation. These chemicals, produce positively charged species and neutralise the negatively charged colloidal impurities and bring them down. This is called flocculation. The entire process is called coagulation. The chemicals used for this purpose is called coagulants.

Aluminium sulphate is the common coagulating agent used for removing clay particles.

$\text{Al}_2(\text{SO}_4)_3$ first gets hydrolysed to form gelatinous precipitate of hydroxide. It acts as a 'Floc' or coagulant which entraps finely divided clay particles, settled at the bottom that can be removed easily.

Other coagulants used for this purpose are

- i) Ferric Sulphate
- ii) Ferrous Sulphate (Copperas)
- iii) Chlorinated Copperas
- iv) Alum
- v) Ammonium Alum
- vi) Sodium Aluminate

5) Filtration

It is a process of removing bacteria, colour, taste, odour, fine suspended particles, etc., by passing the water through filter beds containing fine sand, coarse sand, fine gravel and coarse gravel. The porous material used is called filtering medium and the equipment used for filtration is known as filter.

A sand filter is shown in Fig. 1.5.

Fig.1.5 Filtration Process through Sand Filter

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 logging of impurities in the pores of the sand bed. When the rate of flow becomes very slow, the filtration is stopped and the bed is cleaned by scraping the top layer of the sand bed and replacing it with clean sand.

6) Sterilisation (or) Disinfection

The complete removal or destruction of harmful bacteria is known as sterilisation or disinfection process.

The chemicals used for this purpose are disinfectant or sterilizer. The sterilizers used for sterilizing water are bleaching power, chlorine, ultra violet rays and ozone.

i) Boiling process

When water is boiled for 10–15 minutes, all the harmful bacteria are destroyed.

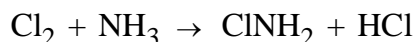
Disadvantages

- ✱ The taste of drinking water is altered.
- ✱ It is not suitable for municipal water supply because the quantity of water is very high.

ii) Chlorination

The process of adding chlorine to water is called chlorination. Chlorination can be done by the following methods.

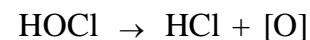
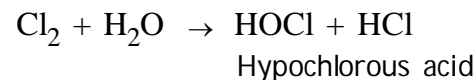
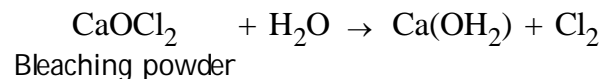
- a) **Adding chlorine gas** : Chlorine gas can be bubbled in the water which acts as very good disinfectant.
- b) **Adding chloramine** : When chlorine and ammonia are mixed in the ratio of 2:1, a compound chloramine is formed.

**Chloramine**

Chloramine compounds decompose slowly to give chlorine. This chlorine completely destroys the harmful bacteria for long time. Hence, it is a better disinfectant than chlorine.

- c) **Adding bleaching powder** : When bleaching powder is added to water, hypochlorous acid (HOCl) is produced. It acts as a powerful germicide. Hypochlorous acid ruptures the cell membrane of

the disease producing microbes and prohibits the metabolic activities of bacteria. So, all the bacteria are killed and water is sterilized.

***Bleaching powder has certain limitations***

- ✧ It is highly unstable and during the storage chlorine may escape.
- ✧ It introduces calcium content in water which increases the hardness.
- ✧ Adding excess of bleaching powder to water gives disagreeable odour and taste.

1.11.1 Break-point chlorination

Water contains bacteria, organic matters, reducing substances (like Fe^{2+} , H_2S , etc.) and free ammonia. When chlorine is added to water, the results obtained can be depicted graphically (Fig.1.6.) The graph shows the relationship between the amount of chlorine added to water and the residual chlorine.

From the graph, the applied chlorine is used to kill the bacteria and oxidize all the reducing substances present in the water, where there is no free residual chlorine.

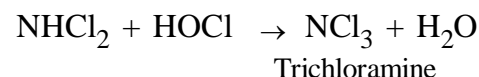
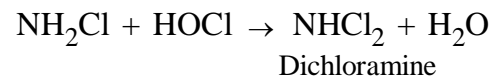
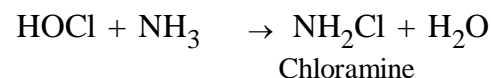
Fig. 1.6 Break Point Chlorination

As the amount of applied chlorine increases, the amount of combined residual chlorine also increases. This is due to the formation of chloramine and other chloro compounds.

At one point, on further chlorination, the oxidation of chloramine and other impurities occurs and the combined residual chlorine gradually decreases. It reaches the minimum point at which oxidation of chloramine and other organic compounds are completed. This minimum point is called the break point chlorination.

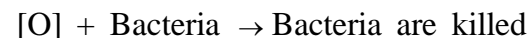
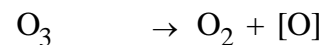
The reason for decrease in the concentration of combined residual chlorine is due to decomposition of organic compounds which lowers the chlorine concentration. These organic compounds are responsible for the bad taste and odour in water.

Thus, break point chlorination eliminates bad taste and odour from the water.



d) Ozone (O₃) Treatment

Ozone is a powerful disinfectant. It is readily absorbed by water. Ozone is highly unstable and decomposes to give nascent oxygen which is capable of destroying bacteria.



Advantages

- * O₃ is a sterilizing agent and also a bleaching, decolourising and deodourising agent. It improves water taste.
- * If excess of ozone is present in water, it is not harmful because it decomposes to give oxygen.

Disadvantages

- * This process is highly expensive.
- * Ozone is unstable and cannot be stored for long time.
- * It cannot be used in large scale.

e) UV-rays

UV-rays are produced by passing electric current through mercury vapour lamp. Water is exposed to uv-radiation which destroys the harmful bacteria. However, it is not an efficient method because UV-rays cannot penetrate into large depth of water. Therefore, the UV-rays are used to clean the swimming pool water.

Advantages

- * No need for chemicals.
- * No odour or colour is developed by the uv-rays.

Disadvantages

- * Careful operation is needed.
- * High cost.
- * Turbid water cannot be treated.

Some important compounds and their molecular weight

Ca(HCO ₃) ₂	- 162	Mg(HCO ₃) ₂	- 146
Ca(NO ₃) ₂	- 164	Mg(NO ₃) ₂	- 148
CaCO ₃	- 100	MgSO ₄	- 120
CaSO ₄	- 136	MgCl ₂	- 95
CaCl ₂	- 111	MgCO ₃	- 84
Ca ²⁺	- 40		
Mg ²⁺	- 24		

PROBLEMS AND SOLUTIONS**PROBLEMS BASED ON HARDNESS**

- 1) **Molecular weights of some hardness producing salts. Sample of water contains 120 mgs of MgSO₄ per litre. Calculate the hardness interms of CaCO₃ equivalent.**

Solution :

Given data:

The amount of MgSO₄ = 120 mg/l

$$\left[\begin{array}{l} \text{The amount} \\ \text{of hardness} \\ \text{in terms} \\ \text{of CaCO}_3 \\ \text{equivalent} \end{array} \right] = \frac{\text{The amount of hardness producing salt} \times 100}{\text{Molecular weight of hardness producing salt}}$$

$$= \frac{120 \times 100}{120} = 100 \text{ mg/l}$$

- 2) **If a sample of water contains 50 mgs of Ca²⁺ ions per litre. Calculate its hardness interms of CaCO₃ equivalent.**

Solution:

The amount of Ca²⁺ ions = 50 mg/l

The molecular weight of calcium ion = 40

$$\left[\therefore \text{The amount of hardness} \right. \\ \left. \text{interms of CaCO}_3 \text{ equivalent} \right] = \frac{50 \times 100}{40} = 125 \text{ mg/l}$$

- 3) A water sample contains 204 mgs of CaSO_4 and 73 mgs of $\text{Mg}(\text{HCO}_3)_2$ per litre. What is the total hardness in terms of CaCO_3 equivalent?

Solution:

$$\begin{aligned}\text{Amount of } \text{CaSO}_4 \text{ in terms of } \text{CaCO}_3 \text{ equivalent} &= \frac{204 \times 100}{136} \\ &= 150 \text{ mg/l}\end{aligned}$$

$$\begin{aligned}\text{Amount of } \text{Mg}(\text{HCO}_3)_2 \text{ in terms of } \text{CaCO}_3 \text{ equivalent} &= \frac{73 \times 100}{146} \\ &= 50 \text{ mg/l}\end{aligned}$$

$$\text{Temporary hardness} = \text{Mg}(\text{HCO}_3)_2 = 50 \text{ mg/l}$$

$$\text{Permanent hardness} = \text{CaSO}_4 = 150 \text{ mg/l}$$

$$\begin{aligned}\text{Total hardness} &= \left[\begin{array}{c} \text{Temporary} \\ \text{Hardness} \end{array} \right] + \left[\begin{array}{c} \text{Permanent} \\ \text{Hardness} \end{array} \right] \\ &= 50 + 150 = 200 \text{ mg/l}\end{aligned}$$

- 4) Calculate the carbonate and non-carbonate hardness of a water sample containing the dissolved salts as given below in mg/l. $\text{Mg}(\text{HCO}_3)_2=7.3$; $\text{Ca}(\text{HCO}_3)_2=40.5$; $\text{CaSO}_4=13.6$, $\text{MgCl}_2=21.75$ and $\text{NaCl}=50$.

Solution :

Amount of hardness of $\text{Mg}(\text{HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{7.3 \times 100}{146} = 5 \text{ mg/l}$$

Amount of hardness of $\text{Ca}(\text{HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{40.5 \times 100}{162} = 25 \text{ mg/l}$$

Amount of hardness of CaSO_4 in terms of CaCO_3 equivalent

$$= \frac{13.6 \times 100}{136} = 10 \text{ mg/l}$$

Amount of hardness of MgCl_2 in terms of CaCO_3 equivalent

$$= \frac{21.75 \times 100}{95} = 22.9 \text{ mg/l}$$

Carbonate hardness = $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2$

$$= 5 + 25 = 30 \text{ mg/l}$$

Non-carbonate hardness = $\text{CaSO}_4 + \text{MgCl}_2$

$$= 10 + 22.9 = 32.9 \text{ mg/l}$$

Total Hardness = Carbonate hardness + Non-carbonate hardness

$$= 30 + 32.9 = \mathbf{62.9 \text{ mg/l.}}$$

- 5) A water sample contains the following dissolved salts in mg/l, $\text{Mg}(\text{HCO}_3)_2 = 73$, $\text{CaCl}_2 = 111$, $\text{Ca}(\text{HCO}_3)_2 = 81$ and $\text{MgSO}_4 = 40$. Calculate the temporary and permanent hardness of the water (At wts. of Ca, Mg, O, C, Cl, S and H are 40, 24, 16, 12, 35.5, 32 and 1 respectively).

Solution :

Amount of hardness of $\text{Mg}(\text{HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{73 \times 100}{146} = 50 \text{ mg/l}$$

Amount of hardness of CaCl_2 in terms of CaCO_3 equivalent

$$= \frac{111 \times 100}{111} = 100 \text{ mg/l}$$

Amount of hardness of $\text{Ca(HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{81 \times 100}{162} = 50 \text{ mg/l}$$

Amount of hardness of MgSO_4 in terms of CaCO_3 equivalent

$$= \frac{40 \times 100}{120} = 33.33 \text{ mg/l}$$

Temporary Hardness = $\text{Mg(HCO}_3)_2 + \text{Ca(HCO}_3)_2$

$$= 50 + 50 = 100 \text{ mg/l}$$

Permanent Hardness = $\text{CaCl}_2 + \text{MgSO}_4$

$$= 100 + 33.33 = 133.33 \text{ mg/l}$$

- 6) A sample of water is found to contain the following analytical data in mg/l. $\text{Mg(HCO}_3)_2 = 14.6$; $\text{Mg Cl}_2 = 9.5$; $\text{MgSO}_4 = 6$, $\text{Ca(HCO}_3)_2 = 16.2$. Calculate the temporary and permanent hardness of the water sample. (Atomic wts. $\text{Ca} = 40$, $\text{Mg} = 24$, $\text{Cl} = 35.5$, $\text{C} = 12$, $\text{S} = 32$, $\text{O} = 16$ and $\text{H} = 1$).

Solution :

Amount of hardness of $\text{Mg(HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{14.6 \times 100}{146} = 10 \text{ mg/l}$$

Amount of hardness of MgCl_2 in terms of CaCO_3 equivalent

$$= \frac{9.5 \times 100}{95} = 10 \text{ mg/l}$$

Amount of hardness of MgSO_4 in terms of CaCO_3 equivalent

$$= \frac{6 \times 100}{120} = 5 \text{ mg/l}$$

Amount of hardness of $\text{Ca(HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{16.2 \times 100}{162} = 10 \text{ mg/l}$$

Temporary hardness

$$= \text{Mg(HCO}_3)_2 + \text{Ca(HCO}_3)_2$$

$$= 10 + 10 = 20 \text{ mg/l}$$

Permanent hardness

$$= \text{MgCl}_2 + \text{MgSO}_4$$

$$= 10 + 5 = 15 \text{ mg/l}$$

Total Hardness = Temporary Hardness + Permanent hardness

$$= 20 + 15 = 35 \text{ mg/l}$$

- 7) A water sample contains $16.8 \text{ mg/l} = \text{Mg(HCO}_3)_2$, $12 \text{ mg/l} = \text{MgCl}_2$, $29.6 \text{ mg/l} = \text{MgSO}_4$ and $5 \text{ mg/l} = \text{NaCl}$. Calculate the permanent and temporary hardness of water and express it in ppm. (Atomic weight of $\text{Mg} = 25$; $\text{H} = 1$; $\text{C} = 12$; $\text{O} = 16$; $\text{Cl} = 35.5$; $\text{Na} = 23$; $\text{S} = 32$).

Solution:

Amount of hardness of $\text{Mg(HCO}_3)_2$ in terms of CaCO_3 equivalent

$$= \frac{16.8 \times 100}{146} = 11.5 \text{ mg/l}$$

Amount of hardness of MgCl_2 in terms of CaCO_3 equivalent

$$= \frac{12 \times 100}{95} = 12.63 \text{ mg/l}$$

Amount of hardness of MgSO_4 in terms of CaCO_3 equivalent

$$= \frac{29.6 \times 100}{120} = 24.66 \text{ mg/l}$$

NaCl does not contribute any hardness to water.

Hence, it is ignored.

Temporary hardness = $\text{Mg}(\text{HCO}_3)_2 = 11.6 \text{ mg/l}$ or ppm

Permanent hardness = $\text{MgCl}_2 + \text{MgSO}_4$

$$= 12.63 + 24.66$$

$$= \mathbf{37.29 \text{ mg/l or ppm.}}$$

8) How many grams of FeSO_4 dissolved per litre gives 210.5 ppm of hardness? (Fe = 56 ; S = 32, O = 16, Ca = 40, C = 12).

Solution :

Molecule weight of $\text{FeSO}_4 = 136$ ($56 + 16 + 64 = 136$) gm

Molecule weight of $\text{CaCO}_3 = 100$ gm

Amount of hardness of FeSO_4
in terms of CaCO_3 Equivalent = 210.5 ppm

100 ppm of hardness = 136 ppm of FeSO_4

$$210.5 \text{ ppm of hardness} = \frac{136 \times 210.5}{100}$$

$$= \mathbf{286.3 \text{ mg/l}}$$

PROBLEMS BASED ON EDTA TITRATION

9. 50 ml of hard water requires 15 ml of EDTA solution for titration, (1 ml of EDTA = 1 mg of CaCO_3). Calculate the hardness of the water sample.

Solution :

Formula used is

$$\text{Total hardness} = \frac{V_{\text{EDTA}}}{V_{\text{water}}} \times Z \text{ mg} \times 1000 \text{ CaCO}_3 \text{ equivalent}$$

Where, Z = Number of mg of CaCO_3 equivalent per EDTA solution.

1 ml of EDTA = 1 mg of CaCO_3 equivalent

15 ml of EDTA = 15 mg of CaCO_3 equivalent

$$\text{Hardness present in 1 litre} = \frac{15}{15} \times 1 \text{ mg} \times 1000$$

$$= \mathbf{300 \text{ ppm CaCO}_3 \text{ equivalent.}}$$

10) 250 ml of water sample of EDTA titration with Eriochrome Black-T as indicator consumed 13 ml of 0.022 M EDTA solution till end point is reached. Calculate the hardness of water. (1 ml of 0.01 M EDTA = 1 mg of CaCO_3)

Solutions:

Formula used is

$$\text{Total hardness} = \frac{V_{\text{EDTA}}}{V_{\text{water}}} \times Z \text{ mg} \times 1000 \text{ CaCO}_3 \text{ equivalent}$$

Where,

Z = Number of mg of CaCO_3 equivalent per EDTA solution.

1 ml of 0.01 M EDTA = 1 mg of CaCO_3 equivalent

1 ml of 0.022 M EDTA = $\frac{1}{1.01} \times 0.022$ mg of CaCO_3 equivalent

13 ml of 0.022 M EDTA = $\frac{13 \times 2.2 \text{ mg of } \text{CaCO}_3 \times 1000}{250}$

11) 100 ml of water sample requires 20 ml of 0.01 M EDTA for the titration with Eriochrome Black T indicator. 100 ml of the same sample after boiling and filtering requires 10 ml of 0.01 M EDTA. Calculate the total carbonate and non-carbonate hardness of the sample.

Solution:

1 ml of 0.01 M EDTA = 1 mg of CaCO_3 equivalent

20 ml of 0.01 M EDTA = 20 mg of CaCO_3 equivalent

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

So that hardness present in 1 litre water sample = $\frac{20}{100} \times 1000$

= 200 ppm of CaCO_3 equivalent

100 ml of the boiled sample = 10 ml of 0.01 M EDTA

= 10 mg of CaCO_3

Permanent hardness = $\frac{10}{100} \times 1000 = 100$ ppm of CaCO_3

$$\begin{aligned} \left[\begin{array}{c} \text{Carbonate Hardness} \\ \text{Temporary Hardness} \end{array} \right] &= \left[\begin{array}{c} \text{Total} \\ \text{Hardness} \end{array} \right] - \left[\begin{array}{c} \text{Non-Carbonate Hardness} \\ \text{Permanent Hardness} \end{array} \right] \\ &= 200 - 100 \\ &= \mathbf{100 \text{ ppm of } \text{CaCO}_3 \text{ equivalent}} \end{aligned}$$

12) 0.5 gm of CaCO_3 was dissolved in dil. HCl and diluted to 500 ml. 50 ml of this solution requires 48 ml of EDTA solution for titration. 50 ml of a hard water sample requires 15 ml of the same EDTA solution for titration. Calculate the total hardness of water.

Solution:

500 ml of CaCl_2 = 0.5g of CaCO_3 = 500 mg of CaCO_3

1 ml of CaCl_2 solution = $\frac{500\text{mg}}{500} = 1$ mg of CaCO_3 equivalent

50 ml of CaCl_2 solution = 48 ml of EDTA solution

1 ml of EDTA solution = $\frac{50}{48} = 1.0417$ mg of CaCO_3 equivalent

15 ml of EDTA solution = 1.0417 mg of $\text{CaCO}_3 \times 15$
= 15.625 mg of CaCO_3 equivalent

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

So, total hardness present in 1 litre = $\frac{15.625}{50} \times 1000$

= **312.5 ppm of CaCO_3 equivalent**

13) 0.25 g of CaCO_3 is dissolved in dil. HCl and diluted to 250 ml. 100 ml of this hard water sample requires 20 ml of the EDTA solution for titration. The 100 ml of water sample consumes 30 ml of same EDTA solution for titration. 100 ml of the same water sample on boiling and filtering requires 10 ml of EDTA. Calculate the total permanent and temporary hardness.

Solution :

250 ml of CaCl_2 solution contains = 0.25 g of CaCO_3 equivalent
 = 250 mg of CaCO_3 equivalent

1 ml of CaCl_2 solution = $\frac{250 \text{ mg}}{250}$
 = 1 mg of CaCO_3 equivalent

100 ml of CaCl_2 solution = 20 ml of EDTA solution.

Standardisation of EDTA

100 ml of CaCl_2 = 100 mg of CaCO_3 equivalent
 20 ml of EDTA solution = 100 mg of CaCO_3 equivalent

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

Total Hardness:

30 ml of EDTA = 100 ml of water
 = 30×5
 = 150 mg of CaCO_3 equivalent

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

So, the total hardness present in

$$\begin{aligned} 1 \text{ litre water sample} &= \frac{150 \text{ mg}}{100} \times 100 \\ &= 1500 \text{ ppm of } \text{CaCO}_3 \text{ equivalent} \end{aligned}$$

Permanent Hardness

10 ml of EDTA solution = 100 ml of hard water after boiling
 = 10×5 = 50 mg of CaCO_3 equivalent

This is present in 100 ml of hard water.

So, permanent hardness present in 1 litre water sample

$$= \frac{50}{100} \times 1000 = 500 \text{ ppm of } \text{CaCO}_3$$

Temporary Hardness = Total hardness – Permanent hardness
 = $1500 - 500$ = **1000 ppm.**

PROBLEMS BASED ON ALKALINITY

14) 100 ml of water sample, on titration with 0.02 N H_2SO_4 gives a titre value of 7.2 ml to phenolphthalein end-point and 14.4 ml to methyl orange end-point. Calculate the alkalinity of the water sample in terms of CaCO_3 equivalent and comment on the type of alkalinity present.

Solution:

Given data:

Volume of given water sample = 100 ml

Volume of acid consumed to phenolphthalein end point P = 7.2 ml

Volume of acid consumed to methyl orange end-point M = 14.4 ml

Normality of acid (H_2SO_4) = 0.2 N

Normality of water sample = $\frac{14.4 \times 0.2}{100} = 0.00288 \text{ N}$

We know that,

$$\begin{aligned} \text{Alkalinity of water sample} &= \text{Normality of water sample} \times \\ &\quad 50 \times 1000 \text{ ppm} \\ &= 0.00288 \times 50 \times 1000 = \mathbf{144 \text{ ppm}} \end{aligned}$$

It is observed that $P = \frac{1}{2}M$ (i.e., $\frac{14.4}{2} = 7.2 \text{ ml}$)

The alkalinity of water sample is only due to carbonate ions and other ions like OH^- and HCO_3^- are absent.

15) 100 ml of a raw water sample, on titration with 0.02 N sulphuric acid requires 10 ml of the acid to phenolphthalein end-point and 16.0 ml of the acid to methyl orange end-point. Determine the type and extent of alkalinity present in the water sample.

Solution:

Given data:

Volume of given water sample = 100 ml

Volume of H_2SO_4 required to }
phenolphthalein end point } P = 10 ml

Volume of H_2SO_4 required to methyl orange indicator = 16 ml

Normality of H_2SO_4 acid = 0.02 N

From the given data, it is observed that 'P' = 10 ml which is greater than $\left(\frac{M}{2}\right)$ i.e., $P > \frac{1}{2}M$. Hence, the water sample contains OH^- and CO_3^{2-} ions alkalinity only and HCO_3^- ions are absent.

(i) Alkalinity due to OH^-

The volume of acid consumed by OH^- present in the 100 ml water sample can be calculated by using the formula
Substitute the values, we get

$$\left. \begin{array}{l} \text{The volume of acid consumed by } \text{OH}^- \\ \text{present in the 100 ml water sample} \\ \text{can be calculated by using the formula} \\ \text{Substitute the values, we get} \end{array} \right\} = 2P - M$$

$$= 2 \times 10 - 16$$

$$= 20 - 16 = 4 \text{ ml}$$

Volume of acid consumed by OH^- alkalinity ' V_1 ' = 4 ml

Normality of acid ' N_1 ' = 0.02 N

Volume of water sample ' V_2 ' = 100 ml

Normality of water sample due to OH^- ' N_2 ' = $\frac{V_1 N_1}{V_2}$

$$= \frac{4 \times 0.02}{100} = 8 \times 10^{-4} \text{ N}$$

$$\begin{aligned} \left(\text{OH}^- \text{ Alkalinity of sample} \right) &= \left(\text{Normality of water} \right) \times 50 \times 1000 \\ &= 8 \times 10^{-4} \times 50 \times 1000 \\ &= \mathbf{40 \text{ ppm.}} \end{aligned}$$

(ii) Alkalinity due to Carbonate (CO_3^{2-})

The volume of acid consumed due to Carbonate ions present in the water can be calculated by using the formula

$$= 2M - 2P$$

$$= 2 \times 16 - 2 \times 10$$

$$= 32 - 20 = 12 \text{ ml}$$

Volume of acid consumed by CO_3^{2-} ions present in the water sample } 'V₁' = 12 ml

Normality of H_2SO_4 'N₁' = 0.2 N

Volume of water sample 'V₂' = 100 ml

Normality of water sample due to

$$\text{CO}_3^{2-} \text{ alkalinity 'N}_2\text{' = } \frac{V_1 N_1}{V_2}$$

$$= \frac{0.02 \times 12}{100} = \frac{0.24}{100}$$

$$= 2.4 \times 10^{-3} \text{ N}$$

$$\left(\text{Alkalinity of water sample due to } \text{CO}_3^{2-} \right) = \left(\text{Normality of water} \right) \times 50 \times 1000 \text{ ppm}$$

$$= 2.4 \times 10^{-3} \times 50 \times 1000$$

$$= \mathbf{120 \text{ ppm.}}$$

(iii) Total Alkalinity of given water sample

Total alkalinity of water sample = alkalinity due to OH^- ions

+ alkalinity due to CO_3^{2-} ions

$$= 40 + 120 = \mathbf{160 \text{ ppm}}$$

16) A water sample is not alkaline to phenolphthalein. But, 100 ml of the sample on titration with N/100 sulphuric acid, requires 18 ml to methyl orange end-point. What are the types and amount of alkalinity present in the sample.

Solution:

Volume of given water sample = 100 ml

Volume of acid consumed by phenolphthalein end point P = 0 ml

Volume of acid consumed by methyl orange end point M = 18 ml

Normality of acid = 1/100 = 0.01 N

Since, P = 0, the alkalinity due to OH^- and CO_3^{2-} ions are zero i.e., they are absent.

But, the alkalinity of water sample is only due to HCO_3^- ions.

Alkalinity due to bicarbonate ions (HCO_3^-)

Volume of acid consumed 'V₁' = 18 ml

Normality of acid 'N₁' = 0.01 N

Volume of water sample 'V₂' = 100 ml

$$\begin{aligned}
 \text{Normality of water sample} \quad 'N_2' &= \frac{V_1 N_1}{V_2} \\
 &= \frac{18 \times 0.01}{100} = \frac{0.18}{100} \\
 &= 1.8 \times 10^{-3} \text{ N}
 \end{aligned}$$

$$\begin{aligned}
 \left(\text{Alkalinity of water sample due to } \text{HCO}_3^- \right) &= \left(\text{Normality of water sample} \right) \times 50 \times 1000 \text{ ppm} \\
 &= 1.8 \times 10^{-3} \times 50 \times 1000 \\
 &= \mathbf{90 \text{ ppm.}}
 \end{aligned}$$

17) 200 ml of a water sample requires 12 ml of 0.02 N sulphuric acid using phenolphthalein indicator but it directly give pink colouration with methyl orange. Calculate the amount of alkalinity due to OH^- ions.

Solution:

$$\begin{aligned}
 \text{Volume of given water sample} &= 200 \text{ ml} \\
 \text{Volume of acid consumed by} & \\
 \text{Phenolphthalein end point} &P = 12 \text{ ml} \\
 \text{Volume of acid consumed by} & \\
 \text{Methyl orange end point} &M = 12 \text{ ml} \\
 \text{Normality of acid} &= 2/100 \\
 &= 0.02 \text{ N}
 \end{aligned}$$

Since, $P = M$, alkalinity of water sample is only due to hydroxide alkalinity and all other alkalinity are absent.

Alkalinity due to OH^-

Volume of acid consumed ' V_1 ' = 12 ml

Normality of acid ' N_1 ' = 0.02 N

Volume of water sample ' V_2 ' = 200 ml

$$\begin{aligned}
 \text{Normality of water sample} \quad 'N_2' &= \frac{V_1 N_1}{V_2} \\
 &= \frac{12 \times 0.02}{200} = \frac{0.24}{200} \\
 &= 1.2 \times 10^{-3} \text{ N}
 \end{aligned}$$

$$\begin{aligned}
 \left. \begin{array}{l} \text{Alkalinity due to} \\ \text{OH}^- \text{ ion of water sample} \end{array} \right\} &= \left(\text{Normality of water sample} \times \right. \\
 &\quad \left. \text{Eq.wt. of } \text{CaCO}_3 \times 1000 \text{ ppm} \right) \\
 &= 1.2 \times 10^{-3} \times 50 \times 1000 \\
 &= \mathbf{60 \text{ ppm.}}
 \end{aligned}$$

POINTS TO REMEMBER

- ⚠ *The chief sources of water are rain, rivers and lakes (surface water), wells and springs (ground water) and sea water.*
- ⚠ *Various impurities present in water are classified into chemical impurities, physical impurities and biological impurities.*
- ⚠ *The quality of a water is determined by the following parameters: Turbidity, colour, odour, taste, alkalinity, nitrogen, fluoride, hardness, etc.*
- ⚠ *Water which readily produce lathers with soap is called soft water, whereas water which does not produce lather with soap is called hard water. Hardness to water is introduced by the presence of Ca^{2+} and Mg^{2+} ions in water. Hardness can be classified into temporary and permanent hardness.*
- ⚠ *Hardness removal methods include lime-soda process, permutit method, demineralization, desalination, etc.*
- ⚠ *Water is an essential resource for both industrial and domestic purposes.*
- ⚠ **Boiler feed water** : *Water used for production of steam should be free from dissolved salts and gases, suspended impurities, silica and oil. If the raw water is used in boilers, these impurities lead*

to sludge formation, priming and foaming, caustic embrittlement and boiler corrosion. These can be prevented by the removal of dissolved oxygen and carbon dioxide by chemical and mechanical method.

- ⚠ **Water softening methods** : *The process of removing hardness producing salts from water is known as softening or conditioning of water. Since water is a source for industrial purposes, it is mandatory to soften water which makes it free from hardness-producing substances, suspended impurities, dissolved gases, etc. Softening of water can be done by two methods – External treatment and Internal treatment.*
- ⚠ *External treatment involves the removal of hardness producing salts from the water before feeding into boiler. The external treatment methods are Lime-soda process, zeolite or permutit process and demineralization or ion exchange process.*
- ⚠ **Demineralisation (or) Ion exchange process** : *The boiler feed water should be free from all types of impurities. Water obtained by the demineralization process, is completely free from ions.*
- ⚠ *Internal treatment involves adding chemicals directly to the water in the boilers for removing dangerous scale forming salts which is not completely removed by the external treatment for water softening. This method is used to convert scale to sludge which can*

be removed by blow-down operation. Internal conditioning methods include colloidal conditioning, carbonate conditioning, phosphate conditioning, calgon conditioning, etc.

⚠ **Desaltation or Desalination** : The process of removal of dissolved salts (NaCl) from water is described as desalination or desalting. The techniques used for desalination of sea water and brackish water includes reverse osmosis, electro dialysis, distillation, etc.

⚠ **Reverse osmosis** : When two solutions of different concentrations are separated by a semi-permeable membrane, solvent (water) flows from a region of lower concentration to a region of higher concentration. This spontaneous process is called osmosis. The external pressure applied on the concentrated solutions side is greater than osmotic pressure, the solvent flows from higher concentration side to lower concentration side. This process is called reverse osmosis.

⚠ The treatment of water for municipal supply involves screening, aeration, sedimentation, coagulation, filtration, sterilization (or) disinfection, storage and distribution.

SHORT QUESTIONS & ANSWERS

1. Define hardness of water.

Hardness is the characteristic property of water which prevent lather formation with soap solution.

2. What is meant by hard water and soft water?

Water that do not produce lather readily with soap solution is called hard water.

Water readily produces lather with soap solution is called soft water.

3. What are carbonate hardness and non-carbonate hardness?

(or)

What is permanent hardness and temporary hardness?

The hardness which can be removed by simple boiling process is called carbonate hardness (or) temporary hardness. This is mainly due to the presence of bicarbonate salts of calcium and magnesium ions.

The hardness which cannot be removed easily by simple boiling is called non-carbonate hardness (or) permanent hardness. This is mainly due to the presence of soluble salts of calcium and magnesium ions.

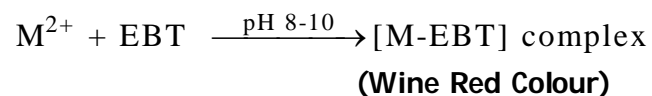
4. What are the salts responsible for carbonate and non-carbonate hardness?

Carbonate hardness is due to the presence of bicarbonates of Ca, Mg and other heavy metal ions. It can be removed by boiling the water.

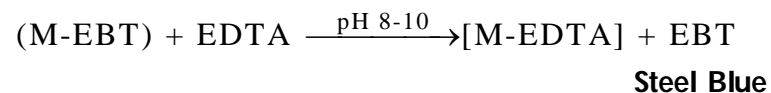
Non-carbonate hardness is due to the presence of soluble salts like chlorides of Ca and Mg, ion, Sulphates of magnesium and hydroxide of calcium ion. It cannot be removed by boiling the water.

5. How Eriochrome-black-T indicator is functioning in EDTA titration?

When EBT indicator is added to the water sample, it forms wine red coloured weak complex with Ca^{2+} and Mg^{2+} ions at pH 8-10.



When this solution is titrated against EDTA, it replaces the indicator from the weak complex and form a stable EDTA complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free. The colour of the true indicator is steel blue. Thus, the end point is the colour change from wine red to steel blue.



6. Why buffer is used in EDTA titration?

The amount of hardness can be determined by titrating the water sample against EDTA using Eriochrome – Black-T indicator at a pH 8-10. In order to maintain the pH, buffer solution ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$) is added. Only at this pH, Ca^{2+} and Mg^{2+} ions forms a complex with EDTA.

7. Define alkalinity.

The ability of water to neutralize the acid is called alkalinity.

8. What are the different types of alkalinity?

Alkalinity of water is classified into three types. They are

- a) Hydroxide alkalinity
- b) Carbonate alkalinity and
- c) Bicarbonate alkalinity

9. Why water should be softened before using in boilers?

If the raw water is supplied directly to the boilers, the following troubles may arise:

- i. Scale and sludge formation
- ii. Priming and foaming (carry over)
- iii. Caustic embattlement
- iv. Boiler corrosion

These problems lead to the breakdown of boilers. So, water should be softened before using in boilers.

10. What are scales and sludges?

Sludge is a soft, loose and slimy precipitate formed within the boiler.

Scales are hard deposits which stick on the inner surface of the boiler.

11. What is meant by priming and foaming?

The process of wet steam formation is called *priming*.

The formation of stable bubbles over the surface of water in boilers is called *foaming*.

12. What is caustic embrittlement? How it can be prevented?

Caustic embrittlement means intercrystalline cracking of boiler metal.

It can be prevented by using sodium phosphate instead of Na_2CO_3 or by adding tannin, lignin and MgSO_4 to boiler water which block the hair cracks thereby preventing infiltration of caustic (NaOH) soda.

13. What is demineralization? Mention the advantages of demineralization.

The process of removal of almost all the ions (both anion and cation) present in hard water is called *demineralization or deionization*.

The major advantages of this process is highly acidic or alkaline water can be treated by this process. The water obtained by this process have very low hardness (nearly 2 ppm).

14. What is coagulation? Give an example.

In order to remove the impurities like finely divided silica, clay and organic matter in water, certain chemicals are added. These chemicals get hydrolysed to form a gelatinous precipitate, which entraps the finely divided clay particles, and settles at the bottom of the container. This process is called coagulation process.

The chemicals used for this purpose is called coagulants.

Example : $\text{Al}_2(\text{SO}_4)_3$

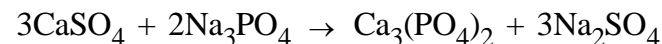
15. What are boiler compounds? Mention their significance.

The removal of scale forming substance by adding chemicals directly into boiler is called internal treatment. The chemicals used for this purpose is called boiler compounds.

These boiler compounds convert the insoluble carbonates and hydroxides of calcium and magnesium salts into soluble compounds or loose precipitates which avoid the breakdown of the boilers.

16. What is phosphate conditioning?

In high pressure boilers, scale formation can be avoided by adding sodium phosphate to boiler water. The scale forming Ca^{2+} and Mg^{2+} salts react with phosphate to give soft sludges of calcium and magnesium phosphate which can be removed by blow-down operation.

**17. What is disinfection process? How is it carried out by UV-treatment?**

The complete removal or destruction of harmful bacteria is known as sterilization, or disinfection.

UV-treatment and chlorine addition is an example of disinfection process. UV-radiations are produced by passing electric current through mercury vapour lamp. When water is exposed to UV-radiation which destroys the harmful bacteria. UV-rays are used to clean the swimming pool water.

18. Define the term break point chlorination.

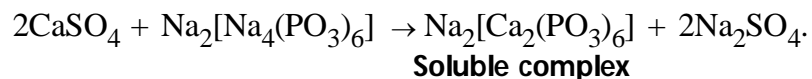
Minimum amount of bleaching powder (chlorine) required for complete destruction of harmful organisms and oxidation of organic compounds in water is called *break point chlorination*. The amount of chlorine added to the water should be greater than the break point.

19. What is desalination?

The process of removing common salt from water is known as desalination.

20. What is calgon? How does it functions in water treatment?

Calgon is sodium hexametaphosphate $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$. This substance reacts with calcium ions and forms a highly soluble complex. Thus, it prevents the precipitation of scale forming salt.

**21. How will you prevent the scales and sludges?**

Scales formation can be prevented by using softened water and sludge can be removed by blow down operation.

22. What is reverse osmosis?

When two solutions of different concentration are separated by a semi-permeable membrane (which allows only solvent not solute), the solvent (water) that flows from lower concentration side to higher concentration side is due to osmosis. The driving force involved in this process is called osmotic pressure. If a hydrostatic pressure in excess of osmotic pressure is applied on the higher concentration

side, the solvent flow is reversed (i.e., solvent flows from higher concentration side to lower concentration side). This process is called reverse osmosis.

23. What are the disadvantages of ion-exchange process?

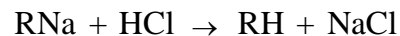
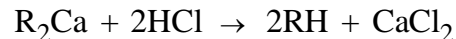
- ✧ The turbid water cannot be treated by this method because turbidity blocks, the surface of resins and reduces the output.
- ✧ The equipment is costly and more expensive chemicals are needed.
- ✧ Water containing Fe and Mn cannot be treated because they form stable compound with the resins.

24. What is blow down operation?

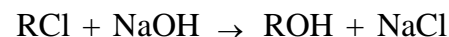
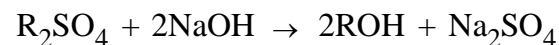
Blow down operation is the process of removing a portion of concentrated water by fresh water frequently from the boiler.

25. How exhausted ion-exchange resins are regenerated?

When the cation exchange resin is exhausted, it can be regenerated by passing a solution of dil. HCl or dil. H_2SO_4 .



Similarly, when the anion exchange resin is exhausted, it can be regenerated by passing a solution of dil. NaOH.



Both the column are washed with deionised water and the regenerated ion exchange resins are used again.

26. What is boiler corrosion?

Boiler corrosion is the decay of boiler materials by chemical or electrochemical attack of its environment.

27. Differentiate the sludge and scale.

No.	Sludge	Scale
1.	They are soft deposits.	Scales are hard deposits
2.	They can be removed easily.	It is very difficult to remove the scales.
3.	Sludges are loose precipitate. So, they are less dangerous.	Scales are bad conductor of heat. So, they are more dangerous.
4.	Sludges are formed by the substances like MgCl_2 , CaCl_2 , etc.	Scales are formed by substances like CaSO_4 , Mg(OH)_2 , etc.

28. Give examples of disinfection process.

The important disinfection processes are chlorination, UV-treatment and ozone treatment.

29. What are the constituents responsible for alkalinity of water?

Alkalinity of water is attributed due to the presence of carbonates (CO_3^{2-}), bicarbonates (HCO_3^-) and hydroxide (OH^-) ions.

30. Distinguish between soft and demineralised water.

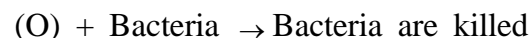
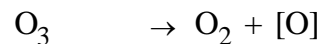
No.	Soft water	Demineralised water
1.	It contains ion like Na^+ , K^+ , etc.	It does not have any ions.
2.	The total dissolved salts are higher.	The total dissolved salts are very low (2 to 10 ppm).
3.	It cannot be used as boiler water, because the NaCl , Na_2SO_4 , etc., present in the water causes caustic embrittlement.	It can be used as boiler feed water.

31. Distinguish between soft and hard water.

No.	Soft water	Hard water
1.	It produce lather readily with soap solution.	It does not produce lather readily with soap solution.
2.	It does not produce white precipitate with soap solution	It produce white precipitate with soap solution.
3.	It can be used for drinking, washing, etc.	It can not be used for drinking, washing, etc.

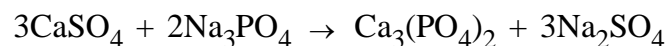
32. How is water sterilised by ozone?

Ozone is bubbled in the water. It can be readily adsorbed by water. Then, ozone decomposes to give nascent oxygen which is capable of destroying bacteria.



33. Name an internal treatment method used for high pressure boiler and explain.

In high pressure boilers, phosphate conditioning is adopted to avoid the scale and sludge formation. It can be done by adding sodium phosphate to boiler water. The scale forming Ca^{2+} and Mg^{2+} salts react with phosphate to give soft sludges of calcium and magnesium phosphate which can be removed by blow-down operation.

**34. List the disadvantages of using hard water in boilers.**

If raw water is supplied directly to the boilers, the following troubles may arise:

- i) Scale and sludge formation
- ii) Priming and foaming (carry over)
- iii) Caustic embrittlement
- iv) Boiler corrosion.

35. What are ion-exchange resins? Give examples.

Ion-exchange resins are long chain, cross linked, insoluble organic polymers with microporous structure.

The function groups attached in the chains are capable to exchange their ions with other ions.

Cation exchangers - Examples: Sulphonated coals, sulphonated polystyrene, phenol-formaldehyde resins, etc.

Anion exchangers - Examples: Urea-formaldehyde, Melamine formaldehyde, resins, crosslinked quaternary ammonium salts, etc.

36. What are the cause of priming?

Priming is cause by

- ✧ The presence of large amount of dissolved salts.
- ✧ High steam velocity.
- ✧ Sudden boiling.
- ✧ Improper boiler design.
- ✧ Sudden increase in steam production rate.

37. What are the causes of foaming?

Foaming is caused by the presence of oil, grease and finely divided particles.

38. How do you prevent the priming?

Priming can be controlled and prevented by

- ✧ Fitting mechanical steam purifier.
- ✧ Avoiding rapid change in steam production rate.
- ✧ Maintaining the water level lower in boilers.
- ✧ Using treated water.

39. How do you prevent the foaming?

Foaming is prevented by

- i. Adding coagulants like sodium aluminate or aluminium hydroxide.
- ii. Adding antifoaming agents like castor oil or synthetic polyamides.

40. What is softening of water?

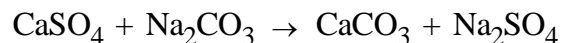
The process of removing hardness producing salts from water is known as softening of water.

41. Distinguish between external treatment and internal treatment of boiler water.

No.	External Treatment	Internal Treatment
1.	External treatment of water is carried out before its entry into the boiler.	Internal treatment of water is carried out within the boiler itself.
2.	It includes soda - lime process, zeolite process and ion exchange process.	It includes colloidal conditioning, carbonate conditioning, phosphate conditioning, calgon conditioning and sodium aluminate treatment.
3.	High pressure boiler requires external treatment.	Low pressure boilers requires internal treatment.
4.	It is the preventive method.	It is the corrective method.

42. What is carbonate conditioning?

In low pressure boilers, scale formation can be avoided by adding Na_2CO_3 to boiler water. The scale forming salt like CaSO_4 is converted into CaCO_3 which can be removed easily by blow-down operation.

**43. What is brackish water?**

The quantity of dissolved solids present in the water is greater than 1000 ppm and less than 35000 ppm, therefore, the water is called as Brackish water.

This water containing dissolved salts with peculiar salty or brackish taste is called as brackish water. It is totally unfit for drinking purpose.

44. What is sedimentation process?

It is a process of removing suspended impurities by allowing the water to stand for 4–6 hours in a large settling tank. All the suspended particles settle down at the bottom due to the force of gravity. They are easily removed by filtration. Sedimentation removes 70 to 75% of the suspended matter in the water.

45. What is filter and filtration?

It is a process of removing bacteria, colour, taste, odour, fine suspended particles, etc., by passing the water through filter beds containing fine sand, coarse sand, fine gravel and coarse gravel. The porous material used is called the filtering medium and the equipment used for filtration is known as filter.

46. Why is hardness expressed in terms of calcium carbonate equivalent?

The concentration of hardness producing salts is expressed in terms of CaCO_3 equivalent. CaCO_3 is used as a standard because of the following factors:

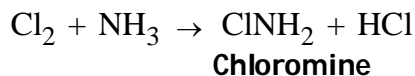
- i. Its molecular weight is 100 and equivalent weight is 50 which are whole number, so the calculations in water analysis can be simplified.
- ii. It is the most insoluble salt, that can be precipitated in water treatment.

47. What is meant by disinfectant?

The complete removal or destruction of harmful bacteria by the addition of certain chemicals is known as sterilisation. The chemical used for this purpose is called disinfectant.

48. What are the advantages of using chloramine as a disinfectant?

When chlorine and ammonia are mixed in the ratio of 2:1, a compound chloramine is formed. Chloramine compounds decompose slowly to give chlorine. This chlorine completely destroy the harmful bacteria for long time. Hence, it is a better disinfectant than chlorine.



50. Give two differences between temporary and permanent hardness.

S.No.	Carbonate hardness (or) Temporary hardness	Non-carbonate hardness (or) Permanent hardness
1.	It is due to bicarbonates of calcium and magnesium.	It is due to chlorides and sulphates of calcium and magnesium.
2.	It can be removed by boiling the water.	It cannot be removed by boiling the water.

ANNA UNIVERSITY QUESTIONS

1. What is the hardness of a solution containing 0.777 grams of NaCl and 0.7 grams of MgCl_2 per 250 ml?
[TAU. Jan.2011]
2. Define desalination. [TAU. Jan.2011]
3. Describe the principle and method involved in the determination of different types and amount of alkalinity of water.
[TAU Jan.2011]
4. What are boiler troubles? How they are caused? Suggest the steps to minimize the boiler troubles. [TAU Jan.2011]
5. What is meant by sterilization of water? What are the chemicals that are normally used for this purpose? Explain break-point chlorination. [TAU Jan.2011]
6. How is internal treatment of boiler water carried out using phosphate, calgon and carbonate? [TAU Jan.2011]
7. Explain the necessity for sterilization of domestic water and discuss the various methods of sterilization. Discuss in detail about the break-point chlorination.
[Chen. AU. June.2009]
8. Explain the process of sterilization and disinfection of water. [TAU Jan.2009]
9. Give an account of internal treatment of boiler water.
[TNVAU Jan.2009]

10. Describe the reverse osmosis method for desalination of brackish water. *[TAU Jan.2009, TAU, May 2009, Chen. AU June 2009]*
 11. Describe briefly the various methods of internal conditioning of boiler feed water.*[Chen. AU June 2009]*
 12. 100 ml of a water sample requires 20 ml of 0.01 M EDTA for the titration with Eriochrome black-T indicator. 100 ml of the same water sample after boiling and filtering required 10 ml of 0.01 M EDTA. Calculate the total, carbonate and non-carbonate hardness of the water sample. *[Chen. AU June 2009]*
 13. How the temporary and permanent hardness of water determined? *[Chen. AU June 2009]*
 14. What is meant by reverse osmosis? Explain the purification of water by reverse osmosis. *[Chen. AU June 2009]*
 15. Describe the boiler corrosion caused by dissolved oxygen in water. *[TAU July.2009]*
 16. Explain zeolite process in detail. *[TAU July.2009]*
 17. Discuss the chlorination, ozonation and UV methods of disinfection. *[TAU.AU May.2009]*
 18. Explain the following boiler troubles and suggesting the remedial methods:
 - (i) Sludge and scale formation and
 - (ii) Caustic embrittlement. *[CBE.AU Jan.2009]*
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19. Discuss the disadvantages of using hard water in boilers. *[Chen. AU Dec.2006; TNV.AU Jan.2009]*
 20. Explain phosphate, calgon and carbonate conditioning in detail. *[TAU. Jan.2009, July 2009]*
 21. Explain the EDTA method of estimation of hardness of water. *[Chen. AU Jan.2009] [TNV. AU.May 2009] [TAU Jan.2009] [CBE AU Jan.2009]*
 22. What are scales and sludges? What are their disadvantages? *[TNV. AU. Jan. 2010]*
 23. What is calgon? Why is calgon conditioning better than phosphate conditioning? *[TNV. AU. Jan. 2010]*
 24. 50 ml of sample hard water requires 35 ml of 0.01 M EDTA in the titration. 50 ml of the same sample of water after boiling required 12 ml of 0.01 M EDTA. Calculate total and temporary hardness of water. *[TNV. AU. Jan. 2010]*
 25. Explain the demineralization of water by ion-exchange process. How are exhausted cation and anion exchange resins regenerated? *[TNV. AU. Jan. 2010]*
 26. What is reverse osmosis? How will you purify the sea water by reverse osmosis? Mention its advantages. *[TNV. AU. Jan. 2010]*
 27. What is desalination? With a neat diagram, describe the 'reverse osmosis' method for the desalination of brackish water. *[Chen. AU. Jan. 2010]*
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28. What are ion exchange resins? How are they useful in removing hardness of water. *[Chen. AU. Jan. 2010]*
29. How is temporary hardness of water estimated by EDTA method? *[Chen. AU. Jan. 2010]*
30. What are the requirements of potable water? How will you purify water for drinking purpose? *[Chen. AU. Jan. 2010]*
31. Explain phosphate and carbonate conditioning in detail. *[TCY. AU. Jan. 2010]*
32. What is meant by hardness? How will you determine hardness of water by EDTA method? Explain? *[TCY. AU. Jan. 2010]*
33. How is the softening of water carried out using the zeolite process? *[TCY. AU. Jan. 2010]*
34. What is desalination? Describe desalination by reverse osmosis method with neat diagram. *[TCY. AU. Jan. 2010]*
35. Define hardness of water. *[Coim. AU. May. 2011]*
36. What is calgon conditioning? *[Coim. AU. May. 2011]*
37. Define break point chlorination. *[Coim. AU. May. 2011]*
38. Discuss the troubles in boiler feed water. *[Coim. AU. May. 2011]*
39. Explain reverse osmosis. *[Coim. AU. May. 2011]*
40. Why is hard water unsuitable for boilers? *[Coim. AU. July. 2010]*
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41. What is the cause for alkalinity of natural water? *[Coim. AU. July. 2010]*
42. What is reverse osmosis? *[Coim. AU. July. 2010]*
43. How is ozone used as an excellent disinfectant? *[Coim. AU. July. 2010]*
44. Describe the ion exchange method for the demineralization of water. *[Coim. AU. July. 2010]*
45. What is internal conditioning? Explain phosphate conditioning and carbonate conditioning in detail? *[Coim. AU. July. 2010]*
46. How is water purified for domestic use? *[Coim. AU. July. 2010]*
47. Distinguish any two differences between hard water and soft water. *[Coim. AU. Feb. 2010]*
48. What is phosphate conditioning? *[Coim. AU. Feb. 2010]*
49. How are exhausted ion-exchange resins regenerated? *[Coim. AU. Feb. 2010]*
50. Describe the procedure to estimate hardness by EDTA method. *[Coim. AU. Feb. 2010]*
51. What is desalination? Explain any one method of desalination. *[Coim. AU. Feb. 2010]*
52. Describe in detail various methods of potable water treatment. *[Coim. AU. Feb. 2010]*
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REVIEW QUESTIONS

1. What is the principle of EDTA method? Describe the estimation of hardness of water by EDTA method.
2. Describe the principle involved in the determination of different types of alkalinity of water.
3. Define the term desalination. Describe the desalination by reverse osmosis method.
4. What are boiler troubles? How are they caused? Suggest steps to minimize the boiler troubles.
5. What is meant by sterilization of water? What are the chemicals normally used for this purpose? Explain the break-point chlorination.
6. Explain the various steps involved in the treatment of water for municipal supply with neat sketch.
7. Describe the de-mineralisation process of water. Explain the reactions involved.

