

Water Treatment

"As fire when thrown into water is cooled down and put out, so also a false accusation when brought against a man of the purest and holiest character boils over and is at once dissipated and vanishes"

1 INTRODUCTION

For the existence of all living beings (humans, animals or plants) water is very crucial. Without water we cannot survive. Almost all human activities—domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources are available for ready use. Hence, it is urgently required to use the available water most carefully and economically. This chapter deals in Hardness and its estimation by EDTA method, alkalinity, water softening by zeolite and ion-exchange processes, domestic water treatment and desalination.

2 SPECIFICATIONS FOR WATER

Different uses of water demand different specifications.

Few examples are discussed below :

(i) *Textile industry* needs frequent dyeing of clothes, and the water used by this industry should be soft and free from organic matter. If hard water is used, uniform dyeing is not possible. Because hard water decreases the solubility of acidic dyes. Basic dyes even precipitate out in such hard water. Organic matter imparts foul smell.

If the water contains Fe, Mn, colour or turbidity, it causes uneven dyeing and leaves stains on fabrics. Hence, water should be free from these impurities.

(ii) *Laundries* require soft water, free from colour, Mn and Fe. Because hardness increases consumption of soaps. Salts of Fe and Mn impart a grey or yellow shade to the fabric.

(iii) *Boilers* require water of zero hardness otherwise efficient heat transfer is prevented by scale formation. Untreated water can also lead to corrosion of boiler material, sometimes even explosion can also occur.

(iv) *Paper industry* requires water free from SiO_2 (as it produces cracks in the paper); Turbidity, (Fe and Mn as they affect the brightness and colour of the paper); alkalinity (consumes alum and increases the cost of production); hardness (as Ca and Mg salts increase the ash content of the paper).

(v) *Beverages* require water which should not be alkaline, as it destroys or modifies the taste as it tends to neutralize the fruit acids.

(vi) *Sugar industry* : If hard water (containing sulphates, nitrates etc.) is used in sugar refining it results in the formation of deliquescent sugar. Moreover, these impurities cause difficulty in the crystallization of sugar.

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(vii) *Cooking* : water used for cooking should be free from dissolved salts producing hardness. Fuel requirement is high if hard water is used. Moreover, more time is required for cooking. Also if hard water is used for making tea or coffee, it imparts unpleasant taste and muddy-looking extract.

(viii) *Dairies and Pharmaceutical industries* require ultra pure water which should be colourless, tasteless, odourless and free from pathogenic organisms.

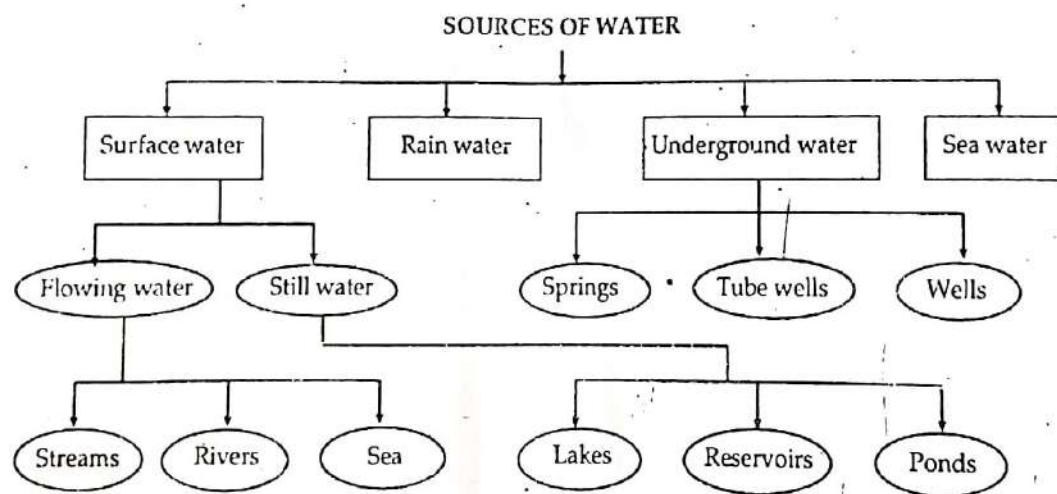
From the specifications of water for different industries, it can be concluded that water needs to be treated to remove all the undesirable impurities. "*Water treatment*" is the process by which all types of undesirable impurities are removed from water and making it fit for domestic or industrial purposes.

An effective water treatment requires a prior knowledge of nature and extent of impurities present in it.

3 SOURCES OF WATER

The main sources of water are :

- (i) *Surface water* : It includes flowing water (streams and rivers) and still water (lakes, ponds and reservoirs).
- (ii) *Underground water* : It includes water from wells and springs.
- (iii) *Rain water* and
- (iv) *Sea water*.



River water contains dissolved minerals like chlorides, sulphates, bicarbonates of sodium, magnesium, calcium and iron. It also contains suspended impurities of sand and rock and organic matter. The composition of river water is not constant. The amount of dissolved impurities in it depends on its contact of the soil. Greater the duration of contact, more soluble are the minerals of soil in it.

Lake water has high quantity of organic matter present in it but lesser amounts of dissolved minerals. Its chemical composition is also constant.

Rain water is obtained as a result of evaporation from the surface water. Probably it is the purest form of natural water. But during its downward journey through the atmosphere it dissolves organic and inorganic suspended particles and considerable amount of industrial gases like (CO_2 , NO_2 , SO_2 etc.). Rain water is expensive to collect and is irregular in supply.

(b) Unlike temporary hardness, permanent hardness is not destroyed on boiling.

(c) It is also known as *non-carbonate* or *non-alkaline hardness*.

(d) The difference between the total hardness and the alkaline hardness gives the *non-alkaline hardness*.

Advantages and disadvantages of hard water are summarized in Table 2 below :

Table 2

S.No.	Hard Water	
	Advantages	Disadvantages
1.	The taste of hard water is usually better than soft water. The label on the bottle of mineral water shows that it contains Mg^{2+} and Ca^{2+} ions and it tastes good.	Hard water produces scum with soap. Thus, the washed clothes look dull. Efficiency of soap decreases in hard water so economy decreases.
2.	The dissolved calcium in hard water can help to produce strong teeth and healthy bones in children.	Boiler feed water should be free from hardness otherwise even explosion can occur.
3.	In old houses, lead piping was used for distribution of water. Hard water coats these with a layer of insoluble $CaCO_3$. This prevents any of the poisonous lead dissolving in the drinking water.	

Degree of Hardness

Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent amount (*equivalents*) of $CaCO_3$.

The reason for choosing $CaCO_3$ as the standard for reporting hardness of water is the ease in calculations as its *molecular weight* is exactly 100. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

$$\left[\frac{\text{Mass of hardness producing substance}}{\text{(in mg/L)}} \right] \times \left[\frac{\text{Chemical equivalent of } CaCO_3}{(= 50)} \right] \times 2$$

$$\text{Equivalents of } CaCO_3 = \frac{[\text{Chemical equivalent of hardness Producing substance}] \times 2}{[\text{Chemical equivalent of hardness Producing substance}] \times 2}$$

$$= \left[\frac{\text{Mass of hardness producing substance}}{\text{in mg/L}} \right] \times \left[\frac{100}{2 \times \text{Chemical equivalents of hardness producing substance}} \right]$$

$$= \left[\frac{\text{Mass of hardness producing substance}}{\text{in mg/L}} \right] \times (\text{Multiplication factor}) \text{ in } \frac{\text{mg}}{\text{L}} \text{ or ppm}$$

Example 1. Given atomic weights of elements as $H = 1$, $C = 12$, $N = 14$, $O = 16$, $Na = 23$, $Mg = 24$, $Al = 27$, $S = 32$, $Cl = 35.5$, $Ca = 40$, $Fe = 56$.

Find multiplication factor for converting into equivalents of $CaCO_3$.

For $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaSO_4$, $CaCl_2$, $MgSO_4$, $MgCl_2$, $CaCO_3$, $MgCO_3$, CO_2 , $Mg(NO_3)_2$, HCO_3^- , OH^- , CO_3^{2-} , $NaAlO_2$, $Al_2(SO_4)_3$, $FeSO_4 \cdot 7 H_2O$, H^+

Hint. Step (i) find molar masses and chemical equivalents of hardness producing substance

Step (ii) molar mass of $CaCO_3$ is 100

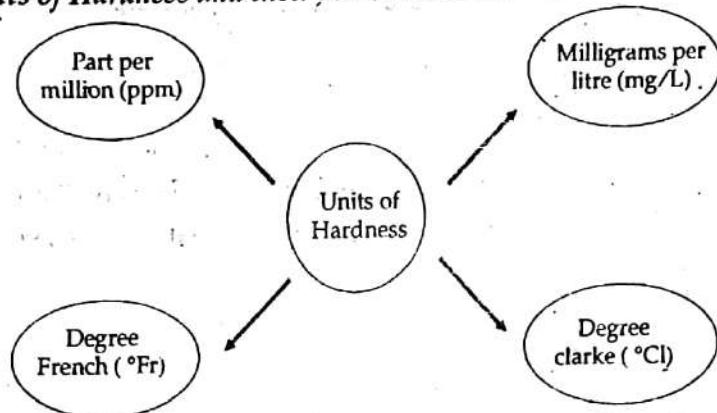
Step (iii) multiplicator factor

$$= \frac{100}{2 \times \text{chemical equivalents of hardness producing substance}}$$

Multiplication factors for different salts are tabulated in Table 3.

Table 3

Dissolved salt/ion	Molar mass	Chemical equivalent	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$MgSO_4$	120	60	100/120
$CaCl_2$	111	55.5	100/111
$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Mg(NO_3)_2$	148	74	100/148
HCO_3^-	61	61	100/122
OH^-	17	17	100/34
CO_3^{2-}	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al_2(SO_4)_3$	342	57	100/114
$FeSO_4 \cdot 7 H_2O$	278	139	100/278
H^+	1	1	100/2

Units of Hardness and their inter-relations :

(i) *Parts per million (ppm)* : It is defined as the number of parts by weight of calcium carbonate present per million (10^6) parts by weight of water,
i.e., 1 ppm = 1 part of CaCO_3 equivalents hardness in (10^6) parts of water.

(ii) *Milligrams per litre (mg/L)* : It is defined as the number of milligrams of CaCO_3 present in one litre of water,
i.e., 1 mg/L = 1 mg of CaCO_3 eq-hardness per L of water. It can be easily proved that 1 mg/L = 1 ppm for water

$$\text{As for water, } 1 \text{ L} = 1 \text{ kg} = 10^6 \text{ mg}$$

$$\therefore 1 \text{ mg of } \text{CaCO}_3 \text{ eq-hardness per L of water}$$

$$= 1 \text{ mg of } \text{CaCO}_3 \text{ eq-hardness per } 10^6 \text{ mg of water}$$

$$= 1 \text{ part of } \text{CaCO}_3 \text{ per } 10^6 \text{ parts of water} = 1 \text{ ppm}$$

$$\text{Hence, } 1 \text{ mg/L} = 1 \text{ ppm}$$

(iii) *Degree clarke (°Cl)* : It is defined as the parts of CaCO_3 equivalent hardness per 70,000 parts of water.

Or It is number of grains of CaCO_3 equivalent hardness per gallon of water.

i.e., 1 °Cl = 1 part of CaCO_3 per 70,000 parts of water.

(iv) *Degree French (°Fr)* : It is defined as the parts of CaCO_3 equivalent hardness per 10^5 parts of water.

i.e., 1 °Fr = 1 part of CaCO_3 equivalent hardness per 10^5 parts of water.

Relationships between various units of hardness :

As 1 ppm = 1 part per 10^6 parts of water

$$1 \text{ } ^\circ\text{Fr} = 1 \text{ part per } 10^5 \text{ part of water}$$

and $1 \text{ } ^\circ\text{Cl} = 1 \text{ part per } 70,000 \text{ parts of water}$

$$\therefore 10^6 \text{ ppm} = 10^5 \text{ } ^\circ\text{Fr} = 70,000 \text{ } ^\circ\text{Cl}$$

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

$\downarrow \rightarrow$	ppm	mg/l	$^\circ\text{Fr}$	$^\circ\text{Cl}$
ppm	1	1	0.1	0.07
mg/l	1	1	0.1	0.07
$^\circ\text{Fr}$	10	10	1	0.7
$^\circ\text{Cl}$	0.07	0.07	0.7	1

5.1 Solved Examples based on Determination of Hardness of Water

Example 1. A water sample contains 408 mg of CaSO_4 per litre. Calculate the hardness in terms of CaCO_3 equivalents.

Solution. Hardness = (mass of CaSO_4 in mg/L) × multiplication factor

$$\begin{aligned} &= (\text{mass of } \text{CaSO}_4 \text{ in mg/L}) \times \left[\frac{\text{chemical equivalents of } \text{CaCO}_3}{\text{chemical equivalents of } \text{CaSO}_4} \right] \\ &= (400 \text{ mg/L}) \times \left[\frac{50}{68} \right] \\ &= 300 \text{ mg/L} = 300 \text{ ppm} \end{aligned}$$

Example 2. How many grams of MgCO_3 dissolved per litre gives 84 ppm of hardness?

Solution. Hardness

$$= (\text{mass of } \text{MgCO}_3 \text{ in mg/L}) \times \left[\frac{\text{chemical equivalent of } \text{CaCO}_3}{\text{chemical equivalent of } \text{MgCO}_3} \right]$$

$$\begin{aligned} \text{Hence, mass of } \text{MgCO}_3 &= \text{Hardness} \times \frac{\text{chemical equivalents of } \text{MgCO}_3}{\text{chemical equivalents of } \text{CaCO}_3} \\ &= (84 \text{ ppm}) \times \left(\frac{42}{50} \right) = 70.56 \text{ ppm} = 70.56 \text{ mg/L} \end{aligned}$$

Thus, 70.56×10^{-3} gms of MgCO_3 dissolved per litre gives 84 ppm of hardness.

Example 3. A sample of water on analysis was found to contain the following impurities:

Impurity	$\text{Ca}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2$	CaSO_4	MgSO_4
Quantity (mg/L)	4	6	8	10
Mol. Wt.	162	146	136	120

Calculate the temporary, permanent and total hardness of water in ppm, $^{\circ}\text{Fr}$ and $^{\circ}\text{Cl}$.

Solution. Step (i) Conversion into CaCO_3 equivalents :

Constituent	Amount mg/L [A]	Multiplication factor [M]	CaCO_3 equivalent = [A] × [M]
$\text{Ca}(\text{HCO}_3)_2$	4	100/162	$4 \times \frac{100}{162} = 2.47 \text{ mg/L}$
$\text{Mg}(\text{HCO}_3)_2$	6	100/146	$6 \times \frac{100}{146} = 4.11 \text{ mg/L}$
CaSO_4	8	100/136	$8 \times \frac{100}{136} = 5.88 \text{ mg/L}$
MgSO_4	10	100/120	$10 \times \frac{100}{120} = 8.33 \text{ mg/L}$

Step (ii) Determination of Temporary Hardness :

As Temporary hardness is due to bicarbonates of Calcium and Magnesium

$$\therefore \text{Temporary hardness} = 2.47 + 4.11 = 6.58 \text{ mg/L}$$

$$\begin{aligned} \text{As } 1 \text{ mg/L} &= 1 \text{ ppm} = 0.1 \text{ }^{\circ}\text{Fr} = 0.07 \text{ }^{\circ}\text{Cl} \\ \text{Hence, Temporary hardness} &= 6.58 \text{ mg/L} = 6.58 \text{ ppm} \\ &= 6.58 \times 0.1 = 0.658 \text{ }^{\circ}\text{Fr} \\ &= 6.58 \times 0.07 = 0.46 \text{ }^{\circ}\text{Cl}. \end{aligned}$$

Step (iii) Determination of Permanent Hardness :

As permanent hardness in this case is due to CaSO_4 and MgSO_4

$$\begin{aligned} \therefore \text{Permanent hardness} &= 5.88 + 8.33 = 14.21 \text{ mg/L} \\ &= 14.21 \text{ ppm} \\ &= 14.21 \times 0.1 = 1.421 \text{ }^{\circ}\text{Fr} \\ &= 14.21 \times 0.07 = 0.995 \text{ }^{\circ}\text{Cl} \end{aligned}$$

Example 4. 200 mL of water sample has a hardness equivalent to 25 mL of 0.08 N MgSO_4 . Find the hardness in ${}^{\circ}\text{Fr}$.

Solution. As Normality is number of gm. equivalents per L of solution.

Hence, number of gm. equivalents of MgSO_4

$$= \text{volume of } \text{MgSO}_4 \times \text{its normality}$$

$$= \frac{25}{1000} \times 0.08 = 2 \times 10^{-3}$$

$$\text{As Number of gm. equivalents} = \frac{\text{Weight in gms.}}{\text{Eq. wt.}}$$

Thus weight in gms. of MgSO_4 present in 200 mL of water sample

$$= (2 \times 10^{-3}) \times \text{Eq. wt. of } \text{MgSO}_4$$

So, wt. in gms. of MgSO_4 per L of water

$$= (2 \times 10^{-3}) \times \text{Eq. wt. of } \text{MgSO}_4 \times \frac{1000}{200} = 10^{-2} \times \text{Eq. wt.}$$

$$\text{Now Hardness} = (\text{Wt. in gms. of } \text{MgSO}_4 \text{ per L of water}) \times \frac{50}{\text{Eq. wt. of } \text{MgSO}_4}$$

$$= (10^{-2} \times \text{Eq. wt. of } \text{MgSO}_4) \times \frac{50}{\text{Eq. wt. of } \text{MgSO}_4}$$

$$= 50 \times 10^{-2} \text{ gm/L}$$

$$= 500 \text{ mg/L}$$

$$= 500 \text{ ppm}$$

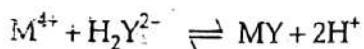
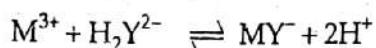
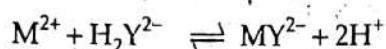
$$= 500 \times 0.1 = 50 {}^{\circ}\text{Fr} \quad (\text{Since } 1 \text{ ppm} = 0.1 {}^{\circ}\text{Fr})$$

6 ESTIMATION OF WATER HARDNESS BY EDTA METHOD

Water hardness is generally caused by the presence of Ca^{2+} and Mg^{2+} ions present in water. Some other polyvalent ions like strontium, iron, aluminium, zinc and manganese etc., also contribute to hardness. But because of their very low concentration in natural water, hardness is generally measured as concentration of only calcium and magnesium ions.

The analysis is done by complexometric titration using standard EDTA as titrant and EBT as an indicator.

Ethylene diaminetetra acetic acid (EDTA) is tetraprotic acid. (Let it is represented by the symbol $H_4 Y$). Because of its limited solubility, it is not used directly. It is usually employed as the soluble disodium salt dihydrate $Na_2 H_2 Y \cdot 2H_2 O$ because it can be obtained in high state of purity (Molecular weight = 372.24) and is a primary standard. The solutions of EDTA are very valuable titrants because the reagent combines with metal ions in a 1 : 1 ratio. Irrespective of the charge on the cation, the resultant complexes have similar structures but differ from one another in the charge they carry. The reactions of cations with EDTA may be written as :



The equilibrium is markedly affected by the pH of the solution, viz, the complexes of EDTA with divalent metals are stable in basic or slightly acidic solutions.

The structures of the anion $H_2 Y^{2-}$ and the complex with divalent metal ion, M^{2+} , are shown in Fig. 1.

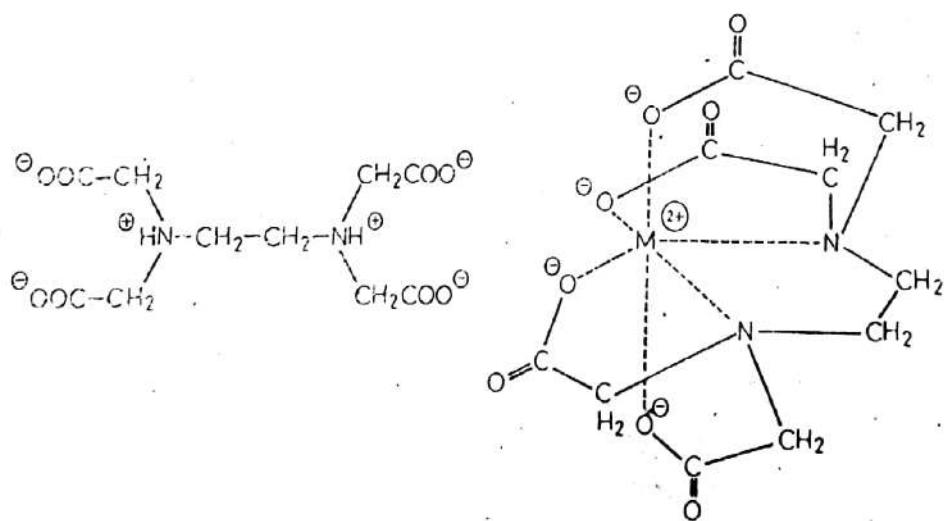


Fig. 1. Structures of ethylene diaminetetraacetic acid (EDTA) and metal-EDTA chelates :
 (A) structure of the dianion of EDTA, $H_2 Y^{2-}$; (B) structure of an M^{2+} -EDTA chelate, MY^{2-} .

We can think of the EDTA anion as surrounding a metal ion like the large claw of a crab grasping its prey. The technical term for such a complex is *chelate*, which comes from the Greek word meaning a pincerlike claw.

The chelates formed by EDTA are sufficiently stable to form the basis for a titrimetric method. The great stability undoubtedly results from the several complexing sites within the molecule that give rise to a cage like structure in which the cation is effectively surrounded and isolated from solvent molecules.

Eriochrome Black T (EBT) : It is a typical metal-ion indicator, chemically it is sodium 1 - (1-hydroxy-2-naphthylazo) -6-nitro-2-naphthol-4-sulphonate. Its structure is shown in Fig. 2.

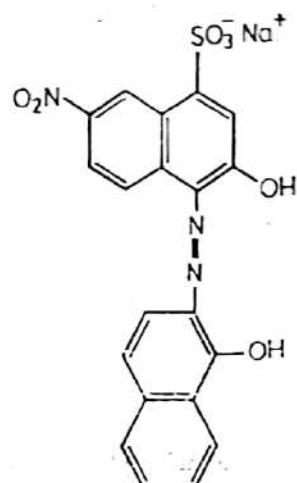
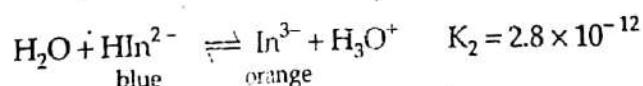
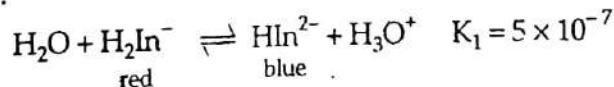
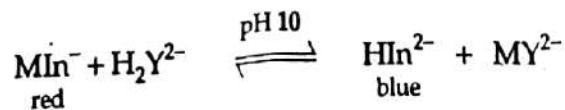


Fig. 2. Eriochrome Black T.

It contains a sulfonic acid group, which is completely ionized in water and two phenolic groups that only partially ionize. Its behaviour as a weak acid is described by the equations :



The acids and their conjugate bases have different colours. EBT also forms complexes with metal ions which are generally wine-red, as is H_2In^- . Thus, EBT behaves as an acid/base indicator as well as metal-ion indicator. For metal ion detection, it is necessary to adjust the pH on the basic side so that the blue form of the species, HIn^{2-} , predominates in the absence of a metal ion. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is wine-red. With the first slight excess of EDTA, the solution turns blue as a consequence of the reaction (buffered at pH 10) :



The EDTA displaces the indicator from the metal-indicator complex because the equilibrium-constant for the formation of the EDTA-metal ion complex is much larger than that for the indicator-metal ion complex, this produces a reasonably sharp colour change at the equivalence point.

A limitation of Eriochrome Black T is that its solutions are not stable. They decompose slowly on standing; refrigeration slows this process. Another indicator, calmagite (structure shown in Fig. 3) does not suffer from this disadvantage. And for all practical purposes, its behaviour is identical to Eriochrome Black T.

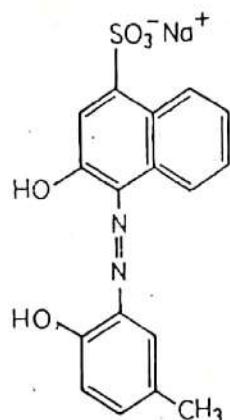
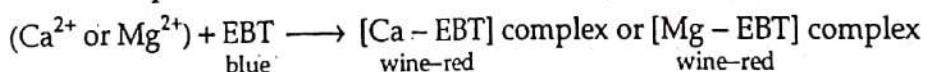


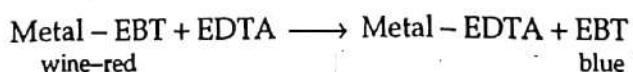
Fig. 3. Calmagite.

Principle of EDTA titrations : The quick, complete and 1 : 1 interaction of metal ions with EDTA leading to the formation of stable complex is the basis of complexometric titrations.

Theory : The hard water is buffered to a pH value of ~10 using $\text{NH}_4\text{OH} - \text{NH}_4\text{Cl}$ buffer and a few drops of EBT indicator solution are added. EBT forms a weak complex with metal ions, which has a wine-red colour.



In the course of the titration of water sample against EDTA, EDTA first combines with free Ca^{2+} or Mg^{2+} ions to give very stable and colourless metal-EDTA complex. After all the free metal ions are consumed, the next drop of added EDTA solution displaces the indicator, EBT, from Metal-EBT complex.



Thus, at the equivalence point, there is change in colour from wine-red (due to Metal-EBT) to blue (due to free EBT).

The *total hardness* is thus determined. For the determination of *permanent hardness*, temporary hardness is first removed by boiling. After the removal of precipitate by filtration, the permanent hardness in the filtrate is determined by titration with EDTA as before. *Temporary hardness* is then determined by subtracting permanent hardness from total hardness.

Procedure :

(i) *Standardization of EDTA solution.* Fill up the burette with EDTA solution after washing and rinsing. Pipette out, 50 mL of standard hard water prepared in such a way that 1 mL of it contains 1 mg of CaCO_3 into a 250 mL conical flask. Add

10 mL of buffer solution and 2-3 drops of indicator (EBT). Titrate this solution against EDTA until the wine-red colour (due to M-EBT complex) changes to blue (due to EBT). Let the volume of EDTA consumed by V_1 mL.

(ii) *Determination of total hardness of water.* As per the same procedure given above, titrate 50 mL of unknown water sample against EDTA. Let the volume of EDTA consumed this time be V_2 mL.

(iii) *Determination of permanent hardness of water.* Take 250 mL of the water sample in a 500 mL beaker and boil it till the volume is reduced to about 50 mL. This step causes all the bicarbonates to decompose respectively into insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$. Filter and wash the precipitate with distilled water and quantitatively collect the filtrate and washings in a 250 mL conical flask and make up the volume to 250 mL with distilled water. Titrate 50 mL of this water sample against EDTA as in step (i). Let the volume used be V_3 mL.

Calculations :

Step (i) Standardization of EDTA solution :

V_1 mL of EDTA = 50 mL of standard hard water.

Since each mL of standard hard water contains 1 mg of CaCO_3 ,

hence, V_1 mL of EDTA = 50 mg of CaCO_3

$$\Rightarrow 1 \text{ mL of EDTA} = \frac{50}{V_1} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness}$$

Step (ii) Determination of total hardness of water :

50 mL of unknown hard water sample = V_2 mL of EDTA

$$= V_2 \times \frac{50}{V_1} \text{ mg of } \text{CaCO}_3 \text{ eq.}$$

\therefore 1,000 mL (or 1 L) of unknown hard water sample

$$= V_2 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000$$

$$= 1000 \frac{V_2}{V_1} \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness}$$

Hence, total hardness of water = $1000 \frac{V_2}{V_1}$ mg/L

or,

$\text{Total hardness of water} = 1000 \frac{V_2}{V_1} \text{ ppm}$

Step (iii) Determination of Permanent hardness of water :

As, 50 mL of boiled water = V_3 mL of EDTA

$$= V_3 \times \frac{50}{V_1} \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1,000 \text{ mL (or 1 L) of boiled water} = V_3 \times \frac{50}{V_1} \times \frac{1}{50} \times 1000 = 1000 \frac{V_3}{V_1} \text{ mg}$$

Hence, permanent hardness of water = $1000 \frac{V_3}{V_1}$ mg/L

or, Permanent hardness of water = $1000 \frac{V_3}{V_1}$ ppm

Step (iv) Determination of Temporary hardness :

Since Temporary hardness = Total hardness - Permanent hardness

$$= 1000 \frac{V_2}{V_1} - 1000 \frac{V_3}{V_1}$$

or, Temporary hardness = $\frac{1000 (V_2 - V_3)}{V_1}$ ppm

Alternative method

As 1.0 mg of pure CaCO_3 was dissolved in 1 mL of distilled water, so the molarity of standard hard water can be easily calculated as given below :

$$S_{\text{std-water}} = \frac{1 \text{ mg } \text{CaCO}_3 / 100 (\text{gm/mol})}{1 \text{ mL}} = 0.01 \text{ M}$$

(since molecular weight of CaCO_3 = 100 gms/mol)

Step (i) Standardization of EDTA solution

$$\begin{aligned} V_{\text{std-water}} \times S_{\text{std-water}} &= V_{\text{EDTA}} \times S_{\text{EDTA}} \\ \Rightarrow 50 \text{ mL} \times 0.01 \text{ M} &= V_1 \text{ mL} \times S_{\text{EDTA}} \\ \Rightarrow S_{\text{EDTA}} &= \frac{0.5}{V_1} \text{ M} \end{aligned}$$

Step (ii) Determination of total hardness of water

$$\begin{aligned} V_{\text{Unknown H}_2\text{O sample}} \times S_{\text{Unknown H}_2\text{O sample}} &= V_{\text{EDTA}} \times S_{\text{EDTA}} \\ \Rightarrow 50 \text{ mL} \times S_{\text{Unknown H}_2\text{O sample}} &= V_2 \text{ mL} \times \frac{0.5}{V_1} \text{ M} \\ \Rightarrow S_{\text{Unknown H}_2\text{O sample}} &= V_2 \times \frac{0.5}{V_1} \times \frac{1}{50} = 0.01 \frac{V_2}{V_1} \text{ M} \end{aligned}$$

We know that (i) molarity \times molecular weight = weight in grams per litre
and (ii) ppm = mg/L

$$\text{Hence } S_{\text{Unknown H}_2\text{O sample}} = 0.01 \times \frac{V_2}{V_1} \times 100 \text{ g/L} = \frac{V_2}{V_1} \text{ g/L}$$

$$= \frac{V_2}{V_1} \times 1000 \text{ mg/L} = 1000 \frac{V_2}{V_1} \text{ ppm.}$$

Thus, total hardness of water = $1000 \frac{V_2}{V_1}$ ppm.

Step (iii) Determination of permanent hardness of water

Given 50 mL of boiled water sample consumes V_3 mL of EDTA so calculation steps similar to as described in step (ii), will give

$$\text{Permanent hardness of water} = 1000 \frac{V_3}{V_1} \text{ ppm}$$

Step (iv) Determination of temporary hardness

As temporary hardness = Total hardness - Permanent hardness

$$= 1000 \frac{V_2}{V_1} - 1000 \frac{V_3}{V_1}$$

$$\Rightarrow \text{Temporary hardness} = 1000 \frac{(V_2 - V_3)}{V_1} \text{ ppm.}$$

Advantages of EDTA method : Advantages of EDTA method for hardness determination are its greater accuracy, convenience and more rapid procedure.

Significance of hardness determination : The determination of hardness is a useful analytical test that provides a measure of the quality of water for household and industrial uses. The test is particularly important to industry because when hard water is heated, it precipitates calcium carbonate, which then clogs boilers and pipes.

6.1 Solved Examples based on Determination of Hardness by EDTA Method

Example 1. 0.28 g of CaCO_3 was dissolved in HCl and the solution was made to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of the hard water sample required 35 ml of the same EDTA solution on titration. After boiling 100 ml of this water, Cooling, Filtering and then Titration required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water.

Solution. Step (i) Standardization of EDTA solution :

Given, 1 L of standard hard water contains 0.28 gm CaCO_3 . Hence, each mL of standard hard water contains 0.28 mg CaCO_3

$$\begin{aligned} \text{As, } 28 \text{ mL of EDTA} &= 100 \text{ mL of standard hard water} \\ &= 100 \times 0.28 = 28 \text{ mg } \text{CaCO}_3 \end{aligned}$$

$$\therefore 1 \text{ mL of EDTA} = \frac{28}{28} = 1 \text{ mg } \text{CaCO}_3 \quad \dots(i)$$

Step (ii) Determination of total hardness of water :

Given, 100 mL of unknown hard water sample = 35 mL of EDTA

$$\begin{aligned} &= 35 \times 1 = 35 \text{ mg } \text{CaCO}_3 \\ &\quad \{\text{By using (i)}\} \end{aligned}$$

\therefore 1,000 mL (or 1L) of unknown hard water sample

$$= \frac{35}{100} \times 1000 = 350 \text{ mg } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, Total hardness = 350 ppm

$\dots(ii)$

Step (i) Determination of permanent hardness

$$100 \text{ mL of boiled water} = 10 \text{ mL of EDTA}$$

$$= 10 \times 1 = 10 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1,000 \text{ mL (or 1 L) of boiled water}$$

$$= \frac{10}{100} \times 1000 = 100 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, Permanent hardness of water = 100 ppm

... (iii)

Step (iv) Determination of Temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 350 - 100$$

$$\Rightarrow \text{Temporary hardness} = 250 \text{ ppm}$$

... (iv)

Example 2. A standard hard water contains 15 g of CaCO_3 per liter. 20 ml of this required 25 ml of EDTA solution, 100 ml of sample water required 18 ml of EDTA solution. The sample after boiling required 12 ml EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm.

Solution. Step (i) Standardization of EDTA solution :

Given 1 L of standard hard water contains 15 gm CaCO_3

$\therefore 1 \text{ mL of standard hard water contains } 15 \text{ mg } \text{CaCO}_3$

Now 25 mL of EDTA = 20 mL of standard hard water

$$= 20 \times 15 = 300 \text{ mg of } \text{CaCO}_3$$

$$\Rightarrow 1 \text{ mL of EDTA} = \frac{300}{25}$$

$$= 12 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness}$$

Step (ii) Determination of total hardness of water :

$$100 \text{ mL of sample water} = 18 \text{ mL of EDTA}$$

$$= 18 \times 12 = 216 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1 \text{ L of sample water} = 2160 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, total hardness of water = 2160 ppm

... (ii)

Step (iii) Determination of Permanent hardness

$$100 \text{ mL of boiled water} = 12 \text{ mL of EDTA}$$

$$= 12 \times 12 = 144 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\therefore 1 \text{ L of boiled water} = 1440 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

Hence, permanent hardness of water = 1440 ppm

... (iii)

Step (iv) Determination of Temporary hardness

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= 2160 - 1440 = 720 \text{ ppm}$$

$$\therefore \text{Temporary hardness} = 720 \text{ ppm}$$

... (iv)

Example 3. 50 ml of standard hard water containing 1 mg of pure CaCO_3 per ml consumed 25 ml of EDTA. 50 ml of a water sample consumed 25 ml of the same EDTA solution. Using eriochrome T as indicator, calculate the total hardness of water sample in ppm.

Solution. Step (i) Standardization of EDTA solution

Given 1 mL of standard hard water contains 1 mg CaCO_3

$$\begin{aligned} \text{Now } 25 \text{ mL of EDTA} &= 50 \text{ mL of standard hard water} \\ &= 50 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness} \end{aligned}$$

$$\text{Hence, } 1 \text{ mL of EDTA} = \frac{50}{25} = 2 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness} \quad \dots(i)$$

Step (ii) Determination of total hardness of water sample

$$\begin{aligned} 50 \text{ mL of sample water} &= 25 \text{ mL of EDTA} \\ &= 25 \times 2 = 50 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness} \end{aligned}$$

$$\text{Hence, } 1 \text{ L of sample water} = \frac{50}{50} \times 1000 = 1000 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\text{Thus, total hardness of water} = 1000 \text{ ppm} \quad \dots(ii)$$

Example 4. Calculate the hardness of a water sample, whose 10 ml required 10 ml of EDTA. 20 ml of CaCl_2 solution, whose strength is equivalent 1.5 g of CaCO_3 per litre, required 30 ml of EDTA solution.

Solution. Step (i) Standardization of EDTA solution

Given 1 L of standard hard water contains = 1.5 gm CaCO_3

\therefore 1 mL of standard hard water contains = 1.5 mg CaCO_3

$$\begin{aligned} \text{Now, } 30 \text{ mL of EDTA} &= 20 \text{ mL of standard hard water (i.e., } \text{CaCl}_2 \text{ solution)} \\ &= 20 \times 1.5 = 30 \text{ mg } \text{CaCO}_3 \end{aligned}$$

$$\text{So, } 1 \text{ mL of EDTA} = \frac{30}{30} = 1 \text{ mg } \text{CaCO}_3 \text{ eq. hardness} \quad \dots(i)$$

Step (ii) Determination of Total hardness of water :

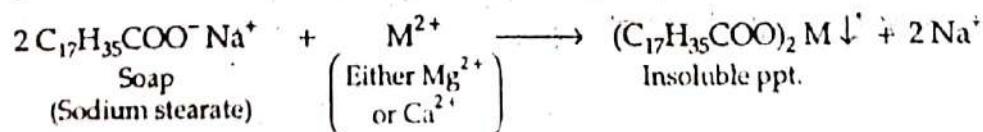
$$\begin{aligned} 10 \text{ mL of sample water} &= 10 \text{ mL of EDTA} \\ &= 10 \times 1 = 10 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness} \end{aligned}$$

$$\therefore 1 \text{ L of sample water} = \frac{10}{10} \times 1000 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness}$$

$$\text{Hence, the total hardness of water sample} = 1000 \text{ ppm}$$

6.2 Estimation of Water Hardness by Clark's Method or Soap Titration Method

The Clark's method is based on the principle that when soap solution is added to hard water, the hardness causing ions (i.e., Ca^{2+} , Mg^{2+} , and other heavy metal ions) are the first to react. As a result, a precipitate of insoluble calcium and magnesium soap is obtained. The process continues as long as there is hardness in the sample of water being titrated. When all hardness causing ions have been precipitated, further addition of soap solution gives lather.



We know that addition of soap solution to water decreases its surface tension. Even in distilled water, formation of lather does not take place till a lower critical value of surface tension is reached. The volume of soap solution required to form lather with distilled water (of zero hardness) is known as *lather factor*.

This volume (corresponding to lather factor) should be subtracted from all titre values. Both total and permanent hardness in a given water sample can be estimated by this method. From these two results, we can also calculate temporary hardness.

Procedure :

Step (i) Standardization of Soap solution :

Burette is first rinsed and filled with soap solution. In a narrow mouth 250 mL glass-stoppered bottle, 50 mL of standard hard water is taken. (The hardness of standard hard water is 1 gm/L). Soap solution is added 0.2 mL at a time to this standard hard water solution. After each addition, the contents of stoppered bottle are vigorously shaken until lather formation starts. Then the addition of soap solution is made at the rate of 0.1 mL at a time till a lather is obtained which persists for 2 minutes. Let the volume of soap solution used be V_1 mL.

Step (ii) Determination of total hardness of water :

The above procedure is repeated by taking 50 mL of given water sample (to be analysed). Suppose the titre value of soap solution be V_2 mL.

Step (iii) Determination of permanent hardness of water :

250 mL of the water sample is taken in 500 mL beaker. It is then boiled till the volume reduces to 50 mL. (Boiling causes all the bicarbonates to decompose respectively into insoluble CaCO_3 and Mg(OH)_2). The precipitate is filtered and washed with distilled water. Simultaneously, the filtrate and washings are quantitatively collected in a 250 mL conical flask. The volume is then made 250 mL by adding distilled water. 50 mL of this water sample is then taken and procedure of step (i) is repeated. Suppose the titre value of soap solution be V_3 mL.

Step (iv) Determination of Lather factor :

50 mL of distilled water of zero hardness is titrated with soap solution. The titration is continued till lather is obtained which lasts for 2 minutes. Let the volume used be V_4 mL. This volume must be subtracted from all the titre values.

Calculations :

Step (i) Standardization of Soap solution :

50 mL of standard hard water $\equiv (V_1 - V_4)$ mL of soap solution.

As standard hard water has 1 gm/L (or 1 mg/mL) CaCO_3 so in 50 mL standard hard water, there are $50 \times 1 = 50$ mg of CaCO_3 .

Thus $(V_1 - V_4)$ mL of soap solution $\equiv 50$ mg of CaCO_3 eq.

$$\Rightarrow 1 \text{ mL of soap solution} = \frac{50}{(V_1 - V_4)} \text{ mg of } \text{CaCO}_3 \text{ eq.} \quad \dots(i)$$

Step (ii) Determination of total hardness of water :

As 50 mL of hard water $\equiv (V_2 - V_4)$ mL of soap solution

$$\equiv (V_2 - V_4) \times \frac{50}{(V_1 - V_4)} \text{ mg of CaCO}_3 \text{ eq.}$$

\therefore 1000 mL (or 1 L) of hard water

$$= (V_2 - V_4) \times \frac{50}{(V_1 - V_4)} \times \frac{1000}{50} \text{ mg of CaCO}_3 \text{ eq.}$$

Thus, total hardness of water = $1000 \frac{(V_2 - V_4)}{(V_1 - V_4)}$ mg/L

$$\Rightarrow \boxed{\text{Total hardness} = 1000 \frac{(V_2 - V_4)}{(V_1 - V_4)} \text{ ppm}} \quad \dots(ii)$$

Step (iii) Determination of permanent hardness :

As 50 mL of boiled water $\equiv (V_3 - V_4)$ mL of soap solution

$$\equiv (V_3 - V_4) \times \frac{50}{(V_1 - V_4)} \text{ mg of CaCO}_3 \text{ eq.}$$

\therefore 1000 mL (or 1L) of boiled water

$$= (V_3 - V_4) \times \frac{50}{(V_1 - V_4)} \times \frac{1000}{50} \text{ mg of CaCO}_3 \text{ eq.}$$

Thus, permanent hardness = $1000 \frac{(V_3 - V_4)}{(V_1 - V_4)}$ mg/L of CaCO₃ eq.

$$\boxed{\text{Permanent hardness} = 1000 \frac{(V_3 - V_4)}{(V_1 - V_4)} \text{ ppm}} \quad \dots(iii)$$

Step (iv) Determination of temporary hardness :

As temporary hardness = Total hardness – permanent hardness

$$= \left[1000 \frac{(V_2 - V_4)}{(V_1 - V_4)} - 1000 \frac{(V_3 - V_4)}{(V_1 - V_4)} \right] \text{ ppm}$$

$$= \left[\frac{1000}{(V_1 - V_4)} [(V_2 - V_4) - (V_3 - V_4)] \right] \text{ ppm} = 1000 \frac{(V_2 - V_3)}{(V_1 - V_4)} \text{ ppm}$$

$$\Rightarrow \boxed{\text{Temporary hardness} = 1000 \frac{(V_2 - V_3)}{(V_1 - V_4)} \text{ ppm}} \quad \dots(iv)$$

Example 1. Estimate different hardnesses present in hard water sample from the following data obtained in soap titration method, when 100 mL of water is titrated with soap solution :

(i) Standard hard water {400 mg/L of CaCO₃} = 36.6 mL,

- (ii) Total hardness = 18.6 mL soap solution,
- (iii) Permanent hardness = 6.2 mL soap solution,
- (iv) Lather factor = 0.6 mL soap solution.

Solution. Step (i) Standardization of soap solution:

$$\text{Given } 1 \text{ L of standard hard water (SHW)} = 400 \text{ mg CaCO}_3 \text{ eq.}$$

$$\therefore 100 \text{ mL of SHW} = 40 \text{ mg CaCO}_3 \text{ eq.}$$

Now volume of soap solution required to precipitate 100 mL of hard water
 $= 36.6 - 0.6 = 36.0 \text{ mL}$

$$\therefore 30 \text{ mL of soap solution} = 40 \text{ mg CaCO}_3 \text{ eq.}$$

$$\Rightarrow 1 \text{ mL of soap solution} = \frac{40}{36} \text{ mg CaCO}_3 \text{ eq.} \quad \dots(i)$$

Step (ii) Determination of total hardness of water:

$$100 \text{ mL of hard water} = 18.6 - 0.6 = 18 \text{ mL soap solution}$$

$$= 18 \times \frac{40}{36} = 20 \text{ mg CaCO}_3 \text{ eq.}$$

$$\therefore 1 \text{ L of hard water} = 200 \text{ mg CaCO}_3 \text{ eq.} \quad \dots(ii)$$

$$\text{Thus, total hardness} = 200 \text{ ppm}$$

Step (iii) Determination of permanent hardness:

$$100 \text{ mL of permanent hard water} = 6.2 - 0.6 = 5.6 \text{ mL soap solution}$$

$$= 5.6 \times \frac{40}{36} = 6.22 \text{ mg CaCO}_3 \text{ eq.}$$

$$\therefore 1 \text{ L of permanent hard water} = 62.2 \text{ mg CaCO}_3 \text{ eq.}$$

$$\text{Thus, permanent hardness} = 62.2 \text{ ppm} \quad \dots(iii)$$

Step (iv) Determination of temporary hardness:

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

$$\text{Temporary hardness} = (200 - 62.2) \text{ ppm} = 137.8 \text{ ppm} \quad \dots(iv)$$

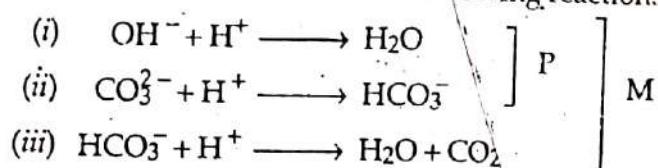
7 ALKALINITY

Theory. By alkalinity of water we mean the total content of those substances in it which causes an increased hydroxide ion concentration $[\text{OH}^-]$ upon dissociation or due to hydrolysis. The alkalinity of water is attributed to the presence of the:

- (i) caustic alkalinity (due to OH^- to CO_3^{2-} ions), and
- (ii) temporary hardness (due to HCO_3^- ions).

These can be estimated separately by titration against standard acid, using phenolphthalein and methyl orange as indicators.

The determination is based on the following reactions :



The titration of the water sample against a standard acid upto phenolphthalein end-point (P) marks the completion of reactions (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one-half of the normal carbonate present.

On the other hand, titration of the water sample against a standard acid to methyl orange end-point (M) marks the completion of reactions (i), (ii) and (iii). Hence the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonate and carbonate ions).

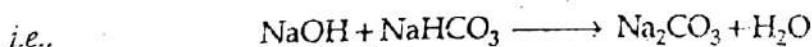
$$\text{Thus, } P = \text{OH}^- \text{ and } \frac{1}{2} \text{CO}_3^{2-}$$

$$\text{and } M = \text{OH}^-, \text{CO}_3^{2-}, \text{HCO}_3^-$$

With respect to the constituents causing alkalinity in water, the following situations may arise :

- (i) OH^- only
- or (ii) CO_3^{2-} only
- or (iii) HCO_3^- only
- or (iv) OH^- and CO_3^{2-} together
- or (v) CO_3^{2-} and HCO_3^- together.

The possibility of OH^- and HCO_3^- together is ruled out, because of the fact that they combine instantaneously to form CO_3^{2-} ions.



Thus, OH^- and HCO_3^- ions cannot exist together in water.

On the basis of same reasoning, all the three (OH^- , CO_3^{2-} and HCO_3^-) cannot exist together.

Procedure :

Pipette out 100 mL of the water sample in a clean titration flask. Add to it 2 to 3 drops of a phenolphthalein indicator. Run in N/50 H_2SO_4 (from a burette), till the pink colour is just discharged. Let the volume of acid used to phenolphthalein end point = V_1 mL. Then to the same solution, add 2 or 3 drops of methyl orange. Continue the titration, till the pink colour reappears. Let extra volume of acid used to methyl orange end point = V_2 mL.

Calculations :

100 mL of water upto phenolphthalein end-point

$$\equiv V_1 \text{ mL of N/50 H}_2\text{SO}_4$$

$$\therefore 100 \text{ mL} \times N_p = V_1 \text{ mL} \times (N/50)$$

$$\text{or normality, } N_p = \frac{V_1 \text{ mL}}{100 \text{ mL}} \times \frac{N}{50} = \frac{V_1}{5000} N$$

Note : Normality (N) = $\frac{\text{gm. Eq.}}{\text{L}} = \frac{x}{\text{Eq. wt.}}$; where x = weight in gms.

$$\Rightarrow \text{strength} \left(\frac{x}{\text{L}} \right) = N \times \text{Eq. wt. and Eq. wt. of CaCO}_3 = \frac{\text{Mol. wt.}}{2} = \frac{100}{2} = 50.$$

\therefore Strength of alkalinity upto phenolphthalein end-point in terms of CaCO_3 equivalent

$$= \frac{V_1}{5000} \times (50 \text{ g/L}) \times 1000 \frac{\text{mg}}{\text{g}}$$

$$P = 10 V_1 \frac{\text{mg}}{\text{L}} = 10 V_1 \text{ ppm}$$

Now 100 mL of water upto methyl orange end-point

$$\equiv (V_1 + V_2) \text{ mL of N/50 H}_2\text{SO}_4$$

$$\therefore 100 \text{ mL} \times N_M = (V_1 + V_2) \text{ mL} \times N/50$$

$$\text{or normality, } N_M = \frac{(V_1 + V_2) \text{ mL}}{100 \text{ mL}} \times N/50 = \frac{(V_1 + V_2)}{5000} N$$

\therefore Strength of total alkalinity in terms of CaCO_3 eq.

$$= \frac{(V_1 + V_2)}{5000} \times 50 \text{ g/L} \times 1000 \frac{\text{mg}}{\text{g}}$$

$$M = 10 (V_1 + V_2) \frac{\text{mg}}{\text{L}} = 10 (V_1 + V_2) \text{ ppm}$$

1. When $P = 0$, both OH^- and CO_3^{2-} are absent and alkalinity in that case is due to HCO_3^- only

2. When $P = M$, only OH^- is present, because neither CO_3^{2-} nor HCO_3^- ions are present.

Thus, alkalinity due to $\text{OH}^- = P = M$

3. When ($P = \frac{1}{2} M$ or $V_1 = V_2$) only CO_3^{2-} is present, since half of carbonate neutralization (i.e., $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$) takes place with phenolphthalein, while complete carbonate neutralization (i.e., $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^- ; \text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$) occurs when methyl orange indicator is used.

Thus, alkalinity due to $\text{CO}_3^{2-} = 2 P$.

4. When $P > \frac{1}{2} M$ or $V_1 > V_2$: In this case, besides CO_3^{2-} , OH^- ions are also present. Now half of CO_3^- (i.e., $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) equal to $(M - P)$.

So, alkalinity due to complete $\text{CO}_3^- = 2(M - P)$

\therefore alkalinity due to $\text{OH}^- = M - 2(M - P) = (2P - M)$.

5. When $P < \frac{1}{2} M$ or $V_1 < V_2$: In this case, besides CO_3^{2-} , HCO_3^- ions are also present.

Now alkalinity due to $\text{CO}_3^{2-} = 2P$

\therefore alkalinity due to $\text{HCO}_3^- = (M - 2P)$.

The results may be summarized in following Table 4 :

Table 4

S.No.	Results of Titrations	Alkalinity due to		
		Hydroxide (OH^-)	Carbonate (CO_3^{2-})	Bicarbonate (HCO_3^-)
1.	$P = 0$	Nil	Nil	M
2.	$P = M$	P or M	Nil	Nil
3.	$P = \frac{1}{2} M$ (or $V_1 = V_2$)	Nil	2P	Nil
4.	$P > \frac{1}{2} M$ (or $V_1 > V_2$)	$(2P - M)$	$2(M - P)$	Nil
5.	$P < \frac{1}{2} M$ (or $V_1 < V_2$)	Nil	2P	$M - 2P$

Drawbacks of using Highly alkaline water

- (a) It may lead to caustic embattlement,
- (b) It may lead to deposition of precipitates and sludges in boiler tubes and pipes.

7.1 Solved Examples based on Determination of Alkalinity of Water

Example 1. 50 mL of a sample of water required 5 mL of N/50 H_2SO_4 using methyl orange as indicator but did not give any colouration with phenolphthalein. What type of alkalinity is present ? Express the same in ppm.

Solution. As the water sample does not give any colouration with phenolphthalein ($P = 0$), hence only HCO_3^- ions are present.

Now, 50 mL of water sample upto methyl orange end-point = 5 mL of N/50 H_2SO_4

$$\therefore 50 \text{ mL} \times N_M = 5 \text{ mL} \times N/50$$

$$\text{or Normality, } N_M = 5 \text{ mL} \times \frac{N}{50} \times \frac{1}{50 \text{ mL}} = \frac{1}{500} N$$

Now, strength of alkalinity upto methyl orange end point (in terms of CaCO_3 equivalents) = $(N_M \times 50)$ g/L

$$\Rightarrow M = \frac{1}{500} \times 50 \text{ g/L} \times 1000 \text{ gm/g}$$

$$\Rightarrow M = 100 \text{ mg/L} = 100 \text{ ppm.}$$

Hence, alkalinity due to HCO_3^- = $M = 100 \text{ ppm}$

Example 2. 200 mL of water sample, on titration with N/50 H_2SO_4 using phenolphthalein as indicator, gave the end point when 10 mL of acid were run down. Another lot of 200 mL of the sample also required 10 mL of the acid to obtain methyl-orange end point. What type of alkalinity is present in the sample and what is its magnitude?

Solution. 200 mL of water upto phenolphthalein end point

$$\equiv 10 \text{ mL of } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$\therefore 200 \text{ mL} \times N_p = 10 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_p = 10 \text{ mL} \times \frac{1}{50} \times \frac{1}{200 \text{ mL}} N = \frac{1}{1000} N$$

$$\text{Hence, } P = N_p \times 50 \times 1000 \text{ ppm}$$

$$= \frac{1}{1000} \times 50 \times 1000 = 50 \text{ ppm} \quad \dots(1)$$

$$\text{Similarly, } M = 50 \text{ ppm} \quad \dots(2)$$

From Equations (1) and (2), As $P = M$

Hence, only OH^- ions are present which are causing alkalinity, and alkalinity due to $\text{OH}^- = 50 \text{ ppm}$.

Example 3. 500 mL of a water sample, on titration with $\frac{N}{50} \text{ H}_2\text{SO}_4$ gave a titre value of 29 mL to phenolphthalein end point and another 500 mL sample on titration with same acid gave a titre value of 58 mL to methyl orange end point. Calculate the alkalinity of the water sample in terms of CaCO_3 and comment on the type of alkalinity present.

Solution. 500 mL of water upto phenolphthalein end-point

$$\equiv 29 \text{ mL of } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$\therefore 500 \text{ mL} \times N_p = 29 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_p = \frac{29 \text{ mL}}{500 \text{ mL}} \times \frac{1}{50} N$$

Now, strength of alkalinity upto phenolphthalein end-point in terms of CaCO_3 equivalent = $N_p \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow P = 58 \text{ ppm} \quad \dots(i)$$

Given, 500 mL of water upto methyl orange end-point = 58 mL of $\frac{N}{50}$ H₂SO₄

$$\therefore 500 \text{ mL} \times N_M = 58 \text{ mL} \times \frac{N}{50}$$

$$\Rightarrow \text{Normality, } N_M = \frac{58 \text{ mL}}{500 \text{ mL}} \times \frac{1}{50} N$$

Now, strength (in terms of CaCO₃ equivalents) = $M = N_M \times 50 \times 1000 \text{ ppm}$

$$M = 116 \text{ ppm} \quad \dots(i)$$

$$\text{From equations (i) and (ii); } P = \frac{1}{2} M$$

Hence, only CO₃²⁻ ions are present

And Alkalinity of water sample due to CO₃²⁻ = $2P = M = 116 \text{ ppm}$

Example 4. A sample of water was alkaline to both phenolphthalein and methyl orange 100 mL of this water sample required 30 mL of N/50 H₂SO₄ for phenolphthalein end point and another 20 mL for complete neutralization. Determine the types and extent of alkalinity present.

Solution. 100 mL of water upto phenolphthalein end-point = 30 mL of $\frac{N}{50}$ H₂SO₄

$$\therefore 100 \text{ mL} \times N_P = 30 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality } N_P = \frac{30 \text{ mL}}{100 \text{ mL}} \times \frac{1}{50} N$$

Now, strength of alkalinity upto phenolphthalein end-point in terms of CaCO₃ equivalent = $N_P \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow P = \frac{30}{100} \times \frac{1}{50} \times 50 \times 1000 = 300 \text{ ppm}$$

$$\Rightarrow P = 300 \text{ ppm} \quad \dots(ii)$$

As, 100 mL of water upto methyl orange end-point

$$= 30 + 20 = 50 \text{ mL of } \frac{N}{50} \text{ H}_2\text{SO}_4$$

$$\therefore 100 \text{ mL} \times N_M = 50 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_M = \frac{50 \text{ mL}}{100 \text{ mL}} \times \frac{1}{50} N$$

Hence, strength (in terms of CaCO₃ equivalents) = $M = N_M \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow M = 500 \text{ ppm} \quad \dots(ii)$$

Since $P > \frac{1}{2} M$. Hence OH⁻ and CO₃²⁻ ions are present.

and Alkalinity due to OH⁻ = $2P - M = 2 \times 300 - 500 = 100 \text{ ppm}$

and Alkalinity due to CO₃²⁻ = $2(M - P) = 2(500 - 300) = 400 \text{ ppm}$

Hence, the given water sample contains : OH⁻ Alkalinity = 100 ppm

CO₃²⁻ Alkalinity = 400 ppm

Example 5. A water sample is alkaline to both phenolphthalein as well as methyl orange. 200 mL of water sample on titration with N/50 HCl required 9.4 mL of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after addition of another 21 mL of the acid solution. Elucidate on the type and extent of alkalinity present in the water.

Solution. 200 mL of water upto phenolphthalein end-point

$$= 9.4 \text{ mL of N/50 HCl}$$

$$\therefore 200 \text{ mL} \times N_p = 9.4 \text{ mL} \times \frac{N}{50}$$

$$\text{or Normality, } N_p = \frac{9.4 \text{ mL}}{200 \text{ mL}} \times \frac{1}{50} N$$

Now, strength of alkalinity upto phenolphthalein end-point in terms of CaCO_3 equivalent $= P = N_p \times 50 \times 1000 \text{ ppm}$

$$\Rightarrow P = 47 \text{ ppm} \quad \dots(i)$$

As, 200 mL of water upto methyl orange end point

$$= 9.4 + 21 = 30.4 \text{ mL of N/50 HCl}$$

$$\therefore 200 \text{ mL} \times N_M = 30.4 \text{ mL} \times N/50$$

$$\text{or Normality, } N_M = \frac{30.4 \text{ mL}}{200 \text{ mL}} \times \frac{1}{50} N$$

Hence, strength of alkalinity upto methyl orange end-point in terms of CaCO_3 equivalent hardness

$$= M = N_M \times 50 \times 1000 \text{ ppm}$$

$$\Rightarrow M = 152 \text{ ppm} \quad \dots(ii)$$

Since $P < \frac{1}{2} M$. Hence CO_3^{2-} and HCO_3^- ions are present.

and Alkalinity due to $\text{CO}_3^{2-} = 2P = 2 \times 47 = 94 \text{ ppm}$

and Alkalinity due to $\text{HCO}_3^- = M - 2P = 152 - 94 = 58 \text{ ppm}$

Hence, the given water sample contains CO_3^{2-} alkalinity = 94 ppm

and HCO_3^- alkalinity = 58 ppm

8 BOILER FEED WATER (WATER FOR STEAM GENERATION)

Water is mainly used in boilers for the generation of steam (for industries and power houses). For such water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits.

A boiler-feed water should correspond with the following composition :

(i) Its hardness should be below 0.2 ppm.

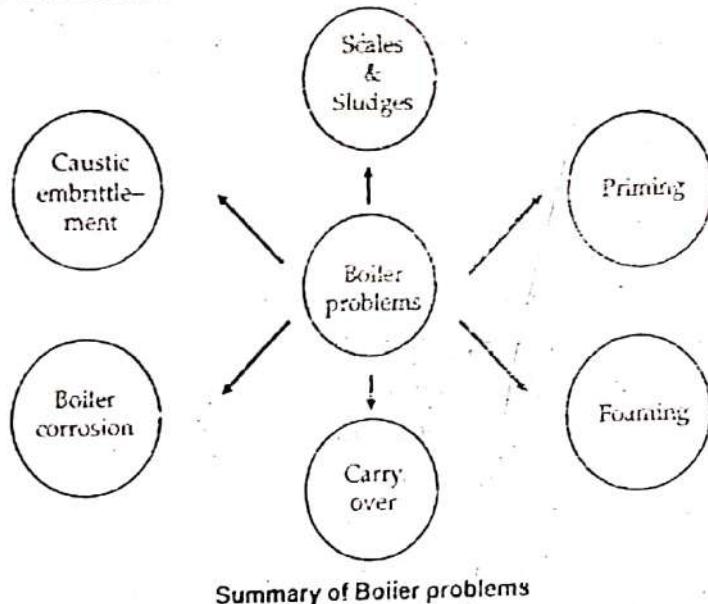
(ii) Its caustic alkalinity (due to OH^-) should lie in between 0.15 and 0.45 ppm.

(iii) Its soda alkalinity (due to Na_2CO_3) should be 0.45 – 1 ppm.

Excess of impurities, if present, in boiler feed water generally cause the following problems :

Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.

9 BOILER PROBLEMS



9.1 Sludge and Scale Formation in Boilers

In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.

If the precipitates formed are soft loose and slimy, these are known as *sludges*; while if the precipitate is hard and adhering on the inner walls, it is called as *scale*.

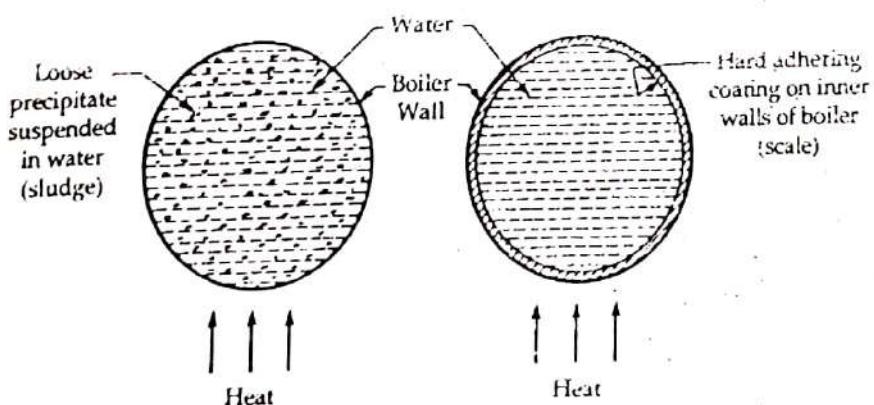
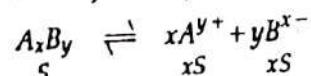


Fig. 4. Sludge and scale formation in boilers.

Note : In general, for an electrolyte, A_xB_y , which ionises as :



The solubility product (K_{SP}) is given by : $K_{SP} = [A^{y+}]^x [B^{x-}]^y$

where $[A^{y+}]$ and $[B^{x-}]$ are the ionic concentrations in a saturated solution. Thus, solubility product of an electrolyte may be defined as "the maximum product of the concentrations of its constituent ions (expressed in moles per Litre) in its solution, when each ionic concentration term being raised to the no. of times the ion occurs in the equation representing the solution of 1 molecule of the electrolyte."

Let S mole/Litre be the solubility of the electrolyte, then concentration,

$$[A^{y+}] = x S \text{ mol/L} \text{ and } [B^{x-}] = y S \text{ mole/L}$$

$$\therefore K_{SP} = [A^{y+}]^x [B^{x-}]^y = [xS]^x [yS]^y = x^x \cdot y^y \cdot S^{x+y}$$

For example, in case of $\text{BaCl}_2 \rightleftharpoons \text{Ba}^{2+} + 2 \text{Cl}^-$; $x=1, y=2$.

$$K_{SP} = 1^1 \cdot 2^2 \cdot S^{1+2} = 4 S^3$$

Cases :

1. If $K_{SP} = [A^{y+}]^x [B^{x-}]^y \Rightarrow$ solution is just saturated
2. If $K_{SP} > [A^{y+}]^x [B^{x-}]^y$ or solubility product > ionic product
 \Rightarrow Solution is unsaturated and more salt can be dissolved in it.
3. If $K_{SP} < [A^{y+}]^x [B^{x-}]^y$ or solubility product < ionic product
 \Rightarrow Solid $A_x B_y$ will precipitate out.

SLUDGE

Sludge is a soft, loose and slimy precipitate formed within the boiler. Sludges are formed by substances which have greater solubilities in hot water than in cold water, e.g., MgCO_3 , MgCl_2 , CaCl_2 , MgSO_4 etc. They are formed at comparatively colder portions of the boiler and get collected at places where the flow rate is slow, they can be easily removed (scrapped off) with a wire brush.

If sludges are formed along-with scales, then former gets entrapped in the latter and both get deposited as scales.

Disadvantages of sludge formation

- (i) Sludges are poor conductors of heat, so they tend to waste a portion of heat generated and thus decrease the efficiency of boiler.
- (ii) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, gauge-glass connection, thereby causing even choking of the pipes.

Prevention of sludge formation

- (i) By using softened water
- (ii) By frequently 'blow-down operation', (i.e., partial removal of concentrated water through a tap at the bottom of boiler, when extent of hardness in the boiler becomes alarmingly high.)

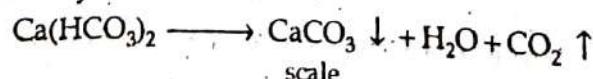
SCALES

Scales are hard deposits firmly sticking to the inner surfaces of the boiler.

They are difficult to remove, even with the help of hammer and chisel, and are the main source of boiler troubles.

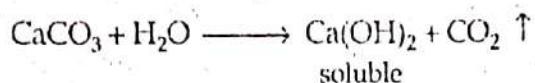
Scales may be formed inside the boiler due to :

- (i) Decomposition of calcium bicarbonate



However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers.

But in high-pressure boilers, CaCO_3 is soluble due to the formation of $\text{Ca}(\text{OH})_2$.



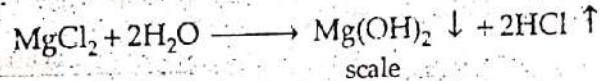
(ii) Deposition of calcium sulphate

The solubility of CaSO_4 in water decreases with increase in temperature. CaSO_4 is soluble in cold water, but almost completely insoluble in super-heated water. [It may be due to increased ionization at high temperature so $k_{sp} < k_{ionic\ prod.}$ and less availability of water molecules for solvation at high temperature.]

Consequently, CaSO_4 gets precipitated as hard scale on the hotter parts of the boiler. This type of scale causes troubles mainly in high-pressure boilers. Calcium sulphate scale is quite adherent and difficult to remove, even with the help of hammer and chisel.

(iii) Hydrolysis of magnesium salts

Dissolved magnesium salts get hydrolysed (at prevailing high temperature inside the boiler) forming magnesium hydroxide precipitate, which forms a soft type of scale, e.g.



(iv) Presence of silica

Even if a small quantity of SiO_2 is present, it may deposit as calcium silicate (CaSiO_3) and/or magnesium silicate (MgSiO_3). These deposits adhere very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

Disadvantages of Scale formation

(i) *Wastage of fuel.* Scales have a poor thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water, excessive or over-heating is done and this causes increase in fuel consumption.

The wastage of fuel being dependent on the thickness and the nature of scale :

Thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

(ii) *Lowering of boiler safety.* Due to scale formation, over-heating of boiler is done in order to maintain a steady supply of steam. It makes the boiler material softer and weaker. This causes distortion of boiler tube and also makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.

(iii) *Decrease in efficiency.* Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of the boiler.

(iv) *Danger of explosion.* When thick scales crack due to uneven expansion, the water comes suddenly in contact with over-heated portion and large amount of steam is formed instantaneously. This results in development of sudden high-pressure which may cause explosion of the boiler.

Removal of Scales

Scales are removed by mechanical methods (*i - iii*) and/or by chemical methods (*iv*).

- (i) If the scales are loosely adhering, it can be removed with the help of scraper or piece of wood or wire brush,
- (ii) If the scales are brittle, it can be removed by giving thermal shocks (*i.e.*, heating the boiler and then suddenly cooling with cold water),
- (iii) If the scales are loosely adhering, they can also be removed by frequent blow-down operation. Blow-down operation is partial removal of hard water through a 'tap' at the bottom of the boiler, when extent of hardness in the boiler becomes alarmingly high. 'Make-up' water is addition of fresh softened water to boiler after blow down operation.
- (iv) If the scales are adherent and hard, they can be removed by dissolving them by adding chemicals *e.g.*, CaCO_3 scales can be dissolved by using 5 – 10% HCl. Calcium sulphate scales can be removed by adding EDTA, since the Ca – EDTA complex is highly soluble in water,

The essential differences between sludges and scales are summarized in Table 5 :

Table 5. Differences between Sludges and Scales

S.No.	Sludges	Scales
1.	Sludges are soft, loose and slimy precipitate.	Scales are hard deposits.
2.	They are non-adherent deposits and can be easily removed.	They stick very firmly to the inner surface of boiler and are very difficult to remove.
3.	Formed by substances like CaCl_2 , MgCl_2 , MgSO_4 , MgCO_3 etc.	Formed by substance like CaSO_4 , Mg(OH)_2 etc.
4.	Formed at comparatively colder portions of the boiler.	Formed generally at heated portions of the boiler.
5.	They decrease the efficiency of boiler but are less dangerous.	Decrease the efficiency of boiler and chances of explosions are also there.
6.	Can be removed by blow-down operation.	Cannot be removed by blow-down operation.

9.2 Priming and Foaming

When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along-with the steam. This process of 'wet-steam' formation, is called *priming*.

Priming is caused by :

- (i) the presence of considerable quantities of dissolved solids (mainly due to suspended impurities and due to dissolved impurities in water).
- (ii) Steam velocities high enough to carry droplets of water into the steam pipe ;
- (iii) Sudden boiling ;
- (iv) Faulty design of boiler.

Priming can be avoided by :

- (i) controlling rapid change in steaming velocities,
- (ii) the proper design of boilers (maintaining low water levels in boilers),
- (iii) ensuring efficient softening and
- (iv) filtration of the boiler-water carried over to the boiler.
- (v) by blowing off sludge or scales from time to time.

Foaming is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily. *Foaming is caused by* the presence of an oil and alkalis in boiler-feed water. Actually oils and alkalis react to form soaps which greatly lowers the surface tension of water and thus increase the foaming tendency of the liquid.

Foaming can be avoided by : (i) the addition of anti-foaming agents, which act by counteracting the reduction in surface tension. For example addition of castor oil (which spreads on the surface of water and therefore) neutralises the surface tension reduction. (ii) The removal of foaming agent (oil) from boiler water.

Traces of oils are generally introduced in boiler feed water through the lubricating materials used for pumps etc. Oils can be removed by the addition of aluminium compounds, like *sodium aluminate* and *aluminium sulphate* which are hydrolysed to form aluminium hydroxide flocks which entrap oil drops. The flocks of Al(OH)_3 containing oil droplets are removed by filtration through anthrafilt filter bed.

9.3 Carry Over

The phenomenon of carrying of water along with impurities by steam is called "carry over". This is mainly due to priming and foaming.

Priming and foaming, usually occur together.

They are *objectionable* because :

- (i) dissolved salts or suspended solids in boiler water are carried by the wet steam to superheater and turbine blades, where they get deposited as water evaporates. This deposit decreases the efficiency of boiler.
- (ii) dissolved salts may enter the parts of other machinery, thereby decreasing their life ;
- (iii) The maintenance of the boiler pressure becomes difficult because of improper judgement of actual height of water column.

9.4 Boiler Corrosion

Boiler corrosion is "decay" or "disintegration" of boiler body material either due to chemical or electrochemical reaction with its environment.

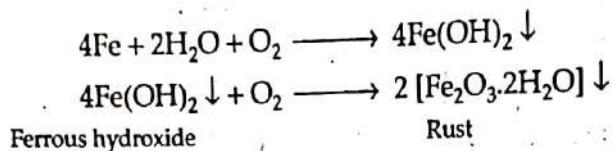
The disadvantages of corrosion are :

- (i) Shortening of boiler life,
- (ii) leakages of the joints and rivets;
- (iii) increased cost of repairs and maintenance.

Corrosion in boilers is due to the following reasons:

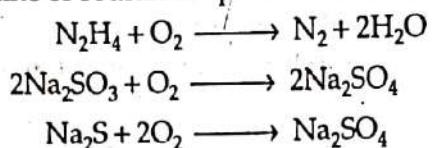
(1) **Dissolved oxygen.** This is the most usual corrosion causing factor. In boilers, oxygen is introduced through the raw water supply. Water usually contains about 8 ppm of dissolved oxygen at room temp. As the water is heated, the

dissolved oxygen is set free and the boiler starts corroding. Dissolved oxygen reacts with the iron of boiler in presence of water and under prevailing high temp. to form ferric oxide (rust).



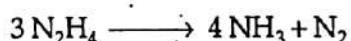
Removal of dissolved oxygen:

(i) By adding hydrazine or sodium sulphite or sodium sulphide. Thus :



Hydrazine is an ideal chemical for the removal of dissolved oxygen. It reacts with oxygen, forming nitrogen and water. Nitrogen is harmless. Consequently, hydrazine removes oxygen without increasing the conc. of dissolved solids/salts.

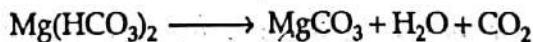
- (i) Pure hydrazine is not used in water treatment because it is an explosive inflammable liquid so 40% Aqueous solution of hydrazine is used which is quite safe.
- (ii) Excess hydrazine must not be used because excess of it decomposes to give NH₃, which causes corrosion of some alloys like brass etc. used in condenser tubes.



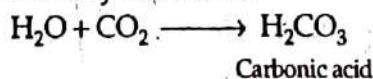
On the other hand, if sodium sulphite or sodium sulphide is used, the sodium sulphate is formed. Under high pressure it decomposes giving SO₂. The SO₂ enters the steam pipes and appears as corrosive sulphurous acid (H₂SO₃) in steam condensate. So as a rule a very low concentration of 5-10 ppm of Na₂SO₃ in the boiler is maintained, rather adding it intermittently.

(ii) *By mechanical deaeration.* This process consists of spraying water over preheated perforated plates stacked in a tower. Removal of dissolved O₂ is ensured by applying high temperature and vacuum.

(2) **Carbon dioxide.** There are two sources of CO₂ in boiler water, viz. dissolved CO₂ in raw water and CO₂ formed by decomposition of bicarbonates in H₂O according to the equation :

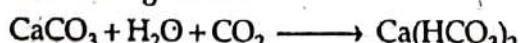


Carbon dioxide in presence of water forms carbonic acid which has a corrosive effect on the boiler material like any other acid.



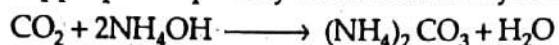
CO₂ can be removed by :

- (i) mechanical de-aeration along with O₂.
- (ii) filtering water through lime-stone

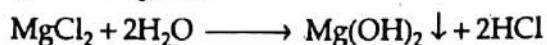


But this method increases hardness

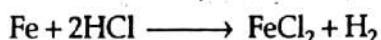
(iii) addition of appropriate quantity of ammonium hydroxide



(3) **Mineral acids.** Magnesium chloride, if present in boiler feed water, can undergo hydrolysis producing HCl



The liberated acid reacts with iron material of the boiler to form ferrous hydroxide which in turn is converted to rust in the following way :



Thus, a small amount of HCl may cause extensive corrosion since HCl is produced in a chain-like manner. Consequently, presence of even a small amount of MgCl₂ cause corrosion of iron to a large extent.

As the boiler water is generally alkaline and hence the acid is usually neutralized. In case, the amount of acid is more, calculated quantity of alkali is added from outside to neutralize the acid for preventing this corrosion.

9.5 Caustic Embrittlement

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

During softening by lime-soda process, it is likely that some residual Na₂CO₃ is still present in the softened water. In high pressure boilers Na₂CO₃ decomposes to give sodium hydroxide and CO₂, and sodium hydroxide thus produced makes the boiler water "caustic".



This caustic water flows into the minute hair-cracks, present in the inner side of boiler, by capillary action. On evaporation of water the dissolved caustic soda concentration increases progressively which attacks the surrounding area, thereby dissolving iron of boiler as sodium ferrate. This causes embrittlement of boiler walls more particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.

Mechanically embrittlement arises due to the setting up of a concentration cell.

With the iron surrounded by dil. NaOH acting as the Cathode, while the iron surrounded by conc. NaOH acting as the anode.

The iron in the anodic part gets dissolved or corroded.

Caustic embrittlement can be prevented :

- (i) by using sodium phosphate as softening reagent, instead of sodium carbonate in external treatment of boiler water.
- (ii) by adding tannin or lignin to boiler water which blocks the hair-cracks in the boiler walls thereby preventing infiltration of caustic soda solution into these areas.

(iii) by adding sodium sulphate to boiler water :

Na_2SO_4 also blocks hair-cracks, thereby preventing infiltration of caustic soda solution in these. It has been observed that caustic cracking can be prevented, if Na_2SO_4 is added to boiler water so that the ratio :

$\frac{[\text{Na}_2\text{SO}_4 \text{ conc.}]}{[\text{NaOH conc.}]}$ is kept as 1 : 1, 2 : 1 and 3 : 1 in boilers working respectively at pressures up to 10, 20 and above 20 atmospheres.

10 WATER SOFTENING

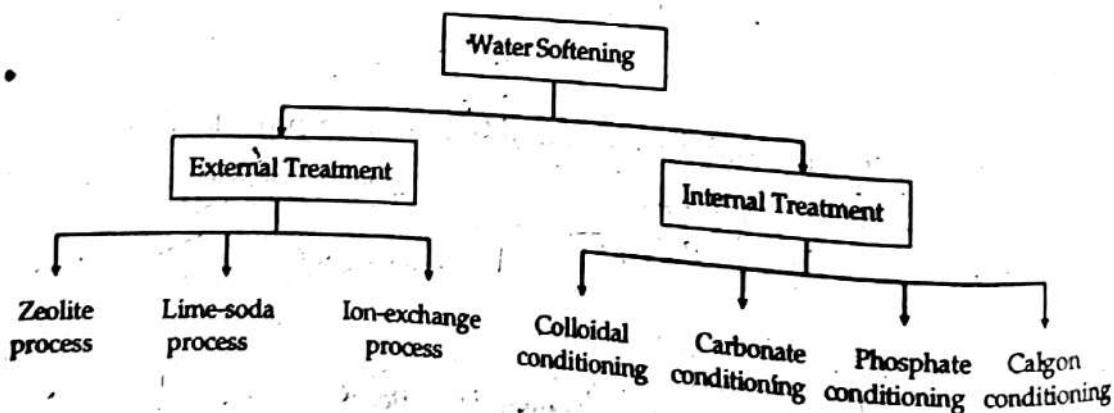
The process whereby we remove or reduce the hardness of water, irrespective of whether it is temporary or permanent is termed as 'softening' of water. It is very essential process since hard water is unsuitable for domestic as well as industrial use. One of the most important applications of water is in steam production for the generation of electricity. For this water need to be fed to industrial boilers. We just cannot feed any water into the industrial boilers because it has been identified that hard water creates large number of problems like scale and sludge formation, priming and foaming etc.

The hardness causing salts can be removed from water by following two ways :

(a) External treatment, and (b) Internal treatment.

The *External treatment* of water is carried out before its entry into the boiler. This treatment prevents boiler problems. It can be done by lime-soda, zeolite or ion-exchange processes. All are preventive methods.

In contrast, the *Internal treatment* of boiler feed water refers to the conditioning of water in the boiler itself by the addition of chemicals. This is essentially a corrective method to remove those salts which are not completely removed by external treatment of water softening. The following conditioning methods are used in the Internal treatment : Colloidal, Phosphate, Calgon and Carbonate conditioning.



The essential difference between the External treatment and Internal treatment methods are summarized in Table 6.

Table 6. Differences between Internal and External treatment methods

S.No.	<i>Internal treatment</i>	<i>External treatment</i>
1.	It is carried out in the boiler itself	It is carried out outside the boiler, before water enters the boiler.
2.	It is required in low-pressure boilers	It is required in high-pressure boilers.
3.	It is a corrective method	It is a preventive method.
4.	It includes colloidal conditioning, carbonate conditioning, Phosphate conditioning, Calgon conditioning etc.	It includes zeolite process, lime-soda process and ion-exchange process.

11 EXTERNAL TREATMENT

It can be done by the following methods :

- (i) Lime-soda process,
- (ii) Zeolite process, and
- (iii) Ion-exchange process

These important methods by which hard water is commonly softened are discussed below :

11.1 Lime-Soda Process

The *basic principle* of this process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling and filtration. For this purpose, a suspension of milk of *lime*, $\text{Ca}(\text{OH})_2$, together with a calculated amount of *sodium carbonate*, Na_2CO_3 (*soda*) is added in requisite amount. Proper mixing of the chemicals and water is carried out. Calcium carbonate, CaCO_3 and magnesium hydroxide $\text{Mg}(\text{OH})_2$ so precipitated are filtered off.

At room temperature, the precipitates formed are very fine. They do not settle down easily and cause difficulty in filtration. If small amount of *coagulants* like Alum [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$] ; Aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3$] or Sodium aluminate [NaAlO_2] are added, they hydrolyse to precipitate of aluminium hydroxide which entraps the fine precipitate of CaCO_3 and $\text{Mg}(\text{OH})_2$. Thus coagulant helps in the formation of coarse precipitates.

There are a number of variations of the lime-soda process :

Like Batch or continuous ; Cold or hot lime soda processes which are briefly described below :

(I) Cold Lime Soda Process

In these processes water is treated with lime and soda at room temperature in the presence of coagulant.

There are four types of cold lime soda softeners which work either in batch process or in continuous process. These are briefly discussed below :

(a) *The intermittent type (Batch process) Cold Lime-Soda Softener.* It consists of a pair of tanks which are used in turn for softening water. Each tank is equipped with a mechanical stirrer, inlets (for raw water and chemicals) and outlets (for soft water

and sludge), see Fig. 5. Raw water and calculated quantities of the chemicals are passed simultaneously into the tank from the opposite sides and the stirring is started with the help of stirrer. For accelerating the process, some sludge (from a previous operation) is also added which acts as nucleus for the fresh precipitation. Reaction is complete by the time tank fills up, and thus stirring is stopped. The sludge (ppt.) formed is allowed to settle down, and is then removed from the tank through the sludge outlet. The softened water is taken out through a floating pipe and sent to the filtering unit. By this batch process, continuous supply of softened water can be ensured by using a pair of tanks planned for alternate cycles of reaction and settling.

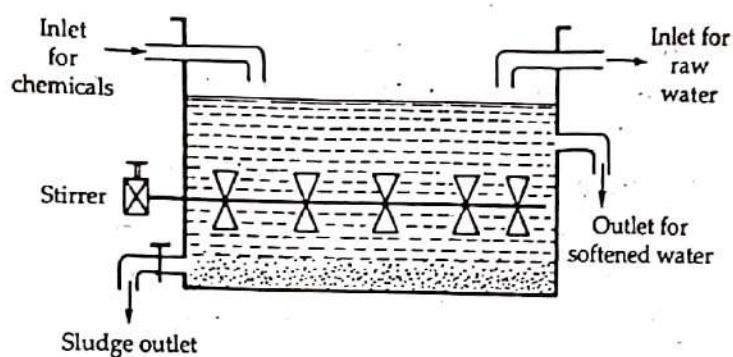


Fig. 5. Intermittent Cold Lime-Soda Softener.

(b) *Continuous cold lime-soda softeners.* (i) *The conventional type.* In this process, raw water and requisite amount of lime, soda and coagulants are fed at room temperature from the top into an inner chamber of vertical circular chamber fitted with a paddle stirrer (see Fig. 6). Vigorous stirring ensures continuous mixing and thus as the raw water and chemicals flow down, softening of water takes place. The

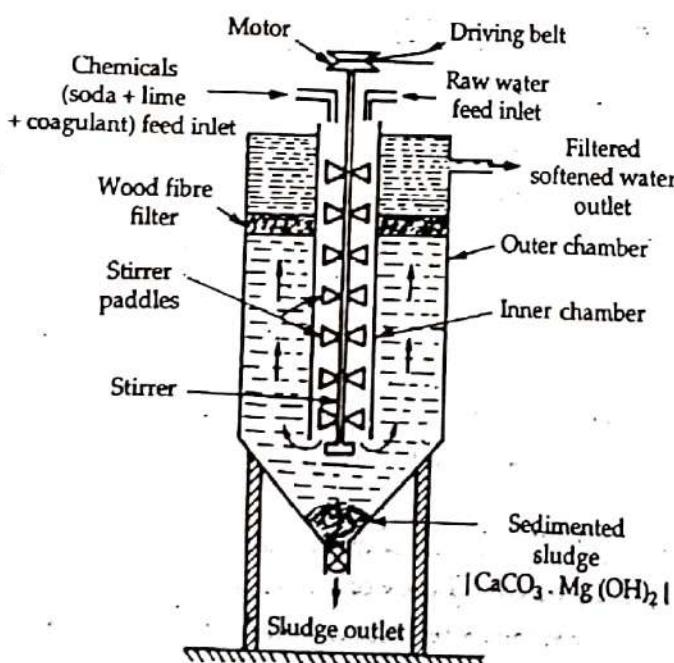


Fig. 6. Continuous cold lime-soda softner.

softened water is allowed to come into the outer co-axial chamber. The softened water, rising up passes through a wood-fiber filter whereby traces of sludges are removed. The sludge settles down in the bottom of outer chamber by the time the softened water reaches up from where it is periodically removed through the sludge outlet. Filtered soft water comes out continuously through the filtered softened water outlet at the top.

(ii) *The sludge-blanket Type.* This process is similar to the above process with a difference that the treated water is filtered upwardly through a suspended sludge blanket composed of previously formed precipitates. This ensures complete utilization of the added lime. But some lime is wasted in the conventional type as it is carried down in the sludge formed by the precipitates before it has time for dissolution and reaction. Silica is removed better in sludge-blanket type. Moreover, the retention period required is just one hour as against four hours with the conventional type softeners.

(iii) *Catalyst or spiractor type cold lime-soda water softener.* This softener consists of a conical tank which may be open (for gravity operation) or closed (for operation under pressure). About two-third of the conical tank is filled with finely divided granular catalyst (0.3 to 0.6 mm diameter) which can be green sand or sand or graded calcite. Inlets for raw water and chemicals are provided near the bottom of the tank. The outlet for soft water is at the top, see Fig. 7.

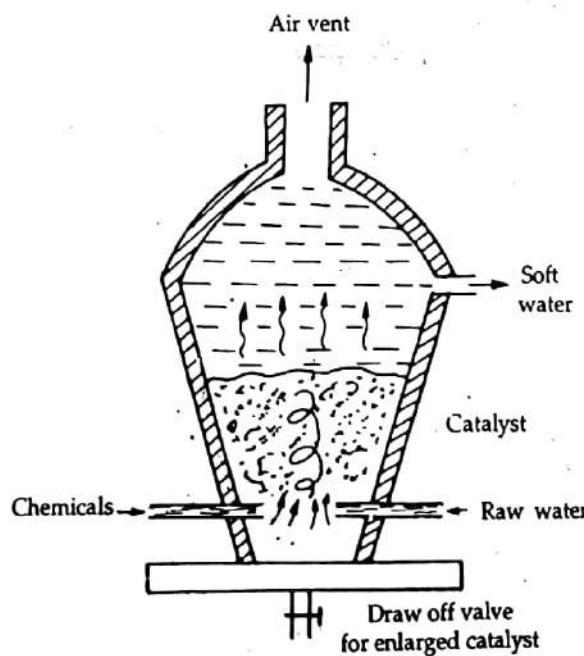


Fig. 7. Catalyst or Spiractor type softener.

Method. The raw water and chemicals enter the tank tangentially near the bottom and spiral upwards through the suspended catalyst bed. The sludge formed deposits on the granular catalyst in an adherent form and hence the granules grow in size. The softened water rises to the top from where it is drawn off. It is to be noted that sludge is formed in the granular shape which drain and dries rapidly and can be handled easily.

(II) Hot Lime-Soda Process

In these processes water is treated with chemicals at a temperature of $94^{\circ} - 100^{\circ}$ C. The softeners used may be of the intermittent type or continuous type. These are briefly discussed below :

(a) *The intermittent type (Batch process) Hot lime-soda softener.* It is similar to the intermittent type cold lime-soda softener except that the heating coils are installed in it for heating water.

(b) *The continuous type Hot lime-soda softener.* This softener essentially consists of three parts :

(i) *Reaction tank.* This tank has three separate inlets, one each for raw water, chemicals and super-heated steam. After all these three are taken in, they are thoroughly mixed. The beginning and completion of reaction occurs in reaction tank.

(ii) *Conical sedimentation tank.* From the reaction tank the contents go to this tank so that sludge settles down.

(iii) *Sand filter.* It has layers of fine and coarse sand which acts as filter and ensures complete removal of sludge from the softened water.

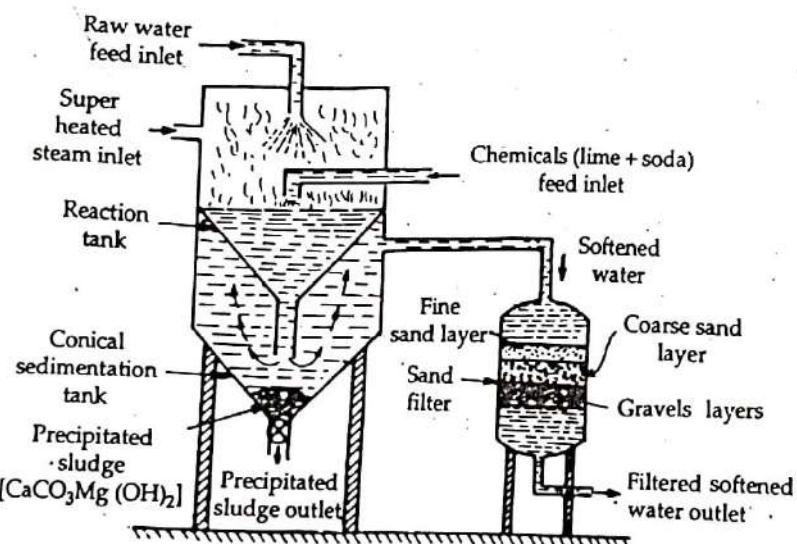


Fig. 8. Continuous hot lime-soda softner.

A soft water with 15-30 ppm of residual hardness is obtained by this process.
Advantages of Hot Lime-Soda processes.

(i) These processes are more rapid in operation. The time taken for completion are 15 minutes and several hours for hot and cold lime soda process respectively.

(ii) Elevated temperature accelerates the actual chemical reactions and reduce the viscosity of the water. This increases the rate of aggregation of the particles. Hence, both the settling rates and filtration rates are increased. Thus the softening capacity of the hot process is several times higher than the cold process.

(iii) The sludge and the precipitate formed settle down rapidly and hence no coagulant is needed.

(iv) Quantity of chemicals required for softening is low.

(v) At the higher temperatures, the dissolved gases such as CO_2 are driven out of the solution to some extent.

(vi) The residual hardness in the softened water is less when it is treated by hot process in comparison to cold lime-soda process.

The main differences between cold and hot lime soda processes are summarized in Table 7.

Table 7: Differences between the Hot and Cold lime-soda process

S.No.	Cold Lime Soda Process	Hot Lime Soda Process
1.	It is done at room temperature. (25 – 30 °C)	It is done at elevated temperatures (94 – 100 °C).
2.	It is a slow process.	It is a rapid process.
3.	The use of coagulants is must.	Coagulants not needed.
4.	Filtration is not easy.	Filtration is easy as the viscosity of water becomes low at elevated temperatures.
5.	Softened water has residual hardness around 60 ppm.	Softened water has residual hardness of 15-30 ppm.
6.	Dissolved gases are not removed.	Dissolved gases such as CO_2 are removed to some extent.
7.	Low softening capacity.	High softening capacity.

Advantages of Lime-soda Process

- (i) Lime-soda process is very economical,
- (ii) Treated water is alkaline and hence has less corrosion tendencies,
- (iii) It removes not only hardness causing salts but also minerals,
- (iv) Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.
- (v) Iron and manganese are also removed from the water to some extent.

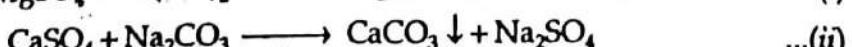
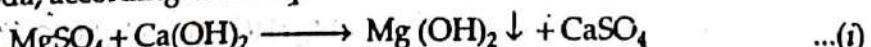
Disadvantages of Lime-Soda Process

- (i) It requires careful operation and skilled supervision for economical and efficient softening.
- (ii) Sludge disposal is a problem.
- (iii) Water softened by this process contains appreciable concentrations of soluble salts, such as sodium sulfate, and cannot be used in high pressure boilers.

Calculation of Lime-Soda Requirements

Example 1. Calculate the amount of lime required for softening of 5000 Litres of hard water containing 72 ppm of MgSO_4 .

Solution. Given hard water contains MgSO_4 so for its softening we require both lime and soda, according to the equations.



Since only amount of lime has to be calculated in this problem, so Equation (i) is important.

Requirement of lime for 1 mole of $MgSO_4 \equiv 1$ mole $Ca(OH)_2$

or requirement of lime for 120 gm of $MgSO_4 \equiv 74$ gm $Ca(OH)_2$

$$\therefore \text{Requirement of lime for } 72 \text{ ppm of } MgSO_4 \equiv \frac{74}{120} \times 72 \text{ ppm or mg/L} \dots(iii)$$

Hence, for softening of 1L of water, lime required is $\frac{74 \times 72}{120}$ mg

Thus, for softening of 5000L of water, lime required is

$$= \frac{74 \times 72}{120} \times 5000 = 222000 \text{ mg} = 222 \text{ gm}$$

Alternative solution.

$$\text{From equation (iii), Lime requirement} = \frac{74}{120} \times 72$$

$$= \frac{74}{100} \times \left(72 \times \frac{100}{120} \right)$$

$$= \frac{74}{100} (\text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}) \text{ mg/L}$$

$$\text{Thus, Lime requirement} = \frac{74}{100} [\text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}] \times \text{vol. of water (in mg)}$$

Step I. Calculation of $CaCO_3$ equivalent

Constituent	Amount	Multiplication factor	$CaCO_3$ equivalent
$MgSO_4$	72 ppm	100/120	$72 \times \frac{100}{120} = 60$ ppm or 60 mg/L

$$\text{Step II. Lime requirement} = \frac{74}{100} [60 \text{ mg/L}] \times 5000 \text{ L}$$

$$= 222,000 \text{ mg} = 222 \text{ gm}$$

Example 2. Calculate the amount of lime required for softening 50,000 litres of hard water containing : $Mg(HCO_3)_2 = 144$ ppm ; $Ca(HCO_3)_2 = 25$ ppm ; $MgCl_2 = 95$ ppm, $CaCl_2 = 111$ ppm ; $Fe_2O_3 = 25$ ppm ; $Na_2SO_4 = 15$ ppm

Solution. Suppose, L stands for Lime $Ca(OH)_2$
and S stands for soda Na_2CO_3 .

Constituent	Reactions	Need
$Mg(HCO_3)_2$	$Mg(HCO_3)_2 + 2 Ca(OH)_2 \rightarrow 2 CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2 H_2O$	2L
$Ca(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2 CaCO_3 \downarrow + 2 H_2O$	L
$MgCl_2$	$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$	L
$CaCl_2$	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2 NaCl$	S

Moreover, Fe_2O_3 and Na_2SO_4 does not causes hardening so they do not need L or S.

$$\begin{aligned} \text{Thus, Lime requirement} &= \frac{74}{100} [2 \times Mg(HCO_3)_2 + Ca(HCO_3)_2 \\ &\quad + MgCl_2 \text{ in terms of } CaCO_3 \text{ eq.}] \times \text{volume of water} \end{aligned}$$

Step I. Conversion into CaCO₃ equivalents

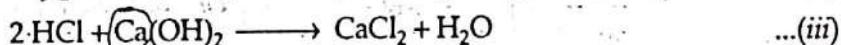
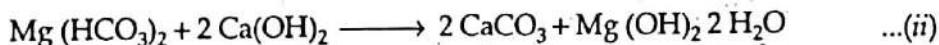
<i>Constituent</i>	<i>Amount</i>	<i>Multiplication factor</i>	<i>CaCO₃ equivalent</i>
Mg(HCO ₃) ₂	144 ppm	100/146	$144 \times \frac{100}{146} = 98.6 \text{ ppm}$
Ca(HCO ₃) ₂	25 ppm	100/162	$25 \times 100/162 = 15.4 \text{ ppm}$
MgCl ₂	95 ppm	100/95	$95 \times 100/95 = 100 \text{ ppm}$

$$\begin{aligned}\text{Step II. Lime requirement} &= \frac{74}{100} [2 \times 98.6 + 15.4 + 100] \text{ mg/L} \times 50,000 \text{ L} \\ &= 1156200 \text{ mg} = 11.57 \text{ kg}\end{aligned}$$

Example 3. Calculate the amount of lime required for softening one Litre of hard water containing : x ppm Al₂(SO₄)₃; y ppm Mg (HCO₃)₂ and z ppm HCl by first deriving the formula.

$$\frac{74}{100} [Al_2(SO_4)_3 + 2Mg(HCO_3)_2 + HCl] \text{ all as CaCO}_3 \text{ equivalent] ppm}$$

Solution. Given hard water contains Al₂(SO₄)₃, Mg (HCO₃)₂ and HCl so for its softening we require lime, according to the equations :



From equation (i), requirement of lime for 1 mole Al₂(SO₄)₃ ≡ 3 mole Ca(OH)₂

or requirement of lime for 342 gm Al₂(SO₄)₃ ≡ 3 × 74 gm Ca(OH)₂

$$\text{requirement of lime for 1 gm } Al_2(SO_4)_3 \equiv \frac{3 \times 74}{342} \text{ gm Ca(OH)}_2$$

$$\text{Thus for } x \text{ ppm } Al_2(SO_4)_3, \text{ requirement of lime} = \frac{74}{114} \times x \text{ ppm or mg/L}$$

$$\frac{74}{100} \left(x \times \frac{100}{114} \right) = \frac{74}{100} (Al_2(SO_4)_3 \text{ as CaCO}_3 \text{ eq.}) \text{ mg/L} \quad \dots(I)$$

From equation (ii) Requirement of lime for 1 mol

$$Mg(HCO_3)_2 \equiv 2 \text{ mol Ca(OH)}_2$$

Requirement of lime for 146 gm Mg (HCO₃)₂ ≡ 2 × 74 gm

$$\text{Requirement of lime for 1 gm } Mg(HCO_3)_2 \equiv \frac{2 \times 74}{146} \text{ gm}$$

$$\text{Requirement of lime for } y \text{ ppm } Mg(HCO_3)_2 \equiv 2 \times \frac{74}{146} \times y \text{ ppm}$$

$$\equiv \frac{74}{100} \left[2y \times \frac{100}{146} \right] = \frac{74}{100} [2Mg(HCO_3)_2 \text{ as CaCO}_3 \text{ eq.}] \frac{\text{mg}}{\text{L}}$$

From equation (iii), Requirement of lime for 2 moles of

$$HCl \equiv 1 \text{ mole Ca(OH)}_2 \quad \dots(II)$$

Requirement of lime for 2×36.5 gm of $\equiv 74$ gm

Requirement of lime for z ppm of $\equiv \frac{74}{73}$ gm

Thus for z ppm, requirement of lime $= \frac{74}{73} \times z$ gm/L

$$= \frac{74}{100} \left[z \times \frac{100}{73} \right] \equiv \frac{74}{100} [HCl \text{ as } CaCO_3 \text{ eq.}] \text{ mg/L} \quad \dots(\text{III})$$

From (I), (II) and (III), total requirement of lime for the given case

$$= \frac{74}{100} [Al_2(SO_4)_3 + 2Mg(HCO_3)_2 + HCl \text{ as } CaCO_3 \text{ equivalents}] \text{ mg/L}$$

$$= \frac{74}{100} \left[x \times \frac{100}{114} + 2y + \frac{100}{146} + z \times \frac{100}{73} \right] \text{ Mg/L}$$

A given hard water sample may contain any combination of different salts or ions. Accordingly, it requires different quantities of lime and soda for effective softening. The various constituents, their chemical reactions with lime and/or soda is summarized in Table 8.

Lime-requirement for softening (in mg/L)

$$= \frac{74}{100} \left[\begin{array}{c} Ca(HCO_3)_2 \\ \text{or} \\ Temp. Ca^{2+} \end{array} \right] + \left[\begin{array}{c} 2Mg(HCO_3)_2 \\ \text{or} \\ 2 \times Temp. Mg^{2+} \end{array} \right]$$

$$+ \text{Perm.} \left\{ \begin{array}{c} Mg^{2+} \\ \text{or} \\ MgCl_2 \text{ or } MgSO_4 \end{array} \right\} + \left\{ \begin{array}{c} Fe^{2+} \text{ or } FeSO_4 \\ \text{or} \\ FeSO_4 \cdot 7H_2O \end{array} \right\} + \left\{ \begin{array}{c} Al^{3+} \\ \text{or} \\ Al_2(SO_4)_3 \end{array} \right\}$$

$$+ CO_2 + \left(\begin{array}{c} H^+ \text{ or } HCl \\ \text{or} \\ H_2SO_4 \end{array} \right) + \left(\begin{array}{c} HCO_3^- \\ \text{or} \\ NaHCO_3 \end{array} \right) - NaAlO_2 \quad \text{all in terms of } CaCO_3 \text{ equivalents}$$

and Soda requirement for softening (in mg/L)

$$= \frac{106}{100} \left[\text{perm.} \left(\begin{array}{c} Ca^{2+} \text{ or } CaCl_2 \\ \text{or} \\ CaSO_4 \end{array} \right) + \left(\begin{array}{c} Mg^{2+} \text{ or } MgCl_2 \\ \text{or} \\ MgSO_4 \end{array} \right) \right]$$

$$+ (Al^{3+} \text{ or } Al_2(SO_4)_3 + \left(\begin{array}{c} Fe^{2+} \\ \text{or} \\ FeSO_4 \end{array} \right) + \left(\begin{array}{c} H^+ \\ \text{or} \\ HCl \text{ or } H_2SO_4 \end{array} \right) - \left(\begin{array}{c} HCO_3^- \\ \text{or} \\ \text{or } NaHCO_3 \end{array} \right))]$$

all in terms of $CaCO_3$ equivalents.

Notes.

1. Substances like $NaCl$, KCl , Na_2SO_4 , SiO_2 , Fe_2O_3 etc. do not impart any hardness and therefore, these do not consume any lime or soda. These should not be taken into consideration for calculating the lime and soda requirements.
2. All the substances causing hardness should be converted into their respective $CaCO_3$ equivalent. For this multiplication factors are required. Multiplication factors for some of the impurities in water which we commonly come across are given in table 3.

WATER TREATMENT

Table 8

S.No.	Constituent	Reactions	Need
1.	$\text{Ca}(\text{HCO}_3)_2$ (Temp. Ca)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{H}_2\text{O}$	L
2.	$\text{Mg}(\text{HCO}_3)_2$ (Temp. Mg)	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
3.	Mg^{2+} (Perm. Mg From MgCl_2 or MgSO_4)	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$	L S (L+S)
	or more specifically and	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaCl}_2$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$	
4.	HCO_3^- (e.g., NaHCO_3)	$2\text{NaHCO}_3 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	(L-S)
5.	Ca^{2+} (Perm. Ca From CaCl_2 or CaSO_4) or more specially:	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{Na}^+$ $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	S

S.No.	Constituent	Reactions	Need
6.	CO ₂	CO ₂ + Ca(OH) ₂ → CaCO ₃ + H ₂ O	L
7.	H ⁺ (free acids like HCl, H ₂ SO ₄ , etc.) or more specifically :	$2 H^+ + Ca(OH)_2 \rightarrow Ca^{2+} + 2 H_2O$ $Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2 Na^+$ $2 HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2 H_2O$ $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2 H_2O$ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + NaCl$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + Na_2SO_4$	(L + S)
	Note: Aluminium and Iron salt may be present in water as contributor of Permanent hardness or they may be added as coagulants.		
8.	FeSO ₄	$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$ $2 Fe(OH)_2 + H_2O + O_2 \rightarrow 2 Fe(OH)_3 \downarrow$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2 Na^+$	(L + S)
9.	Al ₂ (SO ₄) ₃	$Al_2(SO_4)_3 + 3 Ca(OH)_2 \rightarrow 2 Al(OH)_3 \downarrow + 3 CaSO_4$ $3 CaSO_4 + 3 Na_2CO_3 \rightarrow 3 CaCO_3 + 3 Na_2SO_4$	(L + S)
10.	NaAlO ₂	NaAlO ₂ + 2 H ₂ O → Al(OH) ₃ + NaOH because equivalent	- 1 L

Solved Numerical Examples for The Determination of Requirement of Lime & Soda

Example 1. Analysis of water gave the following results. $H_2SO_4 = 196 \text{ mg/l}$, $MgSO_4 = 24 \text{ mg/l}$, $CaSO_4 = 272 \text{ mg/l}$ and $NaCl = 25 \text{ mg/l}$. Water is to be supplied to the town of the population of one lakh only. The daily consumption of water is 50 litre per head. Calculate the cost of lime and soda required for the softening the hard water for town for the month April 2002. If the cost of lime is Rs. 5.00 per kg and cost of soda is Rs. 8.00 per kg.

[MREC 2002]

Solution. Lime requirement per day

$$\begin{aligned} &= \frac{74}{100} [H_2SO_4 + MgSO_4 \text{ as } CaCO_3 \text{ eq}] \times \text{vol. of water} \\ &= \frac{74}{100} \left[196 \times \frac{100}{98} + 24 \times \frac{100}{120} \right] \text{mg/L} \times 50 \text{ L/head} \times 1,00,000 \text{ persons} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \\ &= 814 \text{ kg.} \end{aligned}$$

For the April 2002 month (30 days), total lime requirement

$$= 814 \times 30 = 24420 \text{ kg.}$$

Given cost of lime = Rs. 5.00/kg.

$$\therefore \text{Total cost of lime} = 24420 \text{ kg} \times \frac{5 \text{ Rs.}}{\text{kg}} = 1,22,100 \text{ Rs.}$$

Similarly, cost of soda

$$\begin{aligned} &= \frac{106}{100} [H_2SO_4 + MgSO_4 + CaSO_4 \text{ as } CaCO_3 \text{ eq}] \text{ mg/L} \times 50 \times 10^5 \text{ L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times 30 \times \frac{\text{Rs. 8}}{\text{kg}} \\ &= \frac{106}{100} \left[196 \times \frac{100}{98} + 24 \times \frac{100}{120} + 272 \times \frac{100}{136} \right] \times 50 \times 10^5 \times \frac{1}{10^6} \times 30 \times 8 = 5,34,240 \text{ Rs.} \end{aligned}$$

Example 2. A sample of water was analysed and found to contain temporary magnesium hardness 25 mg/lt. permanent magnesium chloride hardness 15 mg/lt. and permanent calcium sulphate hardness 20 mg/lt., $SiO_2 = 300 \text{ mg/lt.}$ Calculate the lime and soda required for softening 30,000 litres of hard water. (Raj. Univ., 2002)

Solution. Lime requirement

$$\begin{aligned} &= \frac{74}{100} [2 \times \text{temp. Mg} + MgCl_2 \text{ as } CaCO_3 \text{ eq.}] \times \text{vol. of water} \\ &= \frac{74}{100} \left[2 \times 25 \times \frac{100}{24} + 15 \times \frac{100}{95} \right] \text{mg/L} \times 30,000 \text{ L} \times \frac{1 \text{ gm}}{10^3 \text{ mg}} = 4975.53 \text{ gm.} \end{aligned}$$

$$\text{Soda Requirement} = \frac{106}{100} [MgCl_2 + CaSO_4 \text{ as } CaCO_3 \text{ eq.}] \times \text{vol. of water}$$

$$= \frac{106}{100} \left[15 \times \frac{100}{95} + 20 \times \frac{100}{136} \right] \text{mg/L} \times 30,000 \text{ L} \times \frac{1 \text{ gm}}{10^3 \text{ mg}} = 969.75 \text{ gm.}$$

Example 3. Calculate the amount of lime (84% pure) and soda (92% pure) required for treatment of 20,000 litres of water, whose analysis is as follows :

$$\begin{aligned} Ca(HCO_3)_2 &= 40.5 \text{ ppm} ; Mg(HCO_3)_2 = 36.5 \text{ ppm} ; MgSO_4 = 30.0 \text{ ppm} \\ CaSO_4 &= 34.0 \text{ ppm} ; CaCl_2 = 27.75 \text{ ppm} \text{ and } NaCl = 10.00 \text{ ppm.} \end{aligned}$$

Also calculate the temporary and permanent hardness of water sample.

Solution. Temporary hardness

$$= \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2 = 40.5 \times \frac{100}{162} + 36.5 \times \frac{100}{146} = 50 \text{ ppm.}$$

Permanent hardness

$$= \text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2 = 30 \times \frac{100}{120} + 34 \times \frac{100}{136} + 27.75 \times \frac{100}{111} = 75 \text{ ppm}$$

$$\text{Lime } \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2\text{Mg}(\text{HCO}_3)_2 + \text{MgSO}_4]$$

$$= \frac{74}{100} \left[40.5 \times \frac{100}{162} + 2 \times 36.5 \times \frac{100}{146} + 30 \times \frac{100}{120} \right] \times \frac{20,000}{10^6} \times \frac{100}{84} \text{ kg} = 1.762 \text{ kg}$$

$$\text{Soda } = \frac{106}{100} [\text{MgSO}_4 + \text{CaSO}_4 + \text{CaCl}_2] \times \frac{20,000}{10^6} \times \frac{100}{92} \text{ kg}$$

$$= \frac{106}{100} \left[30 \times \frac{100}{120} + 34 \times \frac{100}{136} + 27.25 \times \frac{100}{111} \right] \times \frac{20,000}{10^6} \times \frac{100}{92} = 1.728 \text{ kg.}$$

Example 4. Explain with chemical equations and calculate the amount of lime and soda needed for softening 1,00,000 litres of water containing the following per litre :

$$(i) \text{HCl} = 7.3 \text{ mg/l}; \quad (ii) \text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ mg/l};$$

$$(iii) \text{MgCl}_2 = 9.5 \text{ mg/l}; \quad (iv) \text{NaCl} = 29.25 \text{ mg/l}.$$

Purity of lime is 90% and that of soda is 98%. 10% of chemicals are to be used in excess in order to complete the reaction quickly.

[Raj. Univ., 2001]

Solution. Lime requirement

$$= \frac{74}{100} [\text{HCl} + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ eq.}] \times \text{vol. of water}$$

$$= \frac{74}{100} \left[7.3 \times \frac{100}{73} + 34.2 \times \frac{100}{114} + 9.5 \times \frac{100}{95} \right] \text{mg/L} \times 1,00,000 \text{ L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = 3.7 \text{ kg.}$$

As lime is 90% pure and 10% excess of it was used, so the actual amount of lime needed for softening = $3.7 \times \frac{100}{90} \times \frac{110}{100} = 4.52 \text{ kg}$

Soda requirement

$$= \frac{106}{100} [\text{HCl} + \text{Al}_2(\text{SO}_4)_3 + \text{MgCl}_2 \text{ as CaCO}_3 \text{ eq.}] \times \text{vol. of water}$$

$$= \frac{106}{100} \left[7.3 \times \frac{100}{73} + 34.2 \times \frac{100}{114} + 9.5 \times \frac{100}{95} \right] \text{mg/L} \times 100,000 \text{ L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = 5.3 \text{ kg.}$$

And actual amount of soda needed for softening = $5.3 \times \frac{100}{98} \times \frac{110}{100} = 5.95 \text{ kg.}$

Example 5. Explain with equations and calculate the quantity of quick lime and soda ash required to soften 10,000 litres of water containing :

$$(i) 219 \text{ ppm of magnesium bicarbonate and } 234 \text{ ppm of sodium chloride;}$$

$$(ii) 36 \text{ ppm of Mg}^{2+} \text{ and } 18.3 \text{ ppm of HCO}_3^-;$$

$$(iii) 1.5 \text{ ppm of the free acids, } 144 \text{ ppm of sulphate ions and } 71 \text{ ppm of chloride ions.}$$



$$\text{Lime} = \frac{74}{100} [2 Mg(HCO_3)_2 + Mg^{2+} + HCO_3^- + H^+] \times \frac{10,000}{10^6} \text{ kg}$$

$$= \frac{74}{100} \left[2 \times 219 \times \frac{100}{146} + 36 \times \frac{100}{24} + 18.3 \times \frac{100}{122} + 1.5 \times \frac{100}{2} \right] \times \frac{1}{100} = 3.996 \text{ kg}$$

$$\text{Soda} = \frac{106}{100} [Mg^{2+} - HCO_3^- + H^+] \times \frac{10,000}{10^6} \text{ kg}$$

$$= \frac{106}{100} \left[36 \times \frac{100}{24} - 18.3 \times \frac{100}{122} + 1.5 \times \frac{100}{2} \right] \times \frac{1}{100} = 2.226 \text{ kg.}$$

Example 6. Calculate the amount of lime and soda required for softening one million litres of water containing :

$$H^+ \text{ (Free acidity)} = 1.5 \text{ ppm} ; HCO_3^- = 396.5 \text{ ppm} ; Mg^{+2} = 42.0 \text{ ppm} ; \\ Ca^{+2} = 90.00 \text{ ppm} ; FeSO_4 \cdot 7 H_2O = 14 \text{ ppm.}$$

The purity of lime is 91% and that of soda is 97.2%. Given Atomic mass of :

$$H = 1, Na = 23, Ca = 40, Mg = 24, O = 16, C = 12, S = 32, Fe = 56. \quad [\text{Raj. Univ., 1999}]$$

Solution. Lime requirement

$$= \frac{74}{100} [H^+ + HCO_3^- + Mg^{2+} + FeSO_4 \cdot 7 H_2O \text{ as } CaCO_3 \text{ eq.}] \times \text{vol. of water} \times \frac{100}{91} \\ = \frac{74}{100} \left[1.5 \times \frac{100}{2} + 396.5 \times \frac{100}{122} + 42 \times \frac{100}{24} + 14 \times \frac{100}{278} \right] \text{mg/L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times 10^6 \text{ L} \times \frac{100}{91} \\ = 471.67 \text{ kg.}$$

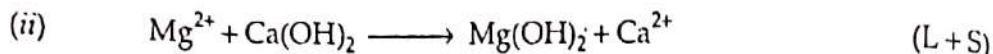
Soda requirement

$$= \frac{106}{100} [H^+ - HCO_3^- + Mg^{2+} + Ca^{2+} + FeSO_4 \cdot 7 H_2O \text{ as } CaCO_3 \text{ eq.}] \times V \times \frac{100}{97.2} \\ = \frac{106}{100} \left[1.5 \times \frac{100}{2} - 396.5 \times \frac{100}{122} + 42 \times \frac{100}{24} + 90 \times \frac{100}{40} + 14 \times \frac{100}{278} \right] \text{mg/L} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times 10^6 \text{ L} \times \frac{100}{97.2} \\ = 169.07 \text{ kg.}$$

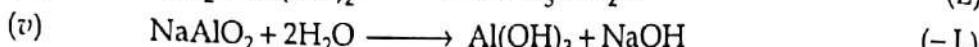
Example 7. Calculate the quantities of lime and soda required for softening 300,000 litres of water, using 20 ppm of sodium aluminate as a coagulant. Impurities in water are as follows :

$$Ca^{2+} = 160 \text{ ppm} ; Mg^{2+} = 96 \text{ ppm} ; HCO_3^- = 403 \text{ ppm} ; dissolved CO_2 = 34 \text{ ppm.}$$





$\therefore \text{S}$ is required for Ca^{2+}



$$\text{Lime} = \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 - \text{NaAlO}_2] \times \frac{V}{10^6} \text{ kg}$$

$$= \frac{74}{100} \left[96 \times \frac{100}{24} + 403 \times \frac{100}{122} + 34 \times \frac{100}{44} - 20 \times \frac{100}{164} \right] \times \frac{3 \times 10^5}{10^6} \text{ kg}$$

$$= 176.58 \text{ kg} = 176.6 \text{ kg.}$$

$$\text{Soda} = \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^-] \times \frac{V}{10^6} \times \text{kg}$$

$$= \frac{106}{100} \left[160 \times \frac{100}{40} + 96 \times \frac{100}{24} - 403 \times \frac{100}{122} \right] \times \frac{3 \times 10^5}{10^6} \text{ kg}$$

$$= 149.36 = 149.4 \text{ kg.}$$

✓ Example 8. Calculate the quantities of lime $[\text{Ca}(\text{OH})_2]$ and soda (anhyd. Na_2CO_3) required for cold softening of 125,000 L of water with the following analysis, using 10 ppm of sodium aluminate as coagulant :

Analysis of raw water : $\text{Ca}^{2+} = 95 \text{ ppm}$; $\text{Mg}^{2+} = 36 \text{ ppm}$; $\text{CO}_2 = 66 \text{ ppm}$; $\text{HCO}_3^- = 264 \text{ ppm}$; $\text{H}^+ = 2 \text{ ppm}$.

Analysis of treated water : $\text{CO}_3^{2-} = 45 \text{ ppm}$; $\text{OH}^- = 34 \text{ ppm}$. Write the chemical equations involved.

Solution. Conversion into CaCO_3 equivalents

Constituent	Amount (ppm)	Multiplication factor	CaCO_3 equivalent
Raw water			
Ca^{2+}	95	100/40	237.5
Mg^{2+}	36	100/24	150
HCO_3^-	264	100/122	216.4
CO_2	66	100/44	150
NaAlO_2	10	100/164	6.098
H^+	2	100/2	100
Treated water			
OH^-	34	100/34	100
CO_3^{2-}	45	100/60	75

\therefore Amount of lime required for just softening

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}^+ - \text{NaAlO}_2 \text{ as } \text{CaCO}_3 \text{ eq}]$$

$$= \frac{74}{100} [150 + 216.4 + 150 + 100 - 6.098]$$

$$= 451.6 \text{ ppm.}$$

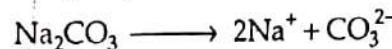
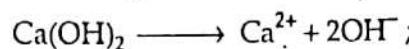
... (i)

Amount of soda required for just softening

$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{H}^+ - \text{HCO}_3^-]$$

$$= \frac{106}{100} [237.5 + 150 + 100 - 216.4] = 287.4 \text{ ppm.} \quad \dots(ii)$$

Reactions involved to get excess OH^- and CO_3^{2-} :



\therefore Lime required for excess OH^- in treated water

$$= \frac{74}{100} [\text{OH}^- \text{ as } \text{CaCO}_3 \text{ eq}] = \frac{74}{100} \times 100 = 74 \text{ ppm} \quad \dots(iii)$$

and soda required for excess OH^- and CO_3^{2-} ions in treated-water

$$= \frac{106}{100} [\text{OH}^- + \text{CO}_3^{2-}] = \frac{106}{100} [100 + 75] = 185.5 \text{ ppm.} \quad \dots(iv)$$

\therefore Total lime requirement for 125,000 L of water

$$= [(i) + (iii)] \times \frac{125,000}{10^6} \text{ kg}$$

$$= (451.6 \times 74) \times .125 = 65.7 \text{ kg}$$

Total soda requirement for 125,000 L of water

$$= [(i) + (iv)] \times .125 \text{ kg}$$

$$= [287.4 + 185.5] \times .125 = 59.1 \text{ kg.}$$

Example 9. A sample of hard water was analysed and following results were obtained :

$\text{Ca}^{2+} = 70 \text{ ppm}$; $\text{Mg}^{2+} = 30 \text{ ppm}$; $\text{CO}_2 = 22 \text{ ppm}$; $\text{HCO}_3^- = 46.36 \text{ ppm}$; Free acidity

= 1.5 ppm.

This water is to be softened by lime-soda process at the rate of 5,000 litres of water per minute. For coagulation 13.9 ppm of commercial grade ferrous sulphate ($\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$) is used as co-agulant. Calculate the quantity of lime and Soda required per hour, the % purity of lime and soda being 80% and 98% respectively. [Raj. Univ., 1998]

Solution. Lime requirement

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{CO}_2 + \text{HCO}_3^- + \text{H}^+ + \text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}] \text{ mg/L} \times \text{Rate (L/min)} \times \frac{60 \text{ min}}{\text{hr.}} \times \frac{100}{80} \times \frac{\text{kg}}{10^6 \text{ mg}}$$

$$= \frac{74}{100} \left[30 \times \frac{100}{24} + 22 \times \frac{100}{44} + 46.36 \times \frac{100}{122} + 1.5 \times \frac{100}{2} + 13.9 \times \frac{100}{278} \right] \times 5000 \times 60 \times \frac{100}{80} \times \frac{1}{10^6}$$

$$= 81.3075 \text{ kg/hr.}$$

Soda requirement

$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} - \text{HCO}_3^- + \text{H}^+ + \text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}] \text{ mg/L} \times \frac{5000 \text{ L}}{\text{min.}} \times \frac{60 \text{ min}}{\text{hr.}} \times \frac{100}{98} \times \frac{1 \text{ kg}}{10^6 \text{ mg}}$$

$$= \frac{106}{100} \left[70 \times \frac{100}{40} + 30 \times \frac{100}{24} - 46.36 \times \frac{100}{122} + 1.5 \times \frac{100}{2} + 13.9 \times \frac{100}{278} \right]$$

$$= 110.975 \text{ kg/hr.}$$

Example 10. Calculate the amount of lime (88.3% pure) and soda (99.2% pure) required to soften 24,000 litres of water per day for a year containing the following :

$$\text{CaCO}_3 = 1.85 \text{ mg/L} ; \quad \text{CaSO}_4 = 0.34 \text{ mg/L} ; \quad \text{MgCO}_3 = 0.42 \text{ mg/L} ; \\ \text{MgCl}_2 = 0.76 \text{ mg/L} ; \text{MgSO}_4 = 0.90 \text{ mg/L} ; \text{NaCl} = 2.34 \text{ mg/L} \text{ and } \text{SiO}_2 = 2.34 \text{ mg/L.}$$

[RGPV, 2001]

Solution. NaCl and SiO₂ do not require lime and soda. CaCO₃ and MgCO₃ impurities are considered as bicarbonates of calcium and magnesium respectively.

Lime requirement

$$= \frac{74}{100} [\text{CaCO}_3 + 2 \times \text{MgCO}_3 + \text{MgCl}_2 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}] \frac{\text{mg}}{\text{L}} \times (24,000 \times 365 \text{ L}) \\ \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{100}{88.3} \\ = \frac{74}{100} \left[1.85 \times \frac{100}{100} + 2 \times 0.42 \times \frac{100}{84} + 0.76 \times \frac{100}{95} + 0.90 \times \frac{100}{120} \right] \times \frac{24,000 \times 365 \times 100}{10^6 \times 88.3} = 32.3 \text{ kg.}$$

Soda requirement

$$= \frac{106}{100} [\text{CaSO}_4 + \text{MgCl}_2 + \text{MgSO}_4 \text{ as CaCO}_3 \text{ eq.}] \frac{\text{mg}}{\text{L}} \times (24,000 \times 365 \text{ L}) \times \frac{1 \text{ kg}}{10^6 \text{ mg}} \times \frac{100}{99.2} \\ = \frac{106}{100} \left[0.34 \times \frac{100}{136} + 0.76 \times \frac{100}{95} + 0.90 \times \frac{100}{120} \right] \times \frac{24,000 \times 365 \times 100}{10^6 \times 99.2} = 16.85 \text{ kg.}$$

11.2 Zeolite or Permutit Process

Zeolites are naturally occurring hydrated sodium alumino silicate minerals (like $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$ where $x = 2 - 10$ & $y = 2 - 6$) capable of exchanging reversibly its sodium ions for hardness-producing ions in water.

Zeolites are also known as *permuts* and in Greek it means 'boiling stone'.

A zeolite crystal can be considered to result from the linking of several SiO₄⁴⁻ tetrahedra, each oxygen of a tetrahedron being shared with an adjacent one. The empirical formula is thus (SiO₂)_n. However, some of the Si⁴⁺ ions may be isomorphostly replaced by Al³⁺ ions and in order to balance the charges an extra positive-ion such as Na⁺ and K⁺ must also be incorporated for every Al³⁺ introduced. The *linking of these tetrahedra results in an open structure with cavities*. The porous nature of the structure permits free movement of water molecules and ions.

Zeolites are of two *types* viz. natural and synthetic.

(i) *Natural zeolites* are non-porous, amorphous and durable for example, natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

(ii) *Synthetic zeolites* are porous and possess a gel structure. They are prepared by heating together sodium carbonate (Na₂CO₃), alumina (Al₂O₃) and silica (SiO₂).

Synthetic zeolites possess higher exchange capacity per unit weight compared to natural zeolites.

Process. For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, housed in a cylindrical unit, see Fig. 9.

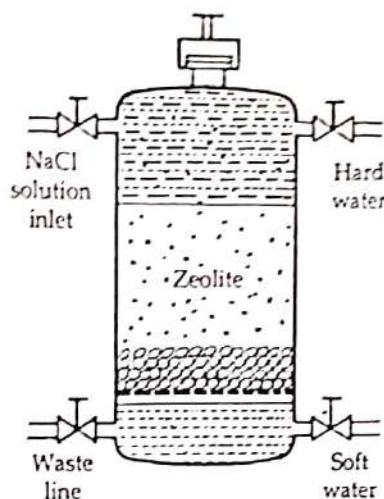


Fig. 9. Zeolite softener.

Zeolite holds sodium ions loosely and can be simply represented as Na_2Ze where Ze represents insoluble radical frame work.

The hardness-causing ions (Ca^{2+} , Mg^{2+} , etc.) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts. In the process, the water becomes free from Ca^{2+} & Mg^{2+} , the main hardness producing cations.

Reactions taking place during the softening process are :



Regeneration. After some time, the zeolite is completely converted into calcium and magnesium zeolites. Eventually, the bed ceases to soften water, i.e., it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated sodium chloride (brine) solution when the following reactions take place.



The washings (containing CaCl_2 and MgCl_2) are led to drain and the regenerated zeolite bed thus obtained is used again for softening purpose. [Instead of NaCl , NaNO_3 , KCl , KNO_3 etc. can also be used for regeneration but NaCl is mostly used because of its low cost and the products of regeneration process (CaCl_2 and MgCl_2) are highly soluble and can be easily rinsed out from the zeolite bed].

The working of zeolite softeners involve alternate cycles of softening run and the regeneration run. The scheme for softening and regeneration processes are represented in Fig. 10 below :

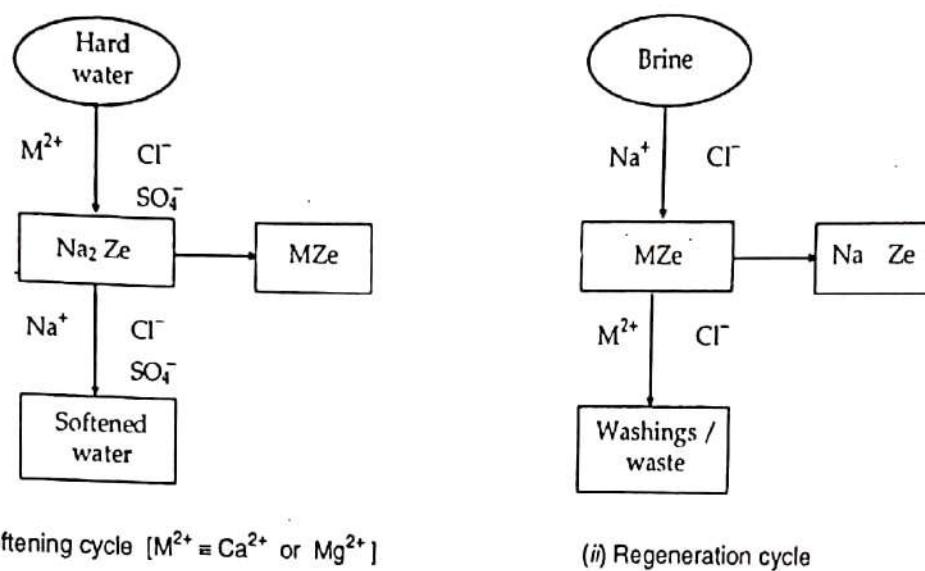
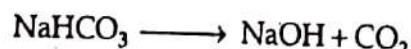


Fig. 10. Scheme for softening of water by zeolite process.

Limitations of zeolite process

- (1) If the supplied water is turbid, the suspended matter must be removed (by coagulation, filtration, etc.) before the water is fed to the zeolite bed. Otherwise the pores of the zeolite bed will get clogged by the turbidity, thereby making it inactive.
- (2) If water contains large quantities of Mn^{2+} and Fe^{2+} , they must be removed first because these ions produce manganese and iron zeolites, which are very difficult to be regenerated.
- (3) Mineral acids, if present in water, destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding the water into the zeolite bed.
- (4) The water to be softened should not be hot as the zeolite tends to dissolve in it.
- (5) Anions are not removed by this process. Thus the bicarbonates present in hard water get converted to $NaHCO_3$, which goes into soft water effluent. If it is used as boiler feed, under the boiler conditions $NaHCO_3$ dissociates to



Both the products are not desirable. Since $NaOH$ may lead to caustic embrittlement and CO_2 makes the condensed water acidic and corrosive. Thus it is desirable to remove temporary hardness before subjecting the raw water to zeolite process.

- (6) Compared to ion-exchange process, water treated by the zeolite process contains 25% more dissolved solids. Moreover, the higher cost of the plant and materials are also limiting factors.

Advantages of zeolite process

- (i) The hardness is nearly completely removed and water of about 10 ppm hardness is produced.
- (ii) The equipment used is compact and occupies less space.
- (iii) It is quite clean and rapid process which requires less time for softening.
- (iv) For maintenance as well as operations, less skill is needed.
- (v) Impurities are not precipitated, so there is no danger of sludge formation.
- (vi) The process automatically adjusts itself to waters of different hardness.

SOLVED EXAMPLES

Example 1. The hardness of 10,000 litres of a sample of water was removed by passing it through a zeolite softener. The zeolite softener then required 200 litres of sodium chloride solution containing 150 gm/litre of NaCl for regeneration. Find the hardness of water sample.

Solution. NaCl contained in 200 L of NaCl solution

$$\begin{aligned} &= 150 \text{ gm/L} \times 200 \text{ L} \\ &= 30,000 \text{ gm of NaCl} \\ &= 30,000 \times \frac{50}{58.5} \\ &= 25,641 \text{ gm equivalents of CaCO}_3 \end{aligned}$$

$$\therefore 10,000 \text{ litres of water} = 25,641 \text{ gm equivalents of CaCO}_3$$

$$\Rightarrow 1 \text{ L of water} = \frac{2.564 \times 10^7}{10,000} \text{ mg/L of CaCO}_3 \text{ eq.}$$

Hence, hardness of water is 2564 ppm.

Example 2. An exhausted zeolite softener was regenerated by passing 150 litres of NaCl solution, having a strength of 150 gm/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 500 ppm.

Solution. 150 L of NaCl contains = $150 \text{ L} \times (150 \text{ g/L})$ of NaCl

$$\begin{aligned} &= 22,500 \text{ gm of NaCl} \\ &= 22,500 \text{ gm} \times \left(\frac{100}{117} \right) \text{ CaCO}_3 \text{ eq.} \\ &= 1.932 \times 10^4 \text{ gm CaCO}_3 \text{ eq.} \\ &= 1.932 \times 10^7 \text{ mg CaCO}_3 \text{ eq.} \end{aligned}$$

Let V litres of 500 ppm (or 500 gm/L) water contains hardness

$$= 1.932 \times 10^7 \text{ mg CaCO}_3 \text{ eq.}$$

$$\therefore \text{Number of litres of hard water, } V = \frac{1.932 \times 10^7}{500} = 38640 \text{ L}$$

Table 9 : Comparison of Zeolite process with lime-soda process

Zeolite process	Lime-soda process
1. This process produces water of 10-15 ppm residual hardness.	Depending on whether it is hot or cold process, water of, generally, 15-50 ppm hardness is obtained.
2. Water treated with zeolite process contains larger amount of sodium salts than in original raw water.	Treated-water contains lesser % of sodium salts.
3. The cost of plant and zeolite are higher. Hence the capital cost is higher.	The capital cost is lower.
4. Operation expenses are lower as cheap NaCl is required for regeneration.	Operation expenses are higher as costly chemicals (lime, soda and coagulant) are consumed.
5. It cannot be used for treating acidic water, because the zeolite material undergoes disintegration.	There is no such limitation.
6. The plant occupies less space as it is compact.	Plant occupies more space, as it depends on the amount of water to be softened.
7. The raw water to be softened must be free from suspended matter ; otherwise the pores of zeolite material are blocked and the bed loses its exchange capacity.	The process is free from such limitation.
8. It can operate under pressure and can be designed for fully automatic operation.	This process cannot be operated under pressure.
9. It involves no problem of settling, coagulation, filtration and removal of the sludges and precipitates.	It involves difficulty in settling, coagulation, filtration and removal of precipitates.
10. Control test comprises only in checking the hardness of treated water. The process adjusts itself to water of different hardness.	In order to meet the changing hardness of incoming water, frequent control and adjustments of reagents is needed.
11. Treated-water contains more NaHCO_3 which creates problem when used as feed water in boilers.	Treated-water is completely free from NaHCO_3 because it is removed in the form of insoluble CaCO_3 and $\text{Mg}(\text{OH})_2$.

11.3 Demineralization or Deionization by Ion-exchange Process

Ion exchange is a process by which ions held on a porous, essentially insoluble solid are exchanged for ions in solution that is brought in contact with it.

Ion-exchange resins are insoluble, cross-linked, high molecular weight, organic polymers with a porous structure, and the "functional groups" attached to the chains are responsible for the *ion-exchange properties*. The ion-exchange resins may be classified as :

(i) *Cation exchange resins (R⁻H⁺)*: They are mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation, become capable to exchange their hydrogen ions with the cations in the water (Fig. 11).

Such resins have acidic functional groups like $-\text{SO}_3\text{H}$, $-\text{COOH}$ or $-\text{OH}$ (phenolic) capable of exchanging the cationic portion of minerals by their hydrogen ions, and hence they are termed as cation exchangers.

Amberlite IR-120 and Dowex-50 are examples of commercially available cation exchange resins.

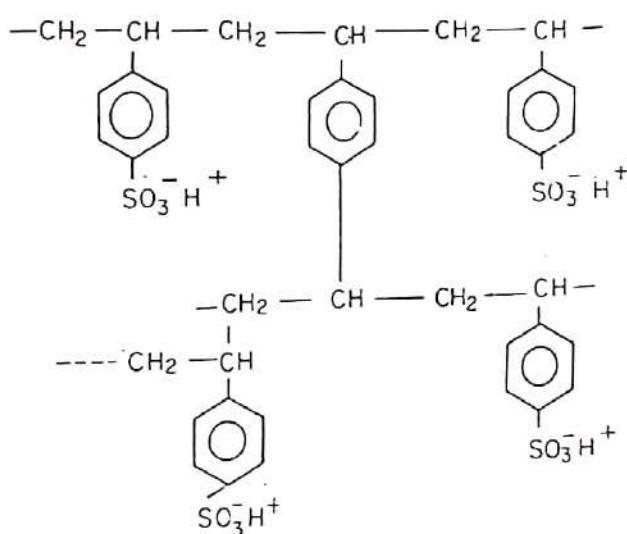


Fig. 11. Sulphonate form of cation-exchanger.

(ii) *Anion exchange resins (R⁺OH⁻)*: They are styrene-divinyl benzene or amine formaldehyde copolymers, which contain basic functional groups such as amino or quaternary ammonium ($-\text{N}^+\text{R}_3$) or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix (Fig. 12). These, after treatment with dil. NaOH solution, become capable to exchange their OH^- anions with anions in water and therefore they are known as anion exchangers.

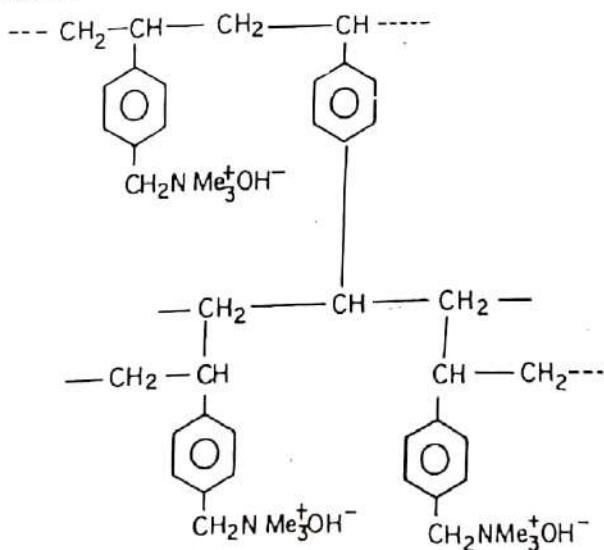


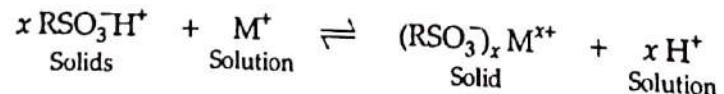
Fig. 12. Hydroxide form of anion-exchanger.

Ambertite-400 and Dowex-3 are examples of commercially available anions exchange resins.

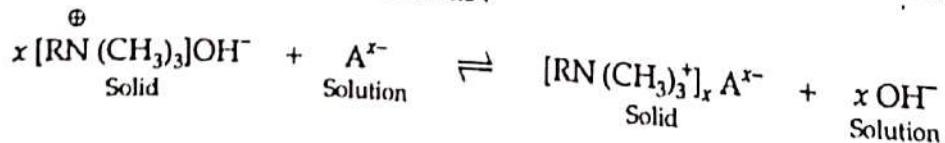
Table 10 : Pros and cons of different Ion-exchangers

	<i>Exchanger</i>	<i>Type</i>	<i>Pros</i>	<i>Cons</i>
1.	Cation exchanger	Strong acid	Useful for any water, Low initial cost, Complete cation removal, Variable capacity, Good physical stability, Good oxidation stability	Low operating efficiency
		Weak acid	Very high capacity High operating efficiency	Useful only for specific water, High initial cost, Partial cation removal, Fixed operating capacity, Poor physical stability,
2.	Anion exchanger	Strong base	Low initial cost, Complete anion removal Variable capacity	Less resistance to organic fouling, Limited life, Thermodynamically unstable, Efficiency or quality,
		Weak base	High operating capacity Excellent resistance to organic fouling Good thermal and oxidation stability	High initial cost, Partial anion removal Does not remove silica or CO_2

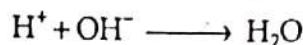
Process. The hard water is first passed through cation exchange column Fig. 13, when all the cations like Ca^{2+} , Mg^{2+} , etc. are removed (taken up by the resin) from it, and equivalent amount of H^+ ions are released from this column to water. Thus



After passing through cation exchange column, the hard water is passed through anion exchange column, when all the anions like SO_4^{2-} , Cl^- , etc. present in the water are removed (taken up by resin) and equivalent amount of OH^- ions are released from this column to water. Thus :



H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule.



Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as *deionized or demineralized water*, and is also free from acidity or alkalinity. Thus it is as pure as distilled water.

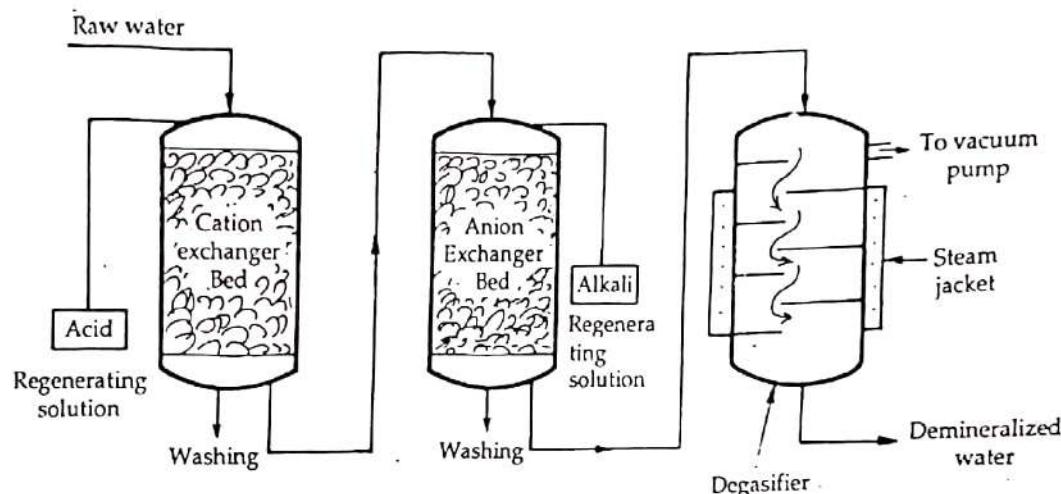


Fig. 13. Demineralization of water.

Finally, the demineralized water is passed through a degasifier, a tower whose sides are heated and which is connected to a vacuum pump. High temperature and low pressure reduces the amount of dissolved gases like CO_2 and O_2 in water.

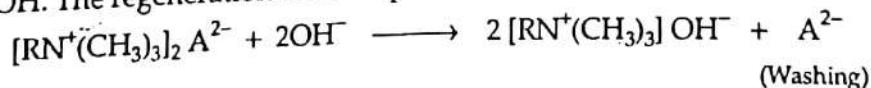
Regeneration. When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be *exhausted*.

The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H_2SO_4 . The regeneration can be represented as :



The column is washed with deionized water and washing (which contains Ca^{2+} , Mg^{2+} , etc. and Cl^- or SO_4^{2-} ions) is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. $NaOH$. The regeneration can be represented as :



The column is washed with deionized water and washing (which contains Na^+ and SO_4^{2-} or Cl^- ions) is passed to sink or drain.

The regenerated ion exchange resins are then used again.

Advantages

- (i) The process can be used to soften highly acidic or alkaline waters.
- (ii) It produces water of very low hardness (say 2 ppm). So, the treated water is very good for use in high pressure boilers.

Disadvantages

- (i) Capital cost is high since chemical and equipment both are costly.
- (ii) If water contains turbidity then the efficiency of the process is reduced.

Mixed bed deioniser. This consists of a single cylinder containing an intimate mixture of strongly acidic cation exchanger and strongly basic anion exchanger. Originally the cation exchanger is in the H^+ form, and the anion exchanger is in the OH^- form. When hard water containing say $CaCl_2$ is poured into the mixed resin bed from the top. Pure water flows out at the bottom. Each Ca^{2+} ion displaces two H^+ ions and each Cl^- displaces one OH^- ions. Exactly equal numbers of H^+ and OH^- are produced, which combine to form water, see Fig. 14.

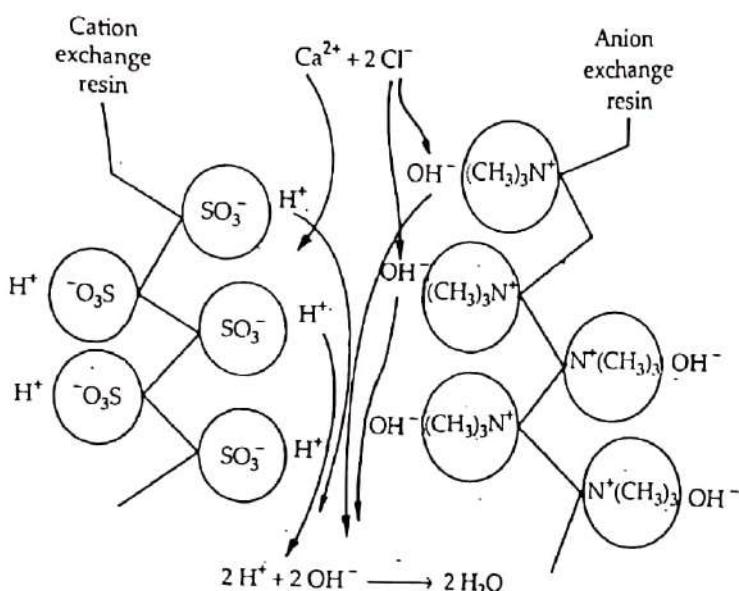


Fig. 14. Deionization of a salt solution using a mixture of cation and anion-exchange resins.
The zigzag lines represent the organic polymer matrix of the resin (most often a styrene-divinylbenzene copolymer), to which the sulfonate ($-SO_3^-$) and quaternary ammonium ($-N^+(CH_3)_3$) groups are chemically bonded.

Regeneration. To regenerate a mixed bed deioniser, it is first necessary to separate the two resins. They are then regenerated separately. The cation exchanger is regenerated by treatment with strong acid like H_2SO_4 and the anion exchanger is regenerated by treatment with a strong base like $NaOH$.

Thus, it might be obvious that mixed bed deionisers are comparatively more convenient to use and are more efficient. But they are more costly too. In many areas, deionization is a simpler and less costly alternative to distillation and is widely used for purifying water used in chemical laboratories.

In domestic water softening by ion exchange, total deionization is not necessary. Only the cations responsible for water hardness need to be removed. So, only a cation-exchanger in Na^+ form is used. Its operation is reversible and regeneration is carried out using readily available, inexpensive $NaCl$ solution (brine).

The Pros and Cons of ion-exchange, zeolite and lime-soda processes are summarized in Table 10.

WATER TREATMENT

Table 11 : Comparison of Ion-exchange, Zeolite and lime-soda process

S.no.	Characteristic	<i>Ion-exchange process</i>	<i>Zeolite process</i>	<i>Lime-soda process</i>
1.	Requirements	Cation and anion exchangers	zeolite	Lime, soda and coagulants
2.	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place	No exchange of ions.
3.	Capital cost	Very high	High	Low
4.	Operating expenses	High	Low	High
5.	Raw water	(i) Should be non-turbid (ii) Both acidic or alkaline water can be treated (iii) Prior knowledge of hardness not required	(i) Should be non-turbid (ii) Should not be acidic (iii) Prior knowledge of hardness not required.	Prior knowledge of hardness is essential
6.	Automation	Possible	Possible	Not possible
7.	Residual hardness	Least (0-2ppm)	Low (0-15 ppm)	High (15-50 ppm)

12 INTERNAL TREATMENT

It means treating the raw water inside the boiler. In this process (also called sequestration), an ion is prohibited to exhibit its original character by 'complexing' or converting it into other more soluble salt by adding appropriate reagent. It can be done by two processes : (a) In the first method, appropriate chemicals are added to the boiler water to precipitate the scale forming impurities in the form of 'sludges', which can be removed by blow-down operation, (b) In the second method, problem causing cations are converted into compounds, which will stay in "dissolved form" in water and thus do not cause any harm.

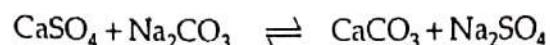
Internal treatment methods are, generally, followed by 'blow-down operations', so that accumulated sludge is removed. Some of the important internal treatment methods are briefly discussed below :

12.1 Colloidal conditioning

Scale formation can be avoided in low pressure boilers by adding substances like kerosene, tannin, agar-agar, etc. which get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by blow-down operation.

12.2 Carbonate conditioning

In *low-pressure boilers*, scale-formation can be avoided by adding sodium carbonate to boiler water, when salts like CaSO_4 etc. are converted into calcium carbonate in equilibrium.



By adding sodium carbonate, the concentration ratio of carbonate ion to sulphate ion is made greater than the solubility product ratio of calcium carbonate to calcium sulphate,

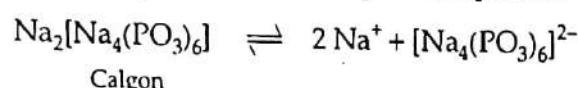
i.e.,

$$[\text{CO}_3^{2-}] / [\text{SO}_4^{2-}] > [\text{CaCO}_3] / [\text{CaSO}_4]$$

deposition of CaSO_4 as scale does not take place because the solution is saturated w.r.t. CaCO_3 and loose sludge of CaCO_3 thus formed can be removed by blow-down operation.

12.3 Calgon Conditioning

It involves in adding sodium hexa meta phosphate (also known as calgon) to boiler water to prevent the scale and sludge formation. Calgon converts the scale forming impurity like CaSO_4 into soluble complex compound.



12.4 Phosphate Conditioning

It is applicable to high-pressure boilers. Scale formation is avoided by adding sodium phosphate, which reacts with magnesium and calcium salts forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphate, the later can be removed by blow-down operation, e.g.,



where $\text{M} = \text{Ca}^{2+}$ or Mg^{2+}

The choice of phosphate salt depends upon the alkalinity of the boiler-feed water. Calcium can be precipitated properly at a pH of 9.5 or above so a phosphate is selected that adjusts pH to optimum value (9.5-10.5).

Trisodium phosphate Na_3PO_4 (*alkaline*) is most suitable for treatment, when the alkalinity of boiler water is low as it is most alkaline in nature. If the alkalinity of boiler water is sufficient, then *disodium phosphate* $[\text{Na}_2\text{HPO}_4$ (*weakly alkaline*)] is selected. But if the alkalinity of boiler water is too high and requires to be reduced, then *sodium dihydrogen phosphate* $[\text{NaH}_2\text{PO}_4$, (*acidic*)] is used.

By adding sodium phosphate, scale formation of calcium sulphate can be prevented. This is because, when we add sodium phosphate, the concentration ratio of phosphate ions to sulphate ions is increased than the solubility product ratio of calcium phosphate to calcium sulphate, i.e.,

$$[\text{PO}_4^{3-}]^{2/3} / [\text{SO}_4^{2-}] > [\text{Ca}_3(\text{PO}_4)_2]^{2/3} / [\text{CaSO}_4]$$

As the water will become saturated w.r.t. calcium phosphate but not w.r.t. calcium sulphate so the solubility product for calcium sulphate will not be reached and hence no scale of calcium sulphate will form.

13 DOMESTIC WATER TREATMENT

Drinking or potable water is fit for human consumption. The common specifications or standards prescribed and recommended for drinking water are as follows :

- (i) It should be colourless and odourless,
- (ii) It should be good in taste,
- (iii) It should not be hot,
- (iv) Its turbidity should be less than 10 ppm,
- (v) It should be free from objectionable dissolved gases like H_2S ,
- (vi) It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salts,
- (vii) Its alkalinity should not be high. pH should be in the range of 7.0 – 8.5.
- (viii) It should be reasonably soft, total hardness should be less than 500 ppm.
- (ix) It should be free from disease-producing microorganisms.
- (x) chloride, Fluoride and sulphate contents should be less than 250 ppm, 1.5 ppm and 250 ppm respectively.

The following table summarises water quality standards :

Table. 12 : Standards for drinking water

S.No.	Parameter	Standard	
		ISI (mg/L)	WHO (mg/L)
1.	Colour, Odour and Taste	Colourless, Odourless and Tasteless	Colourless, Odourless and Tasteless
2.	pH	6.9	6.9
3.	Total dissolved solids	—	1,500
4.	Dissolved oxygen	3.0	—
5.	Chloride	600	250
6.	Sulphate	1,000	400
7.	Nitrate	—	45
8.	Cyanide	0.01	0.2
9.	Fluoride	3.0	1.5
10.	Chromium	0.05	0.05
11.	Lead	0.1	0.05
12.	Arsenic	0.2	0.05

Treatment of Water for Domestic Purposes

Municipalities have to supply potable water. Rivers, lakes and wells are the most common sources of water used by them. Natural water from these sources do not conform to all the required specifications of drinking water. Hence to make these waters – potable, treatment has to be given. Actual treatment methods adopted, depend upon the exact nature of impurities present in raw water. Table 13 lists the types of impurities and the processes to be employed for removing them.

Table 13 : Treatment processes for drinking water

S.No.	Impurity	Process used for removal
1.	Floating matter such as leaves, wood pieces, etc.	Screening
2.	Suspended impurity such as sand, clay etc.	Sedimentation
3.	Fine suspended inorganic matter	Sedimentation with coagulation
4.	Microorganisms and colloidal impurities	Filtration
5.	Pathogenic bacteria	Disinfection

These methods are briefly discussed below :

(i) **Screening.** It is a process of removing floating materials like wood pieces, leaves, etc. from water. Raw water is passed through screens having holes, when the floating matter is retained by them and water is allowed to pass.

(ii) **Sedimentation.** It is the process of removing suspended impurities by allowing the water to stand undisturbed in big tanks for 2 – 8 hours. Most of the particles settle down at the bottom of the tank due to gravitational force, and they are removed. The clear supernatant water is then drawn out from the tank. This process removes only 70-75% of the suspended matter.

(iii) **Sedimentation with coagulation.** Finely divided silica, clay and organic matter do not settle down easily and hence cannot be removed by mere sedimentation. Most of these are in colloidal form and carry negative charge. Thus, they do not coalesce due to mutual repulsions. For their removal coagulation is required. In this process, coagulants like Alum. $[K_2(SO_4)_3 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$ or sodium aluminate ($NaAlO_2$) is added to water which hydrolyses to form a gelatinous precipitate of $Al(OH)_3$. This insoluble, flocculant precipitate descent through the water, absorbs and entangles very fine suspended impurities forming bigger flocs, which settle down easily. Moreover, coagulants like alum provide Al^{3+} ions which neutralize the negatively charged colloidal particles when they come closer and combine to form bigger particles. Due to the force of gravity, these bigger particles settle down. The most commonly used coagulants and their ideal pH range of use are summarized below :

	Chemical coagulants	Ideal pH range of use
(a)	$Al_2(SO_4)_3$ (Alum)	6.5 – 8.5
(b)	$NaAlO_2$ (sodium aluminate)	5.5 – 8.0
(c)	$FeSO_4$ (Ferrous sulphate)	> 8.5

(iv) **Filtration.** For further purification of water and for removing micro-organisms, odour, colour taste and fine-suspended particles, filtration is done. The process of filtration consists of percolating water through beds of fine sand, coarse sand and other granular material. There are different types of filters like gravity filter, slow sand filter, rapid sand filter and pressure filters; the rate of flow of water also increasing in that orders.

Operation of sand filter

A typical sand filter is shown in Fig. 15. It consists of a tank containing beds of fine sand (top layer), coarse sand, fine gravel and coarse gravel (bottom layer). The tank is provided with inlet for sedimented water and an underdrain channel at the bottom for exit of filtered water. Sedimented water entering the sand filter is distributed uniformly over the entire fine sand bed and it flows through the various beds slowly due to gravity. Due to retention of impurities in the pores, the sand pores get eventually clogged and the rate of filtration slowly decreases. When it becomes very slow, filtration is stopped and the bed is cleaned by scraping of a small layer of the sand bed (top layer) and replacing it with clean sand. The scrapped sand is washed with water, dried and stored for reuse at the time of next scrapping operation.

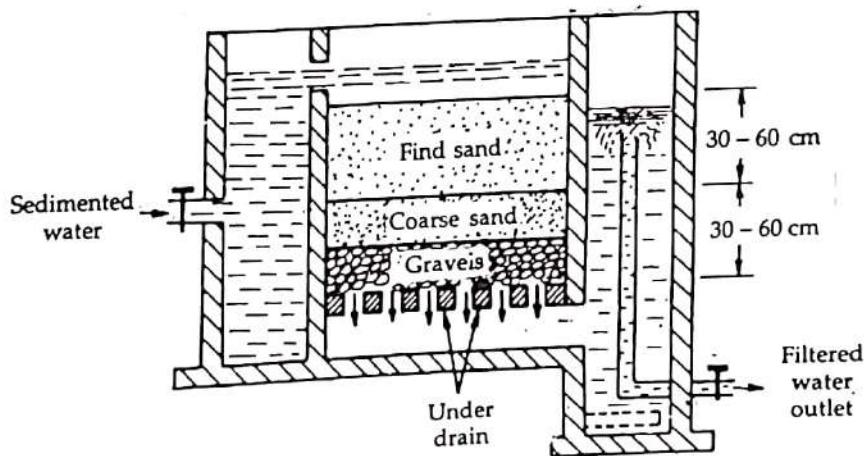


Fig. 15. Sand filter.

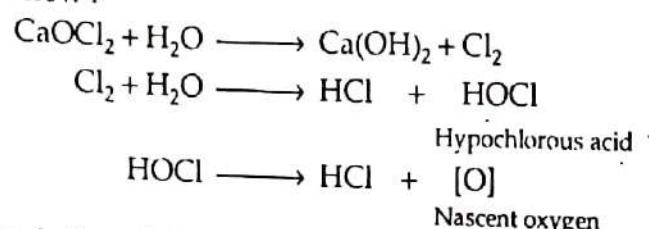
(v) **Removal of micro-organisms.** Even after filtration, water still contains a small percentage of disease producing (pathogenic) bacteria which must be removed or destroyed if the water has to be used for drinking or municipal purposes. The process of destroying/killing the pathogenic bacteria, micro-organisms etc. from the water to make it safe for use is known as *disinfection*. It does not ensure total destruction of all living organisms. On the other hand, *sterilisation* means complete destruction of all living organisms. It is done by boiling the water for a period of time. Sterilisation is a costly process and is used only by individuals particularly during the break up of epidemics in the town or city. It can not be employed in municipal water-works as it kills the bacteria only at the time of boiling but does not provide any protection against future contamination.

Characteristics of an ideal disinfectant

- (i) It should kill the disease producing micro-organisms quickly at room temperature,
- (ii) It should be inexpensive,
- (iii) It should not be toxic to human, and
- (iv) It should provide protection against any contamination in water during conveyance or storage.

Method of disinfection of water

(A) *By adding bleaching powder.* The chemical reaction of bleaching powder in water is given below :



It was earlier believed that nascent oxygen (thus liberated) destroys the pathogens by oxidation. In fact, enzymes in the cells of organisms get deactivated by their chemical reaction with hypochlorous acid. As enzymes are essential for the metabolic process of the micro-organisms so their inactivation results in the death of micro-organisms.

Drawbacks of using bleaching powder : (a) Excess of bleaching powder imparts bad taste and smell to treated water. Thus only calculated quantity of it should be used. (b) It is not stable so it deteriorates due to its continuous decomposition during storage. (c) It introduces calcium in water and thus increases hardness.

(B) *By Chlorination.* Chlorine is the most commonly used disinfectant in water treatment. It can be employed directly as a gas or in the form of concentrated solution in water. It produces hypochlorous acid, which is a powerful germicide. Apparatus used for disinfection by chlorine is known as chlorinator (see Fig. 16). It is a large tower which contains number of baffle plates. From its top, raw water and chlorine solution are introduced. These get thoroughly mixed during their passage through the tower. For filtered water, about 0.3 – 0.5 ppm of Cl_2 is sufficient. Disinfected water is taken out from the outlet at the bottom of chlorinator.

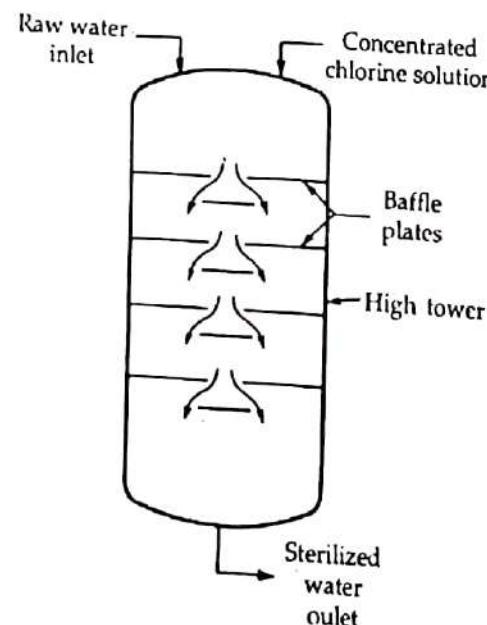


Fig. 16. Chlorinator.

WATER TREATMENT

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Factor affecting efficiency of chlorine

(i) *Temperature of water.* Death rate of micro-organisms (*i.e.*, number of micro-organisms destroyed per unit time) is directly proportional to temperature. Thus,

(ii) *Time of contact.* Death rate of micro-organisms by chlorine is proportional

to the number of micro-organisms remaining alive. Initially, the death rate is maximum and with time, it goes on decreasing.

(iii) *pH of water.* To kill same % of organisms, a small contact period is required at lower pH values (between 5-6.5).

Advantages of using chlorine as disinfectant

(i) The use of chlorine is more effective and economical,

(ii) It is stable, requires small space for storage and does not deteriorate on keeping,

(iii) It can be used at high as well as low temperatures,

(iv) It does not introduce any impurity in treated water

To sum up, chlorine is the most ideal disinfectant.

Disadvantages of using chlorine as disinfectant

(i) If excess of chlorine is added, it produces bad taste and disagreeable odour.

(As a result of chlorination of phenols, leading to the formation of chlorophenols, water acquires a peculiar odour.)

(ii) Excess chlorine produces irritation on mucus membrane,

(iii) It is not effective at higher pH values.

"The treated water should not contain more than 0.1-0.2 ppm of free chlorine".

Break-point chlorination

It means the chlorination of water to such an extent that living organism as well as other organic impurities in water are destroyed. It involves in addition of sufficient amount of chlorine to oxidise organic matter, reducing substances, and free ammonia in raw water, leaving behind mainly free chlorine which possesses disinfecting action against pathogenic bacteria. It is also known as *free-residual chlorination*. A typical relationship between the amount of chlorine added to water and the experimentally determined free residual chlorine is shown in Fig. 17.

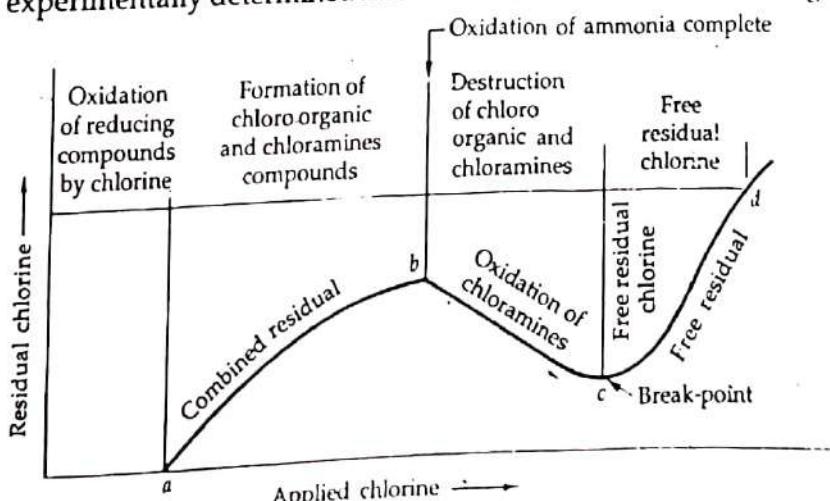


Fig. 17. Break-point chlorination curve:

Initially for lower doses of Cl_2 , there is no free residual chlorine since all the added chlorine gets consumed for doing complete oxidation of reducing substances present in water.

As the amount of chlorine dosage is increased, amount of residual chlorine (experimentally determined) also show steady increase. This stage corresponds to the formation of chloro-organic compounds without oxidising them.

At still higher dose of applied chlorine, oxidation of organic compounds and micro-organisms sets in consequently the amount of free residual chlorine also decreases. When the oxidative destruction is complete it reaches a minima.

After minima, the added chlorine is not used in any reaction. Thus, the residual chlorine keeps increasing in direct proportion to added chlorine.

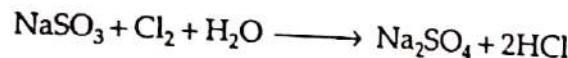
Hence, for effectively killing the micro-organisms, sufficient chlorine (corresponding to minima in the curve) has to be added. Addition of chlorine in such dosages is known as break-point or free residual chlorination.

Advantages of break-point chlorination

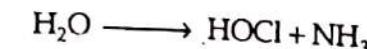
- (i) It ensures complete destruction of organic compounds which impart colour, bad odour and unpleasant taste to water;
- (ii) It completely destroys all the disease producing bacteria; and
- (iii) It prevents the growth of any weeds in water.

De-chlorination

Over chlorinated water can be de-chlorinated by passing it through bed of molecular carbon or by adding activated carbon to water and removing it by filtration after the reaction period. The excess chlorine can also be removed by the addition of small quantities of reducing substances like sulphur dioxide (SO_2), Na_2SO_3 , etc.



(C) *By using Chloramine (ClNH_2)*. Chloramine has better bactericidal action than chlorine



as it is more stable and does not produce any irritating odour. It is obtained by mixing chlorine and ammonia in 2:1 ratio.

(D) *Disinfection by Ozone (O_3)*. Ozone is made by passing silent electric discharge through cold and dry oxygen and is highly unstable, as it liberates nascent oxygen after breakdown $\text{O}_3 \rightarrow \text{O}_2 + [\text{O}]$

In fact ozone is an excellent and harmless disinfectant since it produces nascent oxygen which is a powerful oxidising agent. It oxidises the organic matter present in water and also kills the bacteria. Disinfection of water by ozone is carried out in ozone sterilizer, shown in Fig. 18.

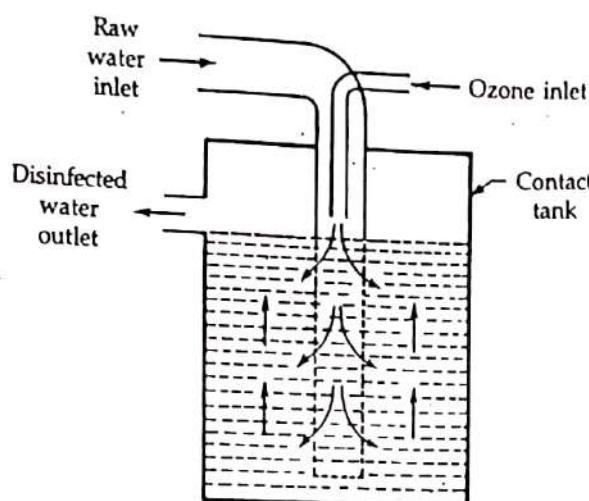


Fig. 18. Ozone sterilizer.

Ozone (2-3 ppm) is injected into the water and the two are allowed to come in contact in a sterilizing tank for about 10-15 minutes. The disinfected water is removed from the outlet at the top of sterilizer. The disinfected water is colourless, odourless and tasteless.

Disinfection of municipal water supply is not done by ozone because it is an expensive method.

(E) *By Ultra-violet light.* UV-light is used as a disinfectant especially for the swimming pool water. As no chemicals are used so this process is quite safe for human skin.

(F) *By potassium permanganate ($KMnO_4$).* $KMnO_4$ is very useful disinfectant especially for water of wells.

To sum up, *municipal water treatment* can be illustrated by *flow diagram* shown below in Fig. 19.

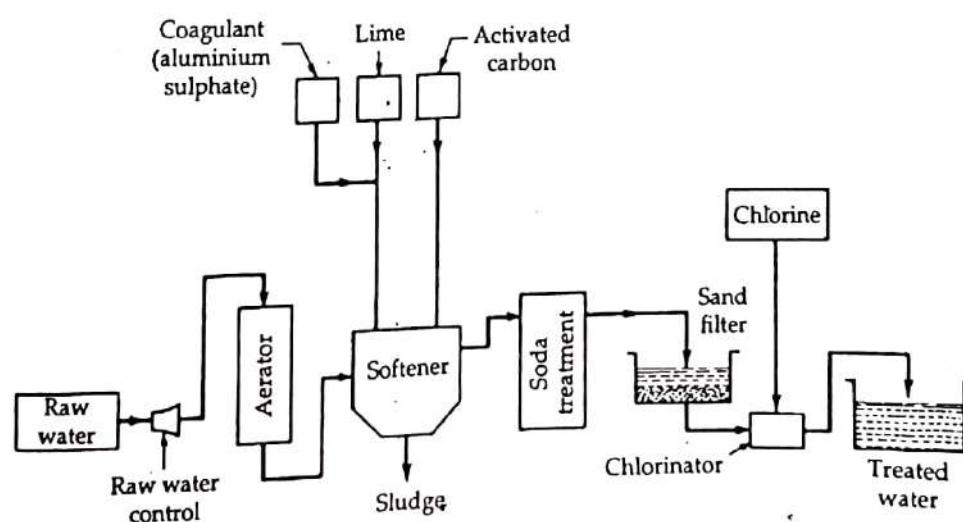
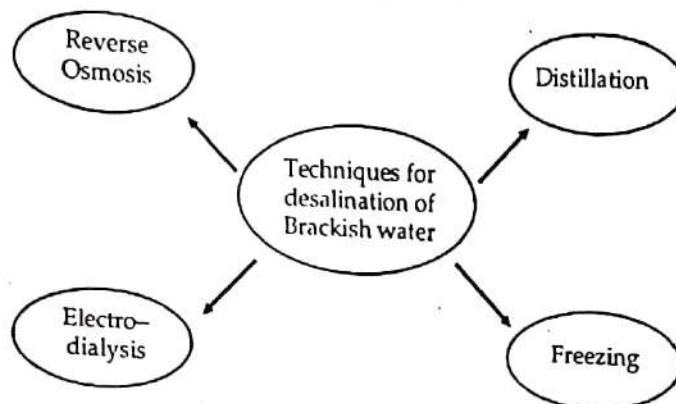


Fig. 19. Flow sheet diagram showing municipal water treatment.

14 DESALINATION OF BRACKISH WATER

Water containing high concentrations of dissolved solids with a peculiar salty or brackish taste is called *brackish water*. Sea water is an example for brackish water as it contains about 3.5% of dissolved salts. Before the removal of these salts, it is unfit for most of the domestic and industrial applications. The removal of dissolved solids (NaCl) from water is known as *desalination process*.

Commonly used techniques for the desalination of brackish water are summarized in figure and discussed thereafter.



Techniques for desalination of Brackish water

(a) **Distillation.** Huge evaporators are used for boiling the brackish water and vapours collected are condensed to get pure water. It is an expensive method for common practice.

(b) **Freezing.** Salt can be separated from brackish water by freezing. This is because when brackish water is cooled, salt is left in the mother liquor and ice crystals are formed. These crystals can be easily separated, washed and melted to get pure water. This method can be practised only in cold climatic areas and is expensive also.

(c) **Electrodialysis.** Electrodialysis is based on the fact that the ions present in saline water migrate towards their respective electrodes, through ion-selective membranes (natural or synthetic) under the influence of applied emf.

The method of electrodialysis can be illustrated with the help of Fig. 20. The unit consists of electrodes (cathode and anode) and thin and rigid ion-selective

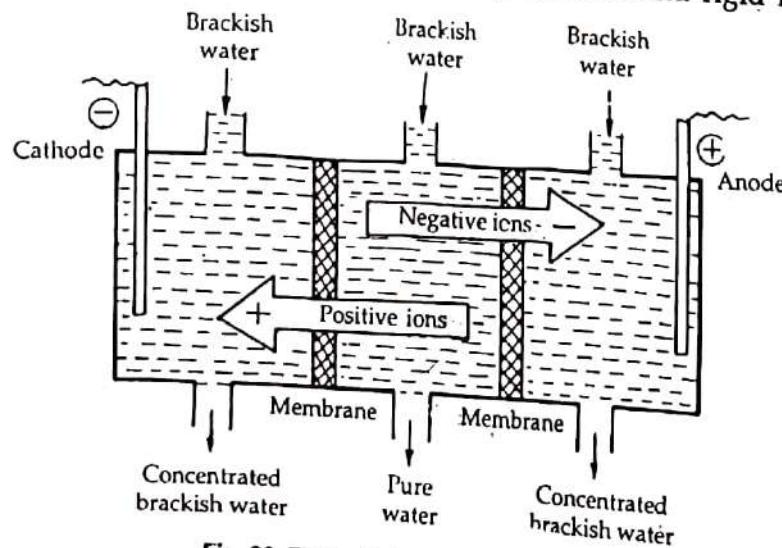


Fig. 20. Electrodialysis of brackish water

membranes which are permeable to either cation or anion. The anode is placed near the anion-selective membrane while the cathode is placed near the cation-selective membrane. [The *anion selective membrane* is embedded with positively charged functional groups such as R_4N^+ and is permeable to anions only. This is due to the presence of fixed functional groups, which carry positive charge, inside the membrane. Similarly, a *cation selective membrane* is based on polystyrene resin embedded with negatively charged functional groups such as RSO_3^- or $RCOO^-$ and is permeable only to cations, while anions stay away as they feel electrostatic repulsion]. Under the influence of an applied emf across the electrodes the cations (Na^+) move towards the cathodes through cation selective membrane and anions (Cl^-) move towards the anode through anion selective membrane (see Fig. 20) the net result is the depletion of ions in the central compartment while it increases in the two side compartments. Desalinated water is periodically drawn out from the central compartment while the concentrated brackish water is replaced by fresh samples.

For practical purposes, an electrodialysis cell is used. It consists of large number of paired sets of ion-selective membranes, see Fig. 21. Under a pressure of about $5-6 \text{ kg/m}^2$, saline water is passed in and we get alternate streams of pure water and concentrated brackish water. The principle is similar to that discussed above:

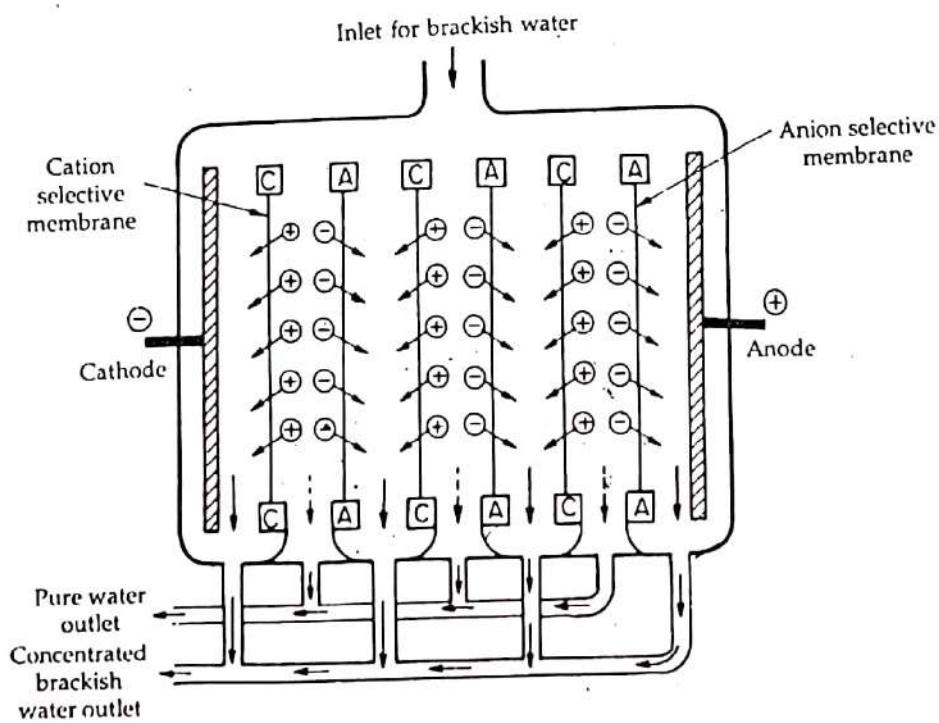


Fig. 21. Electrodialysis cell.

Advantages of desalination by electrodialysis

- (i) This process is economical as per the capital cost and operational expenses are concerned.
- (ii) The unit is compact and the method is best suited.

(d) *Reverse Osmosis.* Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane. (Semi-permeable membrane is selective membrane which does not permit the passage of dissolved solute particles.) The flow continues till the concentration is equal on both the sides. The driving force for osmosis is *osmotic pressure*. However, if a *hydrostatic pressure* in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis of *reverse osmosis*.

For practical purposes, semi-permeable membrane based on thin films of cellulose acetate, polymethyl acrylate and polyamide polymers are used. A pressure of the order of $15\text{-}40 \text{ kg/cm}^2$ is applied (Fig. 22) for separating the water (pure solvent) from its contaminants. The process is also known as *super-or hyper-filtration*.

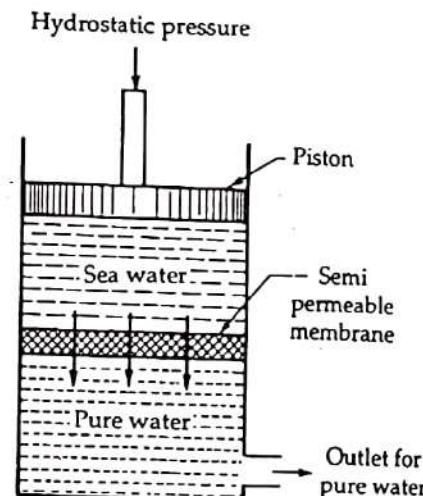


Fig. 22. Reverse Osmosis cell.

Advantages

- (i) Colloidal SiO_2 can be removed by reverse osmosis which even cannot be removed by demineralisation;
- (ii) It is simple and reliable process;
- (iii) Capital and operating expenses are low;
- (iv) The life of the semi-permeable membrane is about 2 years and it can be easily replaced within a few minutes, thereby nearly uninterrupted water supply can be provided.

15 CHEMICAL ANALYSIS OF WATER

15.1 Dissolved Oxygen

It is usually determined by *Winkler's method*. It is based on the fact that dissolved oxygen oxidises potassium iodide (KI) to iodine. The liberated iodine is titrated against standard sodium thiosulphate (also known as hypo) solution using

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starch as indicator. Since dissolved oxygen in water is in the molecular state, it as such cannot oxidise KI. Hence, manganese hydroxide is used as an oxygen carrier to bring about the reaction between KI and oxygen. Manganese hydroxide, in turn, is obtained by the action of KOH on manganese sulphate.



The oxidising agents present in water such as nitrate and ferric ions oxidize Γ to I_2 and give positive error. To overcome this problem, sodium azide is used in alkaline iodide solution to decompose the nitrite or sulphite.



This is known as *Alsterberg's modification*.

The reducing agents like Fe^{2+} ; SO_3^{2-} or S^{2-} can reduce I_2 to Γ and produce negative error. To overcome this problem, KMnO_4 is used for pretreatment. Excess of KMnO_4 is removed by reaction with potassium oxalate. This is known as *Rideat-stewart modification*.

Procedure: Take 250 mL of sample water in a bottle avoiding as far as possible contact with air. Immediately add 2 mL of manganous sulphate solution and 2 mL of alkaline KI solution. Stopper the bottle and shake them thoroughly. When the precipitate is settled, add 2 mL of conc. HCl and shake the bottle until the ppt has completely dissolved. Allow the yellow solution to stand for 5 minutes. Take 100 mL of this solution and titrate against N/100 hypo solution using starch as indicator. End point is the disappearance of blue colour. Let V_2 mL of hypo solution is used.

$$\text{Normality of Hypo solution} = N_2 = \frac{1}{100} \text{ N}$$

$$\text{Volume of sample water taken for titration} = V_1 = 100 \text{ mL}$$

$$\therefore \text{Normality of sample water} = N_1 = \frac{N_2 V_2}{V_1} = \frac{\frac{1}{100} \times V_2}{100}$$

Since equivalent weight of $\text{O}_2 = 8$

Hence, strength of oxygen = $N_1 \times 8 \text{ gm/L}$

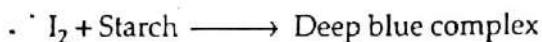
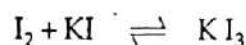
$$= \frac{V_2}{10,000} \times 8 \text{ gm/L}$$

$$= \frac{V_2}{10,000} \times 8 \times 1000 \text{ mg/L}$$

\Rightarrow Amount of dissolved oxygen = $0.8 V_2 \text{ ppm}$

15.2 Free Chlorine

Its estimation is based on the oxidation of potassium iodide by free chlorine, which liberates an equivalent amount of iodine. This liberated iodine is titrated with hypo solution using starch as indicator. End point is the disappearance of blue colour.



Procedure :

- In a 250 mL stoppered conical flask, take about 10 mL of 10% KI solution.
- Stopper the flask and shake it vigorously.
- Remove the stopper and wash the adhering solution into flask, with about 5-10 mL of distilled water.
- Titrate this solution with N/50 Hypo solution using starch as indicator.

End point : Disappearance of blue colour.

Calculations :

$$N_1 V_1 \text{ of water sample} = N_2 V_2 \text{ of hypo solution}$$

$$N_1 \times 50 = N/50 \times V_2$$

$$\text{Hence, normality of (water sample or free chlorine)} = \frac{V_2}{2500} \text{ N}$$

and strength of free chlorine = $N_1 \times 35.5 \text{ gm/L}$

$$= \frac{V_2}{2500} \times 35.5 \times 1000 \text{ mg/L}$$

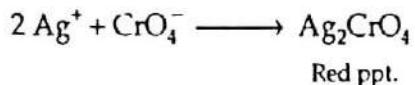
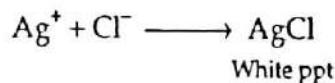
\Rightarrow Strength of free chlorine = $14.2 V_2 \text{ ppm}$.

15.3 Chlorides

The chlorides are estimated by titrating the water sample with standard solution of silver nitrate using potassium chromate as indicator (*Mohr's method*).

The solubility product of AgCl is lower than that of Ag_2CrO_4 . Thus, so long the Cl^- ions are available the less soluble AgCl is precipitated; the Ag^+ ions are not

sufficient for Ag_2CrO_4 to be precipitated. As soon as all the Cl^- ions have been precipitated, even a drop of AgNO_3 added (in excess) gives a red precipitate of silver chromate (Ag_2CrO_4).



Procedure:

(1) Pipette out 100 mL of given Cl^- solution in conical flask add 1 mL of K_2CrO_4 indicator.

(2) Slowly add $\left(\frac{N}{50}\right)$ AgNO_3 solution from the burette. Initially, white ppt. is obtained. Continue the addition of silver nitrate till permanent reddish brown colour is obtained. Let V_2 mL of AgNO_3 gets consumed till end point.

Calculations :

$$(\text{Volume} \times \text{Normality}) \text{ of } \text{Cl}^- = (\text{Volume} \times \text{Normality}) \text{ of } \text{AgNO}_3$$

$$\therefore 100 \times N_1 = V_2 \times \frac{N}{50} \Rightarrow N_1 = \frac{V_2}{5000} N$$

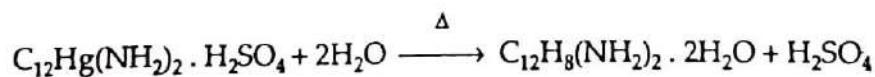
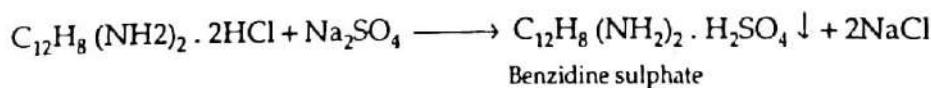
$$\text{Strength of } \text{Cl}^- \text{ ions} = N_1 \times 35.5 \text{ gm/L} = N_1 \times 35.5 \times 1000 \text{ mg/L (or ppm)}$$

$$= \frac{V_2}{5000} \times 35.5 \times 1000 = 7.1 V_2 \text{ ppm}$$

$$\therefore \text{Strength of } \text{Cl}^- \text{ ions} = 7.1 V_2 \text{ ppm.}$$

15.4 Sulphates

The estimation of sulphate ions in water is based on their reaction with benzidine hydrochloride to form benzidine sulphate which is insoluble in cold and soluble in hot H_2SO_4 .



The free sulphonic acid is then titrated against a standard NaOH solution using phenol phthalein as indicator.

Procedure:

- Add 10 mL of benzidine hydrochloride solution to 100 mL of water sample.
- Mix the contents thoroughly and allow the precipitate to settle.
- With the help of whatmann filter paper (No. 4), filter the precipitate.
- Wash the ppt on filter paper with minimum of distilled water to free of acid.

(e) Transfer the ppt along with filter paper to a conical flask.

(f) Add 50 mL of distilled water to above flask and warm the contents to about 50°C to dissolve the precipitate.

(g) Titrate the liberated H₂SO₄ against NaOH (N/50) using phenolphthalein indicator (2-3 drops).

Let V₂ mL of N/50 NaOH solution gets consumed till end pt.

End point. Appearance of permanent pink colour.

Calculations :

$$(\text{Volume} \times \text{Normality}) \text{ of SO}_4^{2-} = (\text{Volume} \times \text{Normality}) \text{ of NaOH}$$

$$\Rightarrow 100 \times N_1 = V_2 \times N/50$$

$$\Rightarrow N_1 = \frac{V_2}{5000} N$$

∴ Strength of SO₄²⁻ ions

$$= N_1 \times \frac{96}{2} \text{ gm/L} = N_1 \times 48 \times 1000 \text{ mg/L}$$

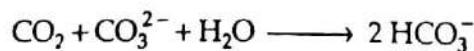
$$= N_1 \times 48 \times 1000 \text{ ppm}$$

$$= \frac{V_2}{5000} \times 48 \times 1000 \text{ ppm} = 9.6 V_2 \text{ ppm}$$

Hence strength of SO₄²⁻ ions = 9.6 V₂ ppm.

15.5 Dissolved CO₂

Carbon dioxide can be determined by titrating with a standard solution of Na₂CO₃. The estimation is based on the following reaction :



The completion of the reaction is indicated by the appearance of pink color by using phenolphthalein as indicator.

Procedure :

(a) In a 250 mL conical flask, pipette out 25 mL of given water sample.

(b) Add 2-3 drops of phenolphthalein indicator and titrate against N/50 Na₂CO₃ solution until the pink colour persists for at least 30 seconds. Take atleast three concordant readings.

(c) Let V mL of N/50 Na₂CO₃ gets consumed till end point.

End Point : Appearance of pink colour which persists for atleast 30 seconds.

Calculations :

$$(\text{Volume} \times \text{Normality}) \text{ of CO}_2 = (\text{Volume} \times \text{Normality}) \text{ of Na}_2\text{CO}_3$$

$$\Rightarrow (25 \text{ mL} \times N_1) = V \times \frac{1}{50}$$

Therefore, Normality of the sample w.r.t. $\text{CO}_2 = N_1 = \frac{V}{50 \times 25}$

$$\text{Strength} = \frac{V}{50 \times 25} \times 22 \text{ gms/L} \times \frac{1000 \text{ mg}}{1 \text{ gm}}$$

or free $\text{CO}_2 = \text{Strength} = 17.6 V \text{ mg/L}$

15.6 Total Dissolved Solids (TDS)

The dissolved solid content of a sample of water is important in deciding whether the water is suitable for boiler feed purposes. Dissolved solids denote mainly the various kinds of minerals present in water. However, some organic substances present in water also contribute to TDS.

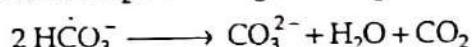
It can be determined by evaporating an aliquot (100 mL) of the filtered sample to dryness and further heating the residue to constant weight at $110^\circ \pm 10^\circ\text{C}$. After cooling (in dessicator), the dish is weighed.

Total dissolved solids present in 100 mL of water

$$\begin{aligned} &= \text{weight of (dish + residue)} - \text{weight of dish} \\ &= w \text{ (gms.)} \end{aligned}$$

$$\therefore \text{TDS (in ppm} = \frac{w}{100} \times 10^6 = 10^4 w \text{ ppm}$$

Limitation : During this heating, the bicarbonate ions are decomposed to give carbonate ions and gaseous CO_2 , according to the equation :



The bicarbonate ions thus yield only carbonate ions.

16 WASTE WATER TREATMENT

The main objectives of waste water treatment are :

- (i) To make sewage inoffensive so that it causes no odour,
- (ii) To prevent the destruction of aquatic life in rivers, canals, etc. into which waste water is generally discharged.
- (iii) To reduce or eliminate danger to the public health by possible contamination of water supplies.

Artificial treatment methods are generally used for waste water treatment.

The main features of this method are :

- (a) To reduce the solid contents of the waste water,
- (b) To remove all nuisance-causing elements, and
- (c) To change the character of the waste water so that it safely be discharged in river, sea or applied on land.

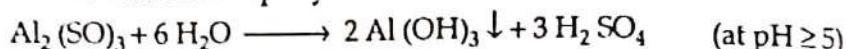
The following steps are generally employed in the artificial sewage treatment :

(A) Preliminary Process

The preliminary processes cause removal of large and coarse solids and inorganic matter suspended in waste water. The waste water is passed through mesh screens to remove gravels, coarse solids, silt, etc. Moreover, for the removal of large suspended floating matter, the waste water is passed through bar screens.

(B) Settling Process

The suspended inorganic and organic solids from the waste water are largely removed by settling process. In settling process, continuous flow type sedimentation tanks are employed. Sometimes, prior to sedimentation, chemical treatment is given to waste water. This helps in more rapid and complete removal of suspended matter. Alum, ferrous sulphate etc. are chemicals which are used for chemical treatment. These chemicals can produce large gelatinous flocs, which entrap finely divided organic matter and settle rapidly.

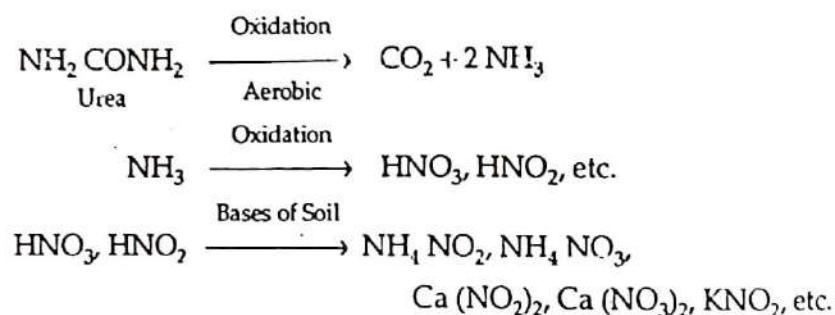


It is important to note that chemical coagulants have the ability to remove colloidal materials.

(C) Biological Treatment Process

It is essentially a aeration process in which aerobic chemical oxidation takes place. In this process, aerobic conditions are maintained all the times by filtering waste water through specially designed sprinkling filters. During this process, the carbon of the organic matter is converted into CO_2 ; the nitrogen into NH_3 and finally into nitrites and nitrates. The dissolved bases, present in the waste water, then form nitrite and nitrate of ammonium, and calcium nitrate etc.

Thus :



Mostly Trickling filters are employed for biological treatment process. Trickling filters are either circular or rectangular in shape and about 2 m deep (Fig. 23). They are filled with any one of the following : Graded clinkers ; broken bricks, blast furnace slag, large anthracite coal or coarse, crushed rock.

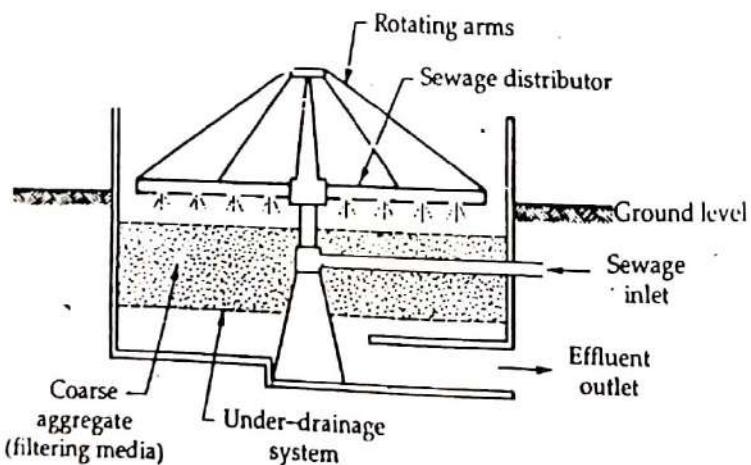


Fig. 23. Trickling filter.

WATER TREATMENT

In the bottom of bed, the underdrain system is provided to collect affluent. Rotating arm distributions are used for delivering waste water to the filters. As the trickled waste water starts percolating downwards, through the filtering media, micro-organism present in waste water grow on the surface of aggregates, using organic material of the sewage as food. Aerobic conditions are maintained and purified water is removed from the bottom. About 90% BOD is removed by normal trickling filters.

Activated Sludge Process

This process is based on the principle that if enough oxygen or air is passed through waste water containing aerobes, slow but complete aerobic oxidation occurs. This oxidation process can be quickened, if this aeration is carried out in the presence of a part of sludge from the previous oxidation process. This sludge is known as *activated sludge* since it contains organic matters inhabited by numerous bacteria, etc.

The activated sludge process consists in mixing the sedimented waste water with proper quantity of activate sludge. This mixture is then sent to the aeration tank, in which the mixed liquor is simultaneously aerated and agitated for 4 to 6 hours. Oxidation of the suspended organic matter takes place during this aeration process. The affluent, after aeration is sent to sedimentation tank. In this tank, sludge is deposited and clean and non-putrefying liquid (*i.e.*, a liquid which is free from bacteria) is drawn off. For seeding fresh batch of sewage, a part of the settled sludge is sent back while the remainder is disposed off by either dumping in sea or spreading uniformly over soil, followed by ploughing in or digestion process.

In this digestion process, the sludge is kept in the absence of air for a prolonged period of about 30 days in a closed tank. The sludge under these conditions suffers anaerobic decomposition yielding gases like methane, hydrogen sulphide, ammonium sulphide and phosphine.

The waste water treatment process is schematically summarized below in Fig. 24.

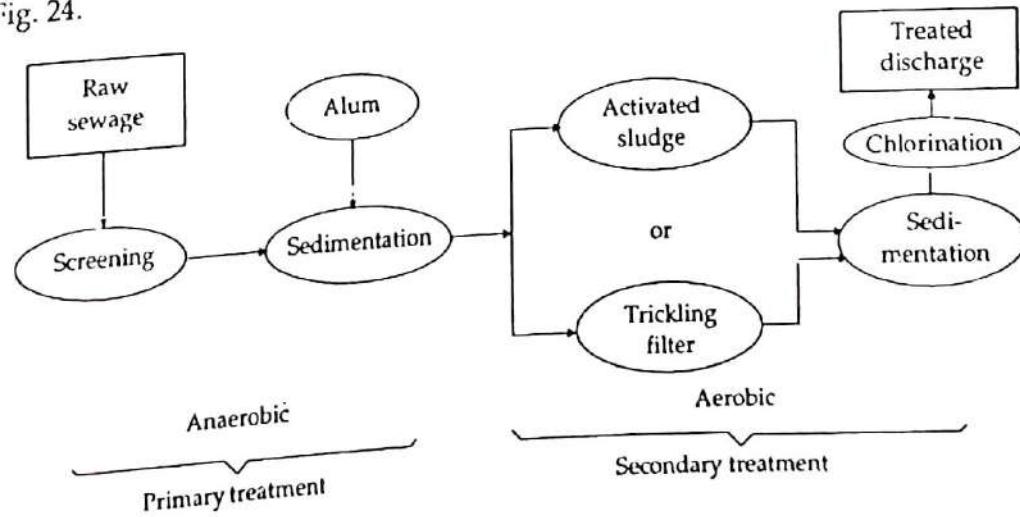


Fig. 24. Flow diagram for sewage treatment.

17 COOLING WATERS (Langlier Index)

One of the major applications of water in industry is for cooling purposes. Requirements of water used for cooling are :

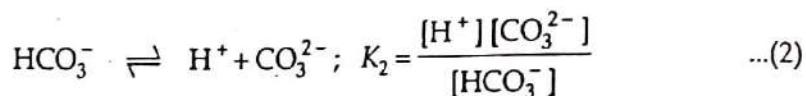
- It should be non-scaling,
- It should be non-corrosive and
- It should be non-staining.

The knowledge of the **Langlier Index** (CaCO_3 saturation index) helps in the prediction of the scaling or corrosive behaviour of natural waters. Water is said to be stable when it neither dissolves nor deposits CaCO_3 . Such stable water will neither remove coatings of CaCO_3 that may protect pipes against corrosion nor lay down deposits of CaCO_3 that may clog pipes.

Let K_{sp} is the solubility product of CaCO_3 ,

$$\text{i.e., } K_{sp} = [\text{Ca}^{2+}] [\text{CO}_3^{2-}] \Rightarrow [\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Ca}^{2+}]} \quad \dots(1)$$

And K_2 is the dissociation constant of the reaction



From equations (1) and (2),

$$\begin{aligned} [\text{H}^+] &= \frac{K_2 [\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{K_2 [\text{HCO}_3^-]}{K_{sp}/[\text{Ca}^{2+}]} = \frac{K_2}{K_{sp}} [\text{HCO}_3^-] [\text{Ca}^{2+}] \\ \Rightarrow -\log [\text{H}^+] &= -\log \left(\frac{K_2}{K_{sp}} \right) - \log [\text{HCO}_3^-] - \log [\text{Ca}^{2+}] \\ \Rightarrow (\text{pH})_s &= \log (K_{sp}/K_2) - \log [\text{HCO}_3^-] - \log [\text{Ca}^{2+}] \end{aligned} \quad \dots(3)$$

The **Langlier Index (LI)**, is defined as the algebraic difference between the actual pH and the saturation pH.

$$\text{LI} = \text{pH} - (\text{pH})_s \quad \dots(4)$$

The saturation pH $(\text{pH})_s$ is calculated by using the formula given in equation (3).

Significance of Langlier Index (LI) :

(A) If $\text{LI} = 0$, the water is stable, i.e., it neither deposits scales of CaCO_3 nor dissolve thin protective coating of CaCO_3 ;

(B) If LI is positive, then it indicates that water has scale-forming tendencies ;

(C) If LI is negative, then it indicates that water has corrosive tendencies.

For cooling purposes, it is usual to adjust the value of LI to be between 0.6 to 1.0.

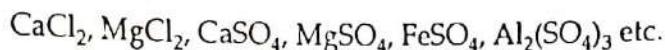
Sea water as a coolant is used only 'once-through' and then discharged to waste. However, cooling waters which are recirculated and used are usually subjected to cold lime process so as to remove only the carbonate hardness.

To avoid corrosion effects, chromates and dichromates are used as corrosion inhibitors in water used as coolant. Sludge (clay and sand) and algae often clog the condensers and heat exchangers. Periodic chlorination is done to counteract the growth of algae and mechanical methods are adopted to remove the sludge.

SOLVED QUESTIONS

Q. 1. What is permanent hardness? Write the constituents responsible for permanent hardness.

Ans. It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Hence, the constituents responsible for permanent hardness are :



Unlike temporary hardness, permanent hardness is not destroyed on boiling.

Q. 2. What is colloidal conditioning?

Ans. Scale formation can be avoided in low pressure boilers by adding substances like kerosene, tannin, agar-agar, etc. which get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by blow-down operation.

Q. 3. Give formula to calculate equivalents of CaCO_3 .

...(1)

Ans. Equivalents of CaCO_3

$$\frac{\left[\begin{array}{l} \text{Mass of hardness} \\ \text{producing substance} \\ (\text{in mg/L}) \end{array} \right] \times \left[\begin{array}{l} \text{Chemical equivalent} \\ \text{of } \text{CaCO}_3 \\ (=50) \end{array} \right] \times 2}{\left[\text{Chemical equivalent of hardness producing substance} \right] \times 2}$$

...(2)

$$= \left[\begin{array}{l} \text{Mass of hardness} \\ \text{producing substance} \\ \text{in mg/L} \end{array} \right] \times \left[\frac{100}{2 \times \text{Chemical equivalents of}} \right. \\ \left. \text{hardness producing substance} \right]$$

...(3)

$$= \left[\begin{array}{l} \text{Mass of hardness} \\ \text{producing substance} \\ \text{in mg/L} \end{array} \right] \times (\text{Multiplication factor}) \text{ in } \frac{\text{mg}}{\text{L}} \text{ or ppm}$$

Q. 4. Briefly describe carbonate conditioning method for water softening.

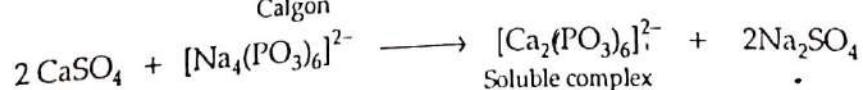
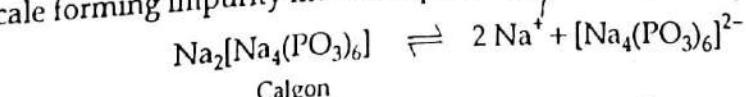
Ans. In *low-pressure boilers*, scale-formation can be avoided by adding sodium carbonate to boiler water, when salts like CaSO_4 etc. are converted into calcium carbonate in equilibrium.



Hence deposition of CaSO_4 as scale does not take place and loose sludge of CaCO_3 can be removed by blow-down operation.

Q. 5. Discuss calgon conditioning.

Ans. It involves in adding sodium hexa meta phosphate (also known as calgon) to boiler water to prevent the scale and sludge formation. Calgon converts the scale forming impurity like CaSO_4 into soluble complex compound.



Q. 6. Give the names of any two coagulants used in Lime-soda process of water softening.

Ans. (i) Sodium aluminate (Na AlO_2), (ii) Alum [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24 \text{H}_2\text{O}$].

Q. 7. Mention the name of impurities present in natural water.

Ans. Impurities present in natural water are :

- (a) Suspended Impurities,
- (b) Colloidal Impurities and
- (c) Dissolved Impurities.

Q. 8. Boiler feed water should be free from dissolved gases as these gases can cause corrosion. Give the names of three such gases.

Ans. (i) Oxygen (O_2), (ii) Carbon dioxide (CO_2), (iii) Sulphur dioxide (SO_2).

Q. 9. Is it possible to remove permanent hardness by either boiling or adding lime alone ?

Ans. No.

Q. 10. Why is demineralization process preferred over zeolite process for softening of water for use in boilers ? Or

Why is water softened by zeolite process unfit for use in boilers ?

Ans. Because zeolite softened water contains large quantities of sodium salts like $NaCl$, Na_2SO_4 etc., which can lead to caustic embrittlement.

Q. 11. CO_2 should not be present in boiler feed water. Why ?

Ans. Carbon dioxide forms carbonic acid (H_2CO_3). As the boiler wall material can be attacked slowly by carbonic acid and become weaker and weaker progressively, so CO_2 should not be present in boiler feed water.

Q. 12. (a) What is meant by softening of water ?

(b) Why is water softened before using in boiler ?

Ans. (a) Softening of water is the process of removing hardness-producing salts from water.

(b) Water should be properly softened before feeding it to boiler otherwise it may cause various boiler problems like

- (i) scale and sludge formation,
- (ii) boiler corrosion,
- (iii) priming and foaming etc.

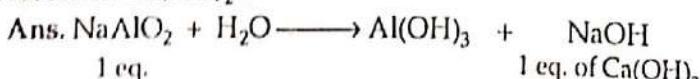
Q. 13. Are coagulants also used in hot lime-soda process ? Give reasons.

Ans. No, because reaction proceeds faster in hot lime-soda process and the precipitate and sludge formed settle down rapidly. Thus, no coagulants are required in hot lime-soda process.

Q. 14. If silica is present in water, what harmful effects it can cause ?

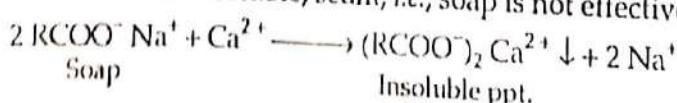
Ans. If silica is present in water, it causes the formation of very firmly sticking deposits of calcium silicate and magnesium silicate scales in the boiler which are very difficult to remove.

Q. 15. Why is presence of $NaAlO_2$ in water equivalent to presence of equivalent of $Ca(OH)_2$?



Q. 16. If the water contains $Ca^{2+}_{(aq)}$ and $HCO_3^-_{(aq)}$ will it be hard water or soft water ? Give reason.

Ans. The given water is hard water. Because when such water is treated with soap solution, it will form white insoluble, scum, i.e., soap is not effective in it.



Moreover, HCO_3^- ions revert to CO_3^{2-} ions on heating and they form precipitate of CaCO_3 by reacting with Ca^{2+} ions in boiler/kettles.

Q. 17. What do you understand by water softening? Why it is an essential process?

Ans. The process whereby we remove or reduce the hardness of water, irrespective of whether it is temporary or permanent is termed as 'softening' of water. It is very essential process since hard water is unsuitable for domestic as well as industrial use. One of the most important applications of water is in steam production for the generation of electricity. For this water need to be fed to industrial boilers. We just cannot feed any water into the industrial boilers because it has been identified that hard water creates large number of problems like scale and sludge formation, priming and foaming etc.

Q. 18. Differentiate between internal and external water treatment methods.

Ans. Differences between Internal and External treatment methods are tabulated below :

S.No.	Internal treatment	External treatment
1.	It is carried out in the boiler itself.	It is carried out outside the boiler, before water enters the boiler.
2.	It is required in low-pressure boilers.	It is required in high-pressure boilers.
3.	It is a corrective method.	It is a preventive method.
4.	It includes colloidal conditioning, carbonate conditioning, Phosphate conditioning, Calgon conditioning etc.	It includes zeolite process, lime-soda process and ion-exchange process.

Q. 19. (a) What is the principle of lime-soda process? (b) Why should we also use coagulants along with lime and soda?

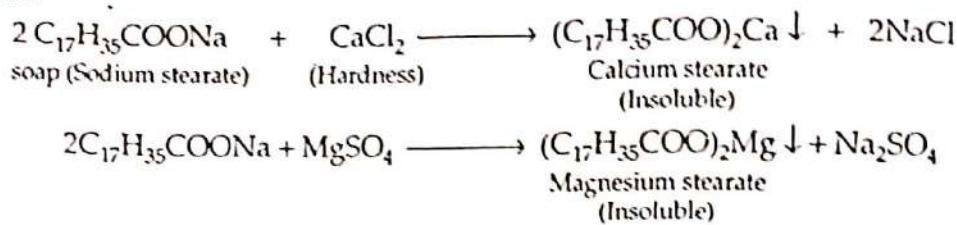
Ans. (a) The basic principle of this process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling and filtration. For this purpose, a suspension of milk of lime, $\text{Ca}(\text{OH})_2$, together with a calculated amount of sodium carbonate, Na_2CO_3 (soda) is added in requisite amount. Proper mixing of the chemicals and water is carried out. Calcium carbonate, CaCO_3 and magnesium hydroxide $\text{Mg}(\text{OH})_2$ so precipitated are filtered off.

(b) At room temperature, the precipitates formed are very fine. They do not settle down easily and cause difficulty in filtration. If small amount of coagulants like Alum [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$]; Aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3$] or Sodium aluminate [NaAlO_2] are added, they hydrolyse to precipitate of aluminium hydroxide which entraps the fine precipitate of CaCO_3 and $\text{Mg}(\text{OH})_2$. Thus coagulant helps in the formation of coarse precipitates.

Q. 20. Why does hard water consumes a lot of soap?

Ans. This is due to presence in water of certain salts of Ca, Mg and other heavy metal ions like Al^{3+} , Fe^{3+} and Mn^{2+} dissolved in it. A sample of hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but on the other hand forms insoluble white scum or precipitate which do not possess any detergent action. This is due to the

formation of insoluble soaps of calcium and magnesium. Typical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below :



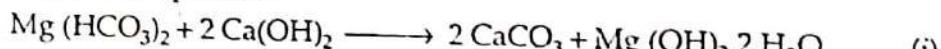
Q. 21. Why do we express hardness of water in terms of CaCO_3 equivalent ?

Ans. Although hardness of water is never present in the form of calcium carbonate because it is insoluble in water, hardness of water is conveniently expressed in terms of equivalent amount (*equivalents*) of CaCO_3 .

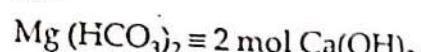
The reason for choosing CaCO_3 as the standard for reporting hardness of water is the ease in calculations as its *molecular weight is exactly 100*. Moreover, it is the most insoluble salt that can be precipitated in water treatment.

Q. 22. Why does magnesium bicarbonate require double amount of lime for softening ?

Ans. Given hard water contains $\text{Mg}(\text{HCO}_3)_2$ so for its softening we require lime, according to the equations :



Thus, from equation Requirement of lime for 1 mol



Q. 23. Write the constituents responsible for the permanent hardness of water. Discuss one treatment method.

Ans. Constituents responsible for permanent hardness are : CaCl_2 , MgCl_2 , CaSO_4 , MgSO_4 , FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$, etc.

Q. 24. Give reasons why alkalinity of water cannot be due to the simultaneous presence of OH^- , CO_3^{2-} and HCO_3^- .

Ans. This is because, OH^- and HCO_3^- ions react to form CO_3^{2-} ions according to :



Q. 25. 20 mL of a water sample was treated with excess of 10% KI solution and then titrated against N/100 hypo solution using starch as indicator. 2.5 mL of hypo was used for starch end point. Calculate the amount of chlorine in water.

Ans. $N_1 V_1$ of water = $N_2 V_2$ of hypo solution

$$\Rightarrow N_1 \times 20 = \frac{N}{100} \times 2.5$$

Hence, normality of water sample having chlorine (N_1)

$$= \frac{1}{100} \times 2.5 \times \frac{1}{20} N = 0.0125 N$$

\therefore Amount of chlorine in water = $N_1 \times 35.5$ gms/L

$$= 0.0125 \times 35.5 = 0.444 \text{ gms/L}$$

WATER TREATMENT

Q. 26. Water should not be soft for drinking purposes, why?

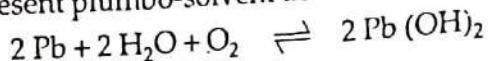
Ans. Water should not be soft for drinking purposes because soft water is *plumbo-solvent*, i.e., it attacks lead used in plumbing.

A partial softening leaving a residual total hardness of about 85 ppm CaCO_3 equivalents is generally used for drinking purposes.

Q. 27. Is there any relationship between $[\text{HCO}_3^-]$ and plumbosolvency?

Ans. In the presence of HCO_3^- ions, the solubility of lead in water is diminished.

We can represent plumbosolvent action as ... (1)

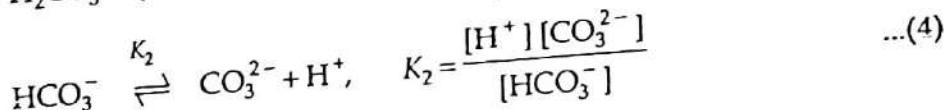
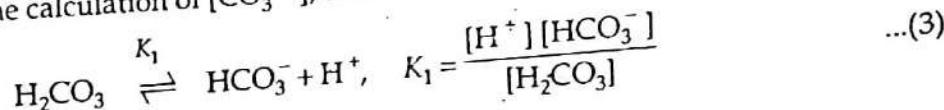


In a solution containing free H_2CO_3 , dissolved CO_2 , Pb^{2+} and NaHCO_3 ,

$$[\text{Pb}^{2+}] [\text{CO}_3^{2-}] = K_{sp} \quad \dots(2)$$

$$\Rightarrow [\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]}$$

For the calculation of $[\text{CO}_3^{2-}]$, consider the following equilibria :



From equations (3) and (4),

$$\frac{K_1}{K_2} = \frac{[\text{HCO}_3^-]^2}{[\text{CO}_3^{2-}] [\text{H}_2\text{CO}_3]} \Rightarrow [\text{CO}_3^{2-}] = \frac{K_2}{K_1} \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3]}$$

Substituting this value of $[\text{CO}_3^{2-}]$ in equation (2), we get

$$[\text{Pb}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = K_{sp} \frac{K_1}{K_2} \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]^2}$$

Hence, the larger the $[\text{HCO}_3^-]$, the lower the concentration of dissolved Pb^{2+} .

Q. 28. What is 'Railway process'?

Ans. Water required to raise steam in locomotives should have low hardness and should be alkaline to reduce corrosion.

The required water is obtained by first adding excess of lime, then excess soda (Na_2CO_3) is added to convert the excess lime into NaOH . This is known as the 'Railway process'.

Q. 29. How scales are formed in the boilers?

Ans. *Explanation by Hall.* On a heated surface, when a bubble of steam is formed, the salts contained in the solution get deposited along the overheated peripheral region of the bubble. When the bubble leaves the surface or bursts deposits the salt as a scale. Deposition of scale proceeds, as evaporation continues.

Explanation by Partridge. When steam bubbles form so rapidly in a given place that the solid deposited under one is not completely washed away by water before the formation of a subsequent bubble, then the scale is produced.

Q. 30. Why the silica, oil and dissolved gases should not be present in the boiler feed water?

Ans. (i) In low pressure boilers (upto 250 psi), small quantities of silica are not objectionable.

But in medium (upto 800 psi) and high (> 800 psi) pressure boilers, silica forms troublesome calcium silicate scale, silica scale or sodium aluminium silicate scale. That's why silica is not desirable in boiler water.

(ii) Oil is not desirable in boiler water because even small quantities of oils form heat-insulating films on the boiler material. The oil may be hydrolyzed to give fatty acids, which may bring in problems of corrosion.

(iii) Dissolved gases like O_2 , H_2S and SO_2 are not desirable in boiler water because oxygen promotes corrosion and H_2S and SO_2 gases attack the boiler material.

Q. 31. Give a table as an overview for waier treatment.

Ans.

Table. Water Treatment (An overview)

<i>Constituent</i>	<i>Difficulties caused</i>	<i>Treatment method(s)</i>
1. Suspended solids	Cause deposit in boilers, heat-exchangers, water lines etc.	Coagulation, settling and filtration.
2. Dissolved solids	Cause foaming in boilers, and process interference.	Any softening method like lime-soda, zeolite or demineralization.
3. Turbidity	Imparts unsightly appearance to water, deposits in water lines, process equipment, etc.	Coagulation, settling and filtration.
4. Hardness	Forms curds with soap, interferes with dyeing, causes scale formation in boilers, heat-exchangers, pipelines etc.	Internal boiler water treatment, softening.
5. Alkalinity	Foaming and carry over of solids with steam, Embrittlement of boiler steel, carbonate and bicarbonate produce CO_2 in steam which causes corrosion in condensate lines.	Acid treatment; softening.
6. Free mineral acids	Corrosion	Neutralization with alkalies.
7. Oxygen	Corrosion	Deareration, sodium sulfite, corrosion inhibitors.
8. Carbon dioxide	Corrosion	Aeration, deareration neutralization with alkalies.

WATER TREATMENT

Q. 32. Write a short note on water quality parameters.

Ans. The quality of water can be decided with the help of certain parameters named as water quality parameters. These are : Colour, pH, Electrical conductivity, Turbidity, Suspended solids, Acidity, Alkalinity, Chlorides, Hardness, Sulphates, Dissolved oxygen, BOD, COD, Residual chloride, Chloride demand, Iron, Nitrogen and Phosphorus compounds, Fluoride and MPN (which indicates bacterial density).

CASE STUDY 6.1**THERMAL POLLUTION AND ECOSYSTEM**

The impairment of the quality of the environmental air or water by raising its temperature is the "thermal pollution". With a thermometer, it is difficult to evaluate the intensity of thermal pollution because what is pleasantly warm for man or some animals can be instant death for other members of the ecosystem. All life processes involve chemical reactions, and the rates of these reactions are very sensitive to changes in temperature. As a rough approximation, for every rise in temperature of 10°C , the rate of a reaction doubles. Over a wide range of environmental temperatures, most warm-blooded animals are able to maintain a constant body temperature, but the entire aquatic ecosystem is very sensitive to temperature changes. All of these organisms respond to temperature increase by speeding up their metabolic processes. Consequently, their need for oxygen and rate of respiration are increased, and as temperatures increase, the solubility of gases in their aquatic environment decreases. As the thermal pollution load in a body of water increases, so will the potential for increased loss of the various members of the aquatic ecosystem.

Let us consider a real example. An industrial electroplating firm dumps 16,000 liters of 2% waste sulphuric acid (H_2SO_4) every month into a holding pond where sufficient lime slurry, $\text{Ca}(\text{OH})_2$, is added to neutralize the acid. The draining is done twice in a month. If we assume that waste water drainage adds heat equivalent to 25% of the standard heat of reaction [$\text{Ca}(\text{OH})_2 + \text{H}_2\text{SO}_4 \text{ (aq)}$] for the sulfuric acid waste, 3×10^4 kCal of heat is added to the lake every month.

EXERCISES

1. (i) Calgon treatment prevents scale formation in boilers, explain.
(ii) Explain (in brief) boiler corrosion.
2. (a) What is the principle of EDTA titrations ? How can the permanent hardness of water be determined by this method ?
(b) Why is $\text{NH}_3 - \text{NH}_4\text{Cl}$ buffer solution is added in determination of hardness of water by EDTA titration ?
3. What are Zeolites ? How do they function in removing hardness of water ? What are the limitations of this process ?

Or

Explain with the help of a neat diagram, how can calorific value of a fuel be determined by Boy's calorimeter ?

4. (a) One gm of CaCO_3 was dissolved in dil HCl and solution diluted to one litre. 50 ml of this solution required 45 ml of EDTA solution, while 50 ml of sample water required 18 ml of EDTA solution. On the other hand, 50 ml of boiled sample water when titrated against EDTA consumed 9 ml of solution. Calculate each type of hardness in ppm.
 (b) Differentiate between scale and sludge.
5. (a) How will you determine the alkalinity of water sample containing hydroxide and carbonate ion ?
 (b) A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 ml of water sample on titration with $\frac{N}{50}$ HCl required 4.7 ml of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after addition of another 10.5 ml of the acid solution. Elucidate on the type and extent of Alkalinity present in the water sample.
6. (a) Give details of the following : (i) Scale and sludge formation (ii) Break Point Chlorination
 (b) Zeolite softeners are not recommended for obtaining feed water for the modern high pressure boilers. Give reasons.
 (c) Why is calgon conditioning better than phosphate conditioning ?
 (d) Calculate the quantity of lime and soda required for cold softening of 10^4 litres of water using 139 ppm of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as a coagulant. The results of the analysis of raw water and softened water are as follows :

<i>Raw water</i>	<i>Softened water</i>
$\text{Mg}^{2+} = 48 \text{ ppm}$	$\text{CO}_3^{2-} = 60 \text{ ppm}$
$\text{Ca}^{2+} = 200 \text{ ppm}$	$\text{OH}^- = 17 \text{ ppm}$
$\text{HCO}_3^- = 488 \text{ ppm}$	
Dissolved $\text{CO}_2 = 44 \text{ ppm}$	
Free HCl = 71 ppm	

7. (a) What do you mean by Priming and Foaming ? How does it take place in boilers ?
 (b) Describe the ion exchange process of water softening.
 (c) 0.28 g of CaCO_3 was dissolved in HCl and the solution was made upto 1 litre with distilled water, 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of Hard water sample required 33 ml of same EDTA solution on titration. After boiling 100 ml of this water cooling, filtering and then titration required 10 ml of EDTA solution. Calculate carbonate and non carbonate hardness of given sample of water in terms of ppm.

8. (a) Explain with equations and calculate the quantity of lime and soda required to soften 10,000 L of water containing

$\text{Mg}(\text{HCO}_3)_2 = 219 \text{ ppm}$, $\text{NaCl} = 234 \text{ ppm}$, $\text{Mg}^{2+} = 36 \text{ ppm}$, $\text{HCO}_3^- = 18.3 \text{ ppm}$,
 $\text{H}^+ = 15 \text{ ppm}$, $\text{SO}_4^{2-} = 144 \text{ ppm}$, $\text{Cl}^- = 71 \text{ ppm}$

- (b) What happens when temporary hard water is boiled ? (Give Equations)
 Or

Write short notes on : (i) Zeolite or Permutit process ; (ii) Scale formation in Boilers.

9. (a) What are complexometric titrations ?
 (b) Explain the principle of EDTA titrations.

WATER TREATMENT

- (c) Is it necessary to maintain the pH of the solution nearly constant by adding a suitable buffer during EDTA titrations ?
- (d) Describe the process of estimation of Ca and Mg with EDTA.
- (e) Write the structures of : (i) Metal-EDTA complex ; (ii) Eriochrome black-T indicator.
10. Explain : Buffer solution ; Buffer action ; Buffer capacity ; Acidic and Basic Buffer solution.

Numerical Problems

Type A : (Based on Hardness of Water)

1. A water sample contains 204 mg of CaSO_4 per liter. Calculate the hardness in terms of CaCO_3 equivalents. (Ans. 150 ppm)
2. How many grams of FeSO_4 dissolved per liter gives 210.5 ppm of hardness ? (Ans. 0.31996 g/L)
3. A sample of water on analysis was found to contain the following impurities expressed in mg/L :

<i>Impurity</i>	$\text{Ca}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2$	CaSO_4	MgSO_4
<i>Quantity</i>	10	8.5	12	14
<i>Mol. Wt.</i>	162	146	136	120

Calculate the temporary, permanent and total hardness of water in mg/L ?

(Ans. 11.99, 20.49 and 32.48 mg/L)

4. A sample of water is found to contain 40.5 mg/L $\text{Ca}(\text{HCO}_3)_2$, 46.5 mg/L $\text{Mg}(\text{HCO}_3)_2$, 27.6 mg/L MgSO_4 , 32.1 mg/L CaSO_4 and 22.45 mg/L CaCl_2 . Calculate the total hardness of water. (Ans. 124.68 ppm)
5. A sample of water on analysis has been found to contain the following in ppm : $\text{Ca}(\text{HCO}_3)_2 = 10.5$; $\text{Mg}(\text{HCO}_3)_2 = 12.5$; $\text{CaSO}_4 = 7.5$; $\text{CaCl}_2 = 8.2$; $\text{MgSO}_4 = 2.6$. Calculate the temporary and permanent hardness in degree French. (Ans. 1.504 and 1.507 degree French)
6. 100 ml of water sample has a hardness equivalent to 12.5 ml of 0.08 N MgSO_4 . What is the hardness in ppm ? (Ans. 500 ppm)

Type B : (Based on Hardness determination by EDTA method)

1. 0.28 g of CaCO_3 was dissolved in HCl and the solution was made to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of the hard water sample required 33 ml of the same EDTA solution on titration. After boiling 100 ml of this water, Cooling, Filtering and then titration required 10 ml of EDTA solution. Calculate the temporary and permanent hardness of water. (Ans. Hardness ; Total = 330, Perm. = 100, Temp. = 230 ppm)
2. A standard hard water contains 15 g of CaCO_3 per liter. 20 ml. Of this required 25 ml. Of EDTA solution. 100 ml. Of sample water required 18 ml. EDTA solution. The same sample after boiling required 12 ml. EDTA solution. Calculate the temporary hardness of the given sample of water, in terms of ppm. (Ans. Temporary hardness = 720 ppm)

3. 50 ml of standard hard water containing 1 mg of pure CaCO_3 per ml consumed 20 ml of EDTA. 50 ml of a water sample consumed 25 ml of the same EDTA solution. Using eriochrome T as indicator, calculate the total hardness of water sample in ppm.
 (Ans. 1250 ppm)
4. Calculate the hardness of a water sample, whose 10 ml required 20 ml of EDTA. 20 ml of CaCl_2 solution, whose strength is equivalent 1.5 g of CaCO_3 per litre, required 30 ml of EDTA solution.
 (Ans. 2000 ppm)
5. One gm of CaCO_3 was dissolved in dil. HCl and the solution diluted to one litre. 50 ml of this solution required 45 ml. of EDTA solution, while 50 ml of the sample water required 18 ml of EDTA solution. On the other hand, 50 ml of boiled sample water when titrated against EDTA consumed 9 ml of solution. Calculate each type of hardness in ppm.
 (Ans. Perm = 200 ppm ; Temperature = 200 ppm)

Type C : (Based on Alkalinity of water)

1. 200 ml. of a sample of water required 20 ml. of N/50 H_2SO_4 using methyl orange as indicator but did not give any colouration with phenolphthalein. What type of alkalinity is present ? Express the same in mg/L.
 (Ans. HCO_3^- = 100 ppm)
2. 200 ml of a sample required 20 ml of N/50 HCl using methyl orange as indicator. Another 200 ml of the same sample required 8 ml of N/50 HCl using phenolphthalein as indicator. Express the alkalinity in terms of mg of CaCO_3 per litre.
 (Ans. 80 ppm (CO_3^{2-}) and 20 ppm (HCO_3^-))
3. A sample of water was alkaline both to phenolphthalein and methyl orange. 50 ml of this water sample required 15 ml of N/50 H_2SO_4 for phenolphthalein end point and another 10 ml for complete neutralisation. Calculate the type of alkalinity in ppm.
 (Ans. 400 ppm (CO_3^{2-}) and 100 ppm OH^-)
4. A water sample is not alkaline to phenolphthalein. However, 100 ml of the sample water on titration with N/50 HCl, required 16.9 ml to obtain the end point, using methyl orange as indicator. What are the types and the amounts of alkalinity present in the sample ?
 (Ans. HCO_3^- = 169 mg/L)
5. A water sample is alkaline to both phenolphthalein as well as methyl orange. 100 ml of water sample on titration with N/50 HCl required 4.7 ml of the acid to phenolphthalein end point. When a few drops of methyl orange are added to the same solution and the titration further continued, the yellow colour of the solution just turned red after addition of another 10.5 ml of the acid solution. Elucidate on the type and extent of alkalinity present in the water sample.
 (Ans. CO_3^{2-} = 94 ppm and HCO_3^- = 58 ppm)
6. 100 ml of a water sample, on titration with N/50 H_2SO_4 gave a titre value of 5.8 ml to phenolphthalein end point and another 100 ml. sample on titration with same acid gave a titre value of 11.6 ml to methyl orange end point. Calculate the alkalinity of the water sample in terms of CaCO_3 and comment on the type of alkalinity present.
 (Ans. CO_3^{2-} = 116 ppm)
7. 100 ml of water sample, on titration with N/50 H_2SO_4 using phenolphthalein as indicator, gave the end point when 5 ml of acid were run down. Another lot of 100 ml of the sample also required 5 ml of the acid to obtain methyl-orange end point. What type of alkalinity is present in the sample and what is its magnitude ?
 (Ans. OH^- = 50 ppm)

Type D : (Based on Lime-Soda Process of Water Softening)

1. Calculate the amount of lime and soda required to soften 25,000 litres of water having following analysis :

$\text{Ca}(\text{HCO}_3)_2 = 4.86 \text{ ppm}$; $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ ppm}$; $\text{CaSO}_4 = 6.8 \text{ ppm}$; $\text{MgCl}_2 = 5.7 \text{ ppm}$;
 $\text{MgSO}_4 = 9.0 \text{ ppm}$; $\text{SiO}_2 = 3.5 \text{ ppm}$; $\text{NaCl} = 5.85 \text{ ppm}$. (Ans. L = 490 g; S = 490 g)

2. Calculate the quantity of lime and soda required for softening 50,000 litres of water containing the following salts per litre :

$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg}$; $\text{Mg}(\text{HCO}_3)_2 = 5 \text{ mg}$; $\text{CaSO}_4 = 13.6 \text{ mg}$; $\text{MgSO}_4 = 12.0 \text{ mg}$;
 $\text{MgCl}_2 = 2.0 \text{ mg}$; and $\text{NaCl} = 4.7 \text{ mg}$. (Ans. L = 1.01 kg; S = 1.17 kg)

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

$\text{Ca}(\text{HCO}_3)_2 = 40.5 \text{ ppm}$; $\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$; $\text{MgSO}_4 = 30.0 \text{ ppm}$;
 $\text{CaSO}_4 = 34.0 \text{ ppm}$; $\text{CaCl}_2 = 27.75 \text{ ppm}$; and $\text{NaCl} = 10.00 \text{ ppm}$.

Also calculate the temporary and permanent hardness of water sample.

(Ans. L = 1.762 kg; S = 1.728 kg; temp. = 50 ppm; perm. = 75 ppm)

4. Calculate the amounts of lime and soda needed for softening 100,000 litres of water containing $\text{HCl} = 7.3 \text{ mg/L}$; $\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ mg/L}$; $\text{MgCl}_2 = 9.5 \text{ mg/L}$;
 $\text{NaCl} = 29.25 \text{ mg/L}$; ($\text{Al} = 27$; $\text{Mg} = 24$; $\text{Na} = 23$; $\text{H} = 1$; $\text{Cl} = 35.5$; $\text{S} = 32$; $\text{O} = 16$).
(Ans. L = 3.7 kg; S = 5.3 kg)

5. Explain with equations and calculate the quantity of quick lime and soda ash required to soften 10,000 litres of water containing :

- (i) 219 ppm of magnesium bicarbonate and 234 ppm of sodium chloride.
(ii) 16 ppm of Mg^{2+} and 18.3 of HCO_3^-
(iii) 1.5 ppm of the free acids, 144 ppm of sulphate ions and 71 ppm of chloride ions.

(Ans. L = 4.0 kg; S = 2.226 kg)

6. A water sample, using $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ as a coagulant at the rate of 278 ppm, gave following data on analysis for raw water :

$\text{Ca}^{2-} = 240 \text{ ppm}$; $\text{Mg}^{2+} = 96 \text{ ppm}$; $\text{CO}_2 = 44 \text{ ppm}$; $\text{HCO}_3^- = 732 \text{ ppm}$.

Calculate the lime and soda required to soften 250,000 litres of water.

(Ans. L = 222 kg; S = 132.5 kg)

7. Calculate the quantities of lime and soda required for softening 300,000 litres of water, using 20 ppm of sodium aluminate as a coagulant. Impurities in water are as follows :
 $\text{Ca}^{2+} = 160 \text{ ppm}$; $\text{Mg}^{2+} = 96 \text{ ppm}$; $\text{HCO}_3^- = 403 \text{ ppm}$; dissolved $\text{CO}_2 = 34 \text{ ppm}$.

(Ans. L = 176.6 kg; S = 149.4 kg)

8. Calculate the quantities of lime ($\text{Ca}(\text{OH})_2$) and soda (anhyd. Na_2CO_3) required for cold softening of 125,000 L of water with the following analysis, using 10 ppm of sodium aluminate as coagulant :

Analysis of raw water : $\text{Ca}^{2+} = 95 \text{ ppm}$; $\text{Mg}^{2+} = 36 \text{ ppm}$; $\text{CO}_2 = 66 \text{ ppm}$;
 $\text{HCO}_3^- = 264 \text{ ppm}$; $\text{H}^+ = 2 \text{ ppm}$

Analysis of treated water : $\text{CO}_3^{2-} = 45 \text{ ppm}$; $\text{OH}^- = 34 \text{ ppm}$. Write the chemical equations involved.

(Ans. L = 65.7 kg; S = 59.1 kg)

9. Calculate the amount of lime and soda required to soften 10,000 litres of water containing the following ions per litre :

$$\text{Mg}^{2+} = 4.8 \text{ mg}; \text{Ca}^{2+} = 16.0 \text{ mg}; \text{HCO}_3^- = 73.2 \text{ mg.}$$

(Ans. L = 592 g; S = Nil)

Examination Questions

- (a) Distinguish between softening and demineralisation of water.
(b) Describe ion-exchange method of demineralisation of water.
(c) A water sample contains :

$$\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/L}; \quad \text{CaCl}_2 = 222 \text{ mg/L}; \\ \text{MgSO}_4 = 120 \text{ mg/L}; \quad \text{Ca}(\text{NO}_3)_2 = 164 \text{ mg/L}.$$

Calculate the quantity of lime (74% pure) and soda (90% pure) for softening 50,000 L of waters.

[GGSIPU, Ist sem., B.Tech., Feb.-March, 2000]

- (a) What is the principle of EDTA titration ? Briefly describe the estimation of hardness of water by EDTA method. What is the role of buffer in EDTA titration ?
(b) A sample of water was alkaline to both phenolphthalein and methyl orange. 50 mL of this water sample required 15 mL of $\frac{N}{50}$ H_2SO_4 for phenolphthalein end-point and another 10 mL for complete neutralization. Calculate the type and amount of alkalinity in ppm. [GGSIPU, Ist sem., B.Tech., Feb.-March, 2000]
- (a) What are boiler scales ? What are ill-effects of scales ? How can scale formation be prevented by :
(i) Phosphate conditioning (ii) Calgon conditioning ?
(b) Write short notes on :
(i) Caustic embrittlement ;
(ii) Priming and foaming. [GGSIPU, Ist sem., B.Tech., Feb.-March, 2000]
- (a) Describe L-S process for water softening. Give the advantages and disadvantages of this process.
(b) Why is hot L-S process better than cold process ?
(c) What are essential requirements of potable water ?

[GGSIPU, Ist sem., B.Tech., Dec., 2000]

- (a) Describe the principle involved in determination of hardness by EDTA method.
(b) 50 mL of standard hard water containing 1 mg of CaCO_3 per mL consumed 20 mL of EDTA solution. 50 mL of water sample consumed 18 mL of EDTA solution. Calculate the temporary and permanent hardness of the sample.

[GGSIPU, Ist sem., B.Tech., Dec., 2000]

- Attempt any seven of the following parts :
(a) What is sterilization of water ? Name three substances for sterilization of water.
(b) Why do we add buffer solution during titration of hard water against EDTA solution ? Name acidic and basic buffers.
(c) What is reverse osmosis ? What are its applications ?
(d) What is calgon conditioning ? How is it better than phosphate conditioning ?
(e) What are zeolites ? Why is water softened by zeolite process unfit for use in boilers ?

- (f) What are flocculants? What happens when alum is dissolved in water?
 (g) What is boiler corrosion? Why should the presence of CO_2 in boiler feed water be avoided?
 (h) What is lime and soda? Why does magnesium bicarbonate require double amount of lime for softening of hard water? [GGSIPU, 1st sem., B.Tech., March, 2001]
7. (a) What are Scales? What are their disadvantages?
 (b) What are internal and external treatments required for prevention of scale formation in boilers?
 (c) A sample of water is collected from a tank and gives the following results on analysis:
 $\text{CO}_2 = 22 \text{ ppm}$, $\text{HCO}_3^- = 365 \text{ ppm}$, $\text{Ca}^{2+} = 40 \text{ ppm}$, $\text{Mg}^{2+} = 48 \text{ ppm}$. Calculate the amount of lime and soda that would be required for softening the water if 139 ppm of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is used as coagulant.
 [At. Wt.: C = 12, O = 16, Ca = 40, Mg = 24, Fe = 56, S = 32]
 (d) Write short note on Ion-exchange resins. [GGSIPU, 1st sem., B.Tech., March, 2000]
8. A sample of water on analysis has been found to contain following in ppm : $\text{Ca}(\text{HCO}_3)_2 = 4.86$; $\text{Mg}(\text{HCO}_3)_2 = 5.84$; $\text{CaSO}_4 = 6.80$; $\text{MgSO}_4 = 8.40$. Calculate the temporary & permanent hardness of the water.
 (At. wt.'s : Ca = 40, Mg = 24, C = 12, S = 32, O = 16, H = 1) [Anna, Jan. 01]
 (Ans. Temp. hardness = 3 ppm ; Permanent hardness = 12 ppm)
9. 50 mL of a sample water consumed 15 mL of 0.01 M EDTA before boiling and 5 mL of the same EDTA after boiling. Calculate the degree of total hardness, permanent hardness and temporary hardness. [Anna, Nov. 2000]
 (Ans. Hardness Total = 300 ppm, Perm. = 100 ppm, Temporary = 200 ppm)
10. If 50 mL of a sample of hard water consumed 15 mL of 0.01 M EDTA. What is the hardness of the water? [Anna, July 2000]
 (Ans. Hardness = 300 ppm)
11. Distinguish between carbonate and non-carbonate hardness of water with example. [Anna, July 2000, Jan. 2001]
12. What is meant by blow down operation and what is its use? [Anna, July 2000]
13. Draw neat & labelled diagram of permuntit (or zeolite process) of softening water. Discuss the chemistry involved in it. Discuss its merits over lime-soda process. [Anna 2000, Jan. 2001]
14. Name any one coagulant used to remove the turbidity of water. [Anna, Nov. 2000]
15. Explain the principle behind the calculation of lime & soda requirement for softening hard water. [Anna, July 2000]
16. Describe in detail the ion exchange process for softening / demineralisation of water. [Anna, July 2000]
17. What is demineralized water? How is it different from soft water? [Anna, Nov. 2000, Jan. 2001]
18. Write short note on reverse osmosis. [Anna, July 2000]
19. What is the principle of EDTA titration? Briefly describe the estimation of hardness of water by EDTA method.

Or

Write a note on complexometric titrations.

[Anna, Jan. 2001]

20. State the various methods of disinfection.
21. What is break-point chlorination ? Explain showing different zones. What are the advantages of break point chlorination ? [Anna, July 2000]
22. (i) Write the constituents responsible for the permanent hardness of water. Discuss one treatment method.
(ii) Why does hard water consumes a lot of soap ?
(iii) Why does magnesium bicarbonate require double amount of lime of softening ? [U.P. Tech., B.Tech, 1st Sem. 2000-01]
23. (a) Write the structure of EDTA.
(b) A sample of ground water has 150 mg/L of Mg^{2+} . Find the total hardness expressed in milli-equivalent per litre and mg/L in terms of $CaCO_3$.
(c) State the zeolite process for the removal of hardness of water. Discuss its merits over soda-lime process. [U.P. Tech., B.Tech, 2nd Sem. 2000-01]
24. (a) Write the names of the substances which impart undesirable odour in waste water and state their removal methods.
(b) Why is it conventional to express hardness of water in terms of $CaCO_3$ at the International level ? Write other units also.
(c) 20 mL of a water sample was treated with excess of 10% KI solution and then titrated against N/100 hypo solution using starch as indicator. 2.5 mL of hypo was used for starch end-point. Calculate the amount of chlorine in water. [U.P. Tech., B.Tech, 1st/2nd Sem. 2000-02]
25. (a) (i) Comment on solubility changes of $CaSO_4$ on variation of temperature in a boiler.
(ii) What is calgon ? What is its application in water treatment ?
(iii) Comment on the use of coagulants in cold-lime soda process.
(iv) Indicate the coloured species among the following :
 Ca -EDTA ; Mg -EDTA ; EDTA ; Mg -EBT ; and EBT (Eriochrome Block-T)
Also give the colours of the coloured species.
(v) What are contributing factors for caustic embrittlement ? How it can be prevented ?
- (b) (i) Find out temporary and permanent hardness of a water sample in ppm of $CaCO_3$ equivalent, which contains
 $CaCl_2 = 2.0 \times 10^{-5} kg/l$, $KHCO_3 = 0.00305 g/500 ml$
 $Mg(HCO_3)_2 = 10^{\circ} Cl$, $Ca(HCO_3)_2 = 0.0162 g/500 ml$
- (ii) 100 ml of a water sample was boiled with 500 ml of N/50 Na_2CO_3 solution. It is then filtered and the filtrate required 50 ml of N/10 HCl for complete neutralization. Calculate the permanent hardness of water sample in ppm.
- Or*
- (b) Calculate the amounts of lime & soda required for the softening of 10^6 litres of water, having the following :
- $HCl = 3.65 ppm$; $Mg(HCO_3)_2 = 2.92 ppm$; $MgSO_4 = 5.4 ppm$;
 $CaSO_4 = 20.0 ppm$; $FeCl_3 = 10 ppm$;
- Treated water has
 $OH^- = 1.7 ppm$ and $CO_3^{2-} = 3.0 ppm$ [J.M.I. B.Tech., Part-I, 2000]

WATER TREATMENT

26. (a) (i) Give General formulae of zeolites. Write down the reaction showing their regeneration:
(ii) How is deionized water obtained from ion exchange process? Give the necessary reactions.
(iii) Why is the presence of $MgCl_2$ in the boiler water objectionable? Show it by giving reactions.
(iv) What is the advantage of break point chlorination? Also give the necessary graph.
(v) Discuss the alkalinity of water in condition $P < \frac{1}{2} M$

- (b) Calculate carbonate and non-carbonate hardness of a water sample in ppm, having the following analysis:

$$Mg(HCO_3)_2 = 1.40 \text{ ppm}; \quad NaHCO_3 = 0.84 \text{ mg/L}$$

$$CaCl_2 = 3 \times 10^{-3} \text{ kg/L}; \quad NaCl = 0.002 \text{ mg/500 ml}$$

$$MgCl_2 = 0.30 \text{ °C}$$

Or

- (b) Calculate the lime and soda requirement of a municipal water sample measuring 10^5 litres and containing the following:

$$AlCl_3 = 1.00 \text{ ppm}; \quad Mg(HCO_3)_2 = 2.00 \text{ ppm};$$

$$Ca(HCO_3)_2 = 3.00 \text{ ppm}; \quad MgSO_4 = 4.00 \text{ ppm};$$

$$CO_2 = 4.4 \text{ ppm}; \quad CaCl_2 = 5.00 \text{ ppm};$$

The treated water has

$$OH^- = 1.7 \text{ ppm}, \quad CO_3^{2-} = 3.0 \text{ ppm}$$

[J.M.I., B.Tech., Part-I, 2001]

27. (a) Calculate the amount of lime and soda required for softening a million litres of hard water which analysed as follows:

Substance	Conc. in mg/L
Ca(HCO ₃) ₂	243
Mg(HCO ₃) ₂	73
CaSO ₄	102
MgCl ₂	95
NaCl	500
FeSO ₄ .7 H ₂ O	139

Purity of lime is 94% and that of soda is 86.0%.

- (b) Why is calgon conditioning better than phosphate conditioning?
(c) What happens when temporary hard water is boiled (give equations)?

[GGSIPU, B.Tech., 1st Sem. Dec. 2001]

28. (a) 200 mL of a sample required 20 mL of N/50 HCl using methyl orange as indicator. Another 200 mL of the same sample required 8 mL of N/50 HCl using phenolphthalein as indicator. Express the alkalinites in terms of mg of $CaCO_3$ per litre.
(b) What are the factors that lead to caustic embrittlement in boilers? How can this be prevented?

- (c) 100 mL of a sample of water required 15 mL of 0.01 M EDTA for titration using Erioph-T as indicator. In another experiment, 100 mL of the same sample was boiled to remove the carbonate hardness, the precipitate was removed and the cold solution required 8.0 mL of 0.01 M EDTA using Erioph-T as Indicator. Calculate in terms of ppm.
 (i) The total hardness, (ii) Permanent and (iii) Carbonate hardness.
- [GGSIPU, B.Tech., 1st Sem., Dec. 2001]
29. (a) What is hardness of water? How is it determined by EDTA method?
 (b) Explain caustic embrittlement in boilers and how it can be avoided.
 (c) Explain with chemical equations and calculate the amount of lime and soda needed for softening 1,00,000 litres of water containing the following per litre:
 (i) $\text{HCl} = 7.3 \text{ mg/litre}$, (ii) $\text{Al}_2(\text{SO}_4)_3 = 34.2 \text{ mg/litre}$,
 (iii) $\text{MgCl}_2 = 9.5 \text{ mg/litre}$,
 (iv) $\text{NaCl} = 29.25 \text{ mg/litre}$
- Purity of lime is 90% and that of soda is 98%. 10% of chemicals are to be used in excess in order to complete the reactions quickly.
- (d) Draw neat & labelled diagram of permuntit or zeolite process.
- [Univ. of Rajasthan, B.E., 1st Sem., May 2001]
30. (a) Explain causes of hardness in water.
 (b) At what stage for which purpose hydrazine is added to high pressure boiler water?
 (c) Give relationship between various units of hardness.
 (d) Describe scale & sludge formation in boiler.
 (e) Explain the function of the following in water treatment:
 (i) Calgon (ii) Bleaching powder
- [R.G.P.V. B.E., 1st Sem. 2001]
31. (a) In the determination of hardness of water by EDTA method, $\text{NH}_3\text{OH}-\text{NH}_4\text{Cl}$ buffer is used. Why?
 (b) Calculate the amount of lime (88.3% pure) and soda (99.2% pure) required to soften 24,000 litres of water per day for a year containing the following:
 $\text{CaCO}_3 = 1.85 \text{ mg/L}$, $\text{CaSO}_4 = 0.34 \text{ mg/L}$,
 $\text{MgCO}_3 = 0.42 \text{ mg/L}$, $\text{MgCl}_2 = 0.76 \text{ mg/L}$,
 $\text{MgSO}_4 = 0.90 \text{ mg/L}$, $\text{NaCl} = 2.34 \text{ mg/L}$, and $\text{SiO}_2 = 2.32 \text{ mg/L}$
 (c) Name the factors which are responsible for corrosion of boiler tubes, plates and pipe lines.
- [RGPV, B.E., 1st Sem., 2001]
32. What are the disadvantages of hard water? Describe one process of softening of hard water.
- [Orissa, B.E., 1st Sem., 1999]
33. (a) Describe two methods for internal treatment of boilers to prevent scale formation.
 (b) Discuss lime-soda process for softening of hard water.
- [Orissa, B.E., 1st Sem., 2000]
34. (a) What are the requirements of water for municipal use? Give an account of treatment plant for raw water for domestic use.
 (b) Write notes on (i) zeolite process for softening water. (ii) Disinfection of drinking water.
- [Orissa, B.E., 1st Sem., 2001]
35. What are different sources of water and how are they polluted? How can water pollution be prevented?
- [Orissa, B.E., 2nd Sem., 1997]

36. (a) How are boiler scale formed ? Discuss the disadvantages of scale formation. Differentiate between a scale and sludge.
 (b) What are the requirements of water for municipal use ? [MREC 2001]
37. (a) Discuss the harms caused by hard water in boilers. Explain with equations how addition of soda-lime to hard water softens it.
 (b) Explain the meaning of Caustic Embrittlement. [Udaipur Univ. 2001]
38. How the degree of hardness of water is expressed ? Name the important methods used for the determination of hardness of water and describe one of them in detail.
 [Udaipur Univ., 2001]
39. (a) Describe the ion-exchange process of softening hard water. What are its advantages ?
 (b) Write note on Caustic Embrittlement. [MREC 2000]
40. (a) Discuss Clark's method for determining the hardness of water.
 (b) Discuss methods of disinfection of water. [Raj. Univ. 2000]
41. Explain scales formation and caustic embrittlement in boilers. What are the methods employed to remove these defects ? [Raj. Univ. 1999]
42. Discuss in detail the process of softening of hard water by lime-soda process. Also give the chemical equations involved in the process. [Raj. Univ. 1999]
43. (a) How hydrogen bonding affects the properties of water ? What are the requisites for drinking water ? How is water purified for drinking purposes by municipalities ?
 (b) Discuss the effect of oil and dissolved silica on boilers and the methods of their removal.
 (c) Write briefly the method employed for determining alkalinity in water due to OH^- , CO_3^{2-} and HCO_3^- . Give reactions. [Jodhpur Univ. 1999]
44. (a) What is meant by carbonate and non-carbonate hardness of water ? Describe the EDTA titration method of determining Calcium and Magnesium hardness of water, explaining the chemistry of the method.
 (b) Describe the method for determining dissolved oxygen in water, explaining the chemical principles. [Jodhpur Univ. 2000]
45. A sample of water contains following impurities :
 $\text{MgCO}_3 = 42 \text{ mg/l}$, $\text{HCO}_3 = 122 \text{ mg/l}$, $\text{MgSO}_4 = 1.20 \text{ mg/l}$,
 $\text{CaCO}_3 = 111 \text{ mg/l}$, $\text{Al}_2(\text{SO}_4)_3 = 228 \text{ mg/l}$, $\text{NaCl} = 35 \text{ mg/L}$,
 Calculate the quantity of lime and soda required for complete softening of 5000 litres of hard water. [MREC 2001] (Ans. Lime = 1.85 kg, Soda = 1.59 kg)
46. A water sample contains following salts dissolved in it :
 $\text{Ca}(\text{HCO}_3)_2 = 0.162 \text{ per litre}$ and $\text{MgCl}_2 = 0.095 \text{ per litre}$.
 How much soda and lime shall be needed to soften 10,000 litres of it ?
 [Udaipur Univ. 2001] (Ans. Lime 1.48 kg, Soda = 1.06 kg)
47. In an experiment to determine the hardness of a sample of water, 25 mL of N/50 Na_2CO_3 solution was added to 100 mL of water sample. After completion of precipitation of the insoluble carbonates, the unreacted Na_2CO_3 was titrated against N/50 H_2SO_4 solution when 10 mL of the acid was required. Calculate the degree of hardness and comment on the nature of hardness so determined.
 [Jodhpur Univ. 1999] (Ans. Hardness = 150 mg/L or ppm)

48. Water having following composition has to be softened by lime-soda process :

$$\text{Ca}(\text{HCO}_3)_2 = 220 \text{ ppm}$$

$$\text{Mg}(\text{HCO}_3)_2 = 56 \text{ ppm}$$

$$\text{MgCl}_2 = 130 \text{ ppm}$$

$$\text{MgSO}_4 = 84 \text{ ppm and}$$

and

$$\text{CaCO}_3 = 98 \text{ ppm.}$$

(Na = 23, Ca = 4, H = 1, C = 12, O = 16, Mg = 24, Cl = 35.5, S = 32)

[Jaipur Univ. 2001] (Ans. Lime = 310 kg, Soda = 296 kg)

49. Calculate the amount of lime and soda required for softening 10,000 literes of water which analysed as follows :

Analysis of raw water

$$\text{Ca}^{+2} = 380 \text{ ppm}$$

$$\text{Mg}^{+2} = 144 \text{ ppm}$$

$$\text{HCO}_3^- = 1500 \text{ ppm}$$

$$\text{Dissolved CO}_2 = 120 \text{ ppm}$$

$$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = 278 \text{ ppm}$$

Analysis of treated water

$$\text{OH}^- = 36 \text{ ppm}$$

$$\text{CO}_3^{+2} = 32 \text{ ppm}$$

[MREC 2000]

50. Calculate the quantities of lime and soda needed for softening 2,000 litres of hard water which analysed as follows :

Analysis of raw water

$$\text{Ca}^{+2} = 160 \text{ ppm}$$

$$\text{Mg}^{+2} = 72 \text{ ppm}$$

$$\text{HCO}_3^- = 732 \text{ ppm}$$

$$\text{dissolved CO}_2 = 44 \text{ ppm}$$

$$\text{HCl} = 7.3 \text{ ppm}$$

Analysis of treated water

$$\text{CO}_3^{+2} = 30 \text{ ppm}$$

$$\text{OH}^- = 17 \text{ ppm}$$

[Raj. Univ. 2000]

51. Calculate the amount of lime and soda required for softening one million litres of water containing :

$$\text{H}^+ (\text{Free acidity}) = 1.5 \text{ ppm},$$

$$\text{HCO}_3^- = 396.5 \text{ ppm}$$

$$\text{Mg}^{+2} = 42.0 \text{ ppm},$$

$$\text{Ca}^{+2} = 90.00 \text{ ppm}$$

$$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = 14 \text{ ppm}$$

The purity of lime is 91% and that of soda is 97.2%. Given Atomic mass of :

$$\text{H} = 1, \text{Na} = 23, \text{Ca} = 40, \text{Mg} = 24, \text{O} = 16, \text{C} = 12, \text{S} = 32, \text{Fe} = 56$$

[Raj. Univ. 1999]

Calculate the amount of lime and soda required for softening one million litres of water containing

$$\text{H}^+ [\text{Free acidity}] = 1.5 \text{ ppm},$$

$$\text{HCO}_3^- = 396.5 \text{ ppm}$$

$$\text{Mg}^{+2} = 42.0 \text{ ppm}$$

$$\text{Ca}^{+2} = 90.00 \text{ ppm}$$

$$\text{FeSO}_4 \cdot 7 \text{H}_2\text{O} = 14 \text{ ppm}$$