

## Water and Its 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".*

### Fundamental Definitions at a Glance

- **Hardness** in water is that characteristic which prevents the lathering of soap. Originally, it was defined as the soap consuming capacity of water sample.
- **Temporary hardness** is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Temporary hardness can be largely removed by mere boiling of water.
- **Permanent hardness** is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Unlike temporary hardness, permanent hardness is not destroyed on boiling.
- **Hard water** is water which does not produce lather with soap solution readily, but forms a white curd.
- **Soft water** is water which lathers easily on shaking with soap solution.
- **Inter-relations between units of hardness**

$$1 \text{ ppm} = 0.1^\circ \text{ Fr} = 0.07^\circ \text{ Cl} = 1 \text{ mg/L}$$
- **Sludges** are soft, loose and slimy precipitate. They are non-adherent deposits and can be easily removed. They are formed by substances like  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{MgCO}_3$ , etc.
- **Scales** are hard deposits. They stick very firmly to the inner surface of boiler and are very difficult to remove. They are formed by substance like  $\text{CaSO}_4$ ,  $\text{Mg(OH)}_2$ ,  $\text{CaCO}_3$ ,  $\text{CaSiO}_3$ , etc.
- **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 *permutits* and in Greek it means 'boiling stone'.

- **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.
- **Calgon conditioning** involves 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  $\text{CaSO}_4$  into soluble complex compound, which are harmless to boiler.
- **Drinking or potable water** is fit for human consumption.

## 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. In this chapter, we will not discuss about heavy water. This chapter deals in sources of water, impurities in water, hardness of water, units of hardness, boiler problems, and water treatment for boiler feed water by calgon process, zeolites and ion-exchange resins.

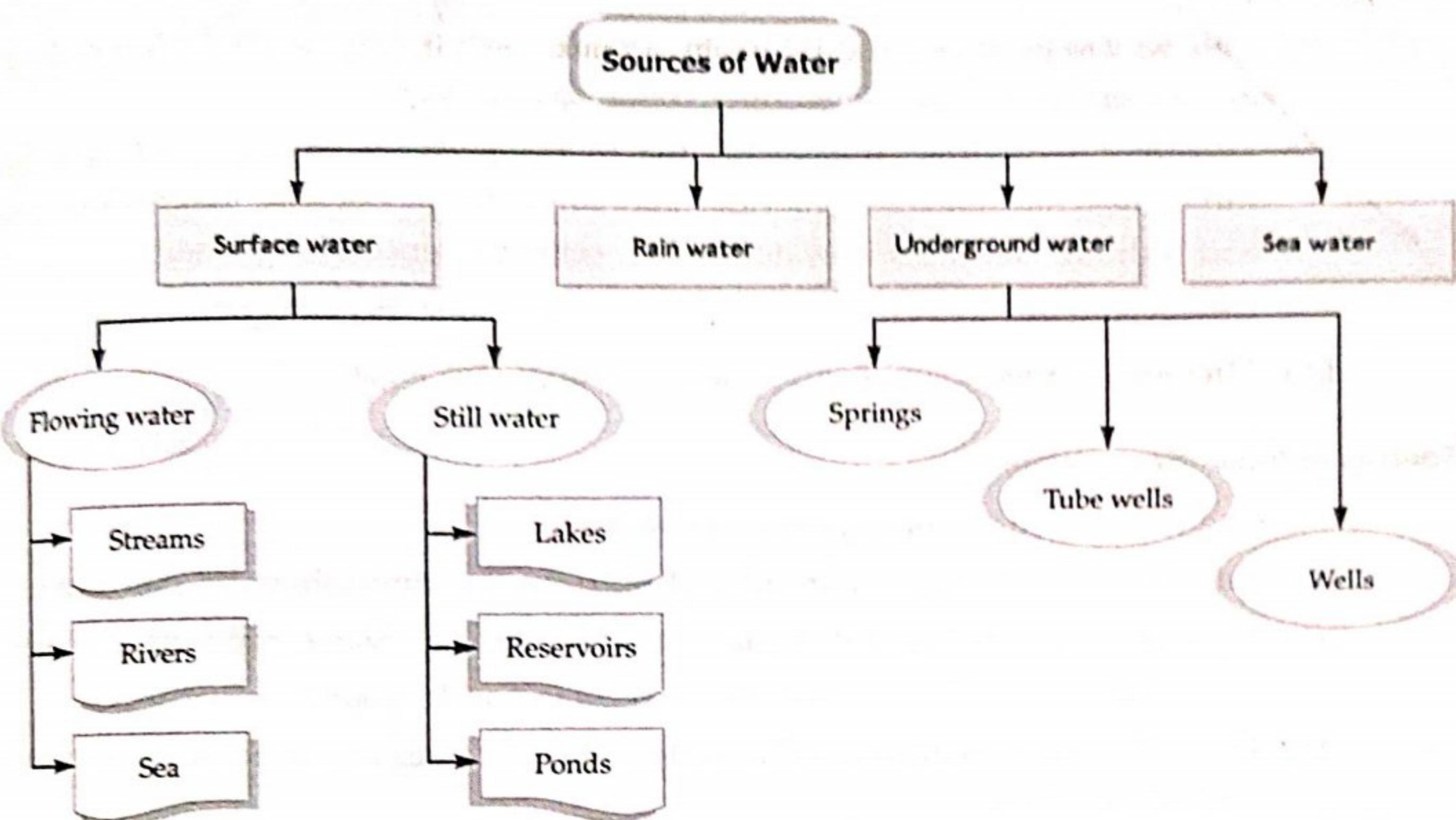
## 2

### SOURCES OF WATER

The important 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. Due to continuous evaporation of water, clouds are formed. Rain occurs as a result of condensation of water from clouds. Rain water is thus free from hardness and surface impurities. Probably *rain water 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<sub>2</sub>, NO<sub>2</sub>, SO<sub>2</sub> etc.)**. Rain water is expensive to collect and is **irregular in supply**.

**Underground water** is free from organic impurities and is clearer in appearance due to the filtering action of the soil. But it contains large amount of dissolved salts.

**Sea water** is very impure due to two reasons : continuous evaporation increases the dissolved impurity content which is further increased by the impurity thrown by rivers as they join sea. It is too saline for most industrial uses except cooling.

### 3 IMPURITIES IN WATER

#### Types of Impurities Present In Water and their effects

The following types of impurities are present in water :

- (i) **Suspended impurities.** These impurities impart turbidity, colour and odour to water. It may be inorganic (clay and sand) or organic (oil globules, vegetable and animal matter) in nature.

- (ii) **Colloidal impurities.** Products from organic waste, finely divided silica and clay etc. are agents which come under colloidal impurities.
- (iii) **Dissolved impurities.** It may be due to the presence of dissolved salts like carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron and sodium. Hardness in water is due to the presence of these salts.  
Dissolved gases like  $O_2$ ,  $CO_2$ , etc. also come under this category.
- (iv) **Microorganisms.** They include bacteria, fungi and algae.

### Sources of Impurities in Water

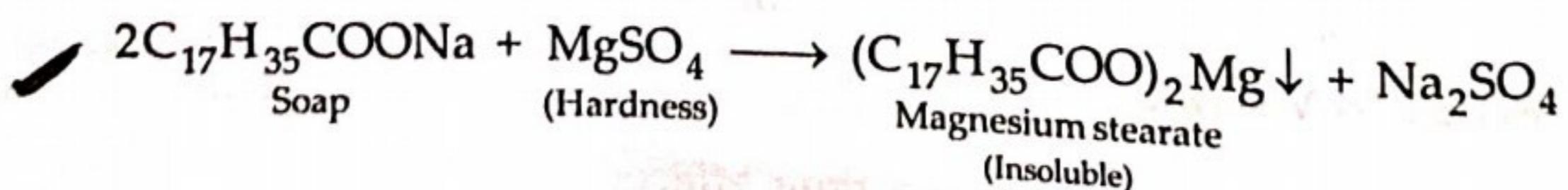
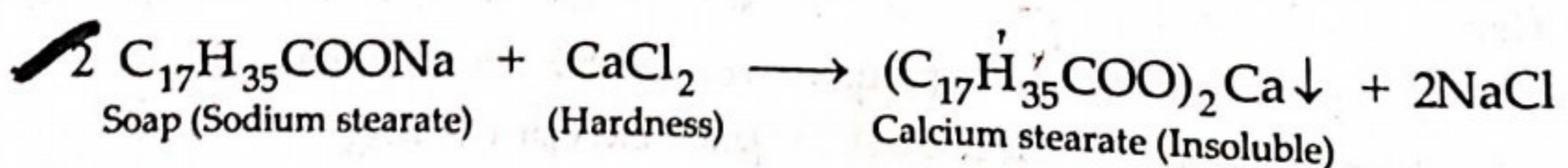
Following are the sources of impurities in water :

- (a) Gases (e.g.,  $O_2$ ,  $CO_2$ , etc.) are picked up from the atmosphere by rain water.
- (b) Decomposition of plant and animal remains introduce organic impurities in water.
- (c) Water takes impurities when it comes in contact with ground, soil or rocks.
- (d) Impurities are also introduced in water when it comes in contact with sewage or industrial waste.

## 4 HARDNESS OF WATER [UPTU, 2003, 09, 11]

Hardness in water is that characteristic, "which prevents the lathering of soap". Originally, it was defined as the soap consuming capacity of water sample.

Hard water consumes a lot of soap [UPTU, 2000]. 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 possesses any detergent action. This is due to the formation of insoluble soaps of calcium and magnesium. Chemical reactions of soap (sodium stearate) with calcium chloride and magnesium sulphate are shown below [UPTU, 2012] :



In fact, any cation which produces insoluble soap with soap solution will contribute to hardness. Thus, on this basis water can be classified into two types : viz., Hard water and Soft water.

The essential differences between the two are summarized in Table 1.

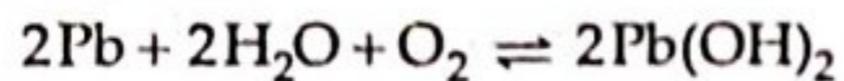
**Table 1** Differences between Hard Water and Soft Water.

S. No.	<i>Hard Water</i>	<i>Soft Water</i>
1.	Water which does not produce lather with soap solution readily, but forms a white <u>curd</u> , is called "hard water".	Water which lathers easily on shaking with soap solution, is called "soft water".
2.	Hard water contains dissolved Calcium and Magnesium salts in it.	Soft water does not contain dissolved Calcium and Magnesium salts in it.
3.	In hard water, cleansing quality of soap is depressed and a lot of it is wasted during Washing and Bathing.	In soft water, cleansing quality of soap is not depressed and so soap is not wasted during washing and bathing.
4.	Due to the presence of dissolved hardness-producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking.	Less fuel and time are required for cooking in soft water.

### Important Question

**Q. Why water should not be soft for drinking purposes ?**

**Ans.** Since soft water is plumbo-solvent (it attacks lead used in plumbing), *via*.



The solubility of Pb in water is diminished in the presence of  $\text{HCO}_3^-$  ions.

#### **NOTE**

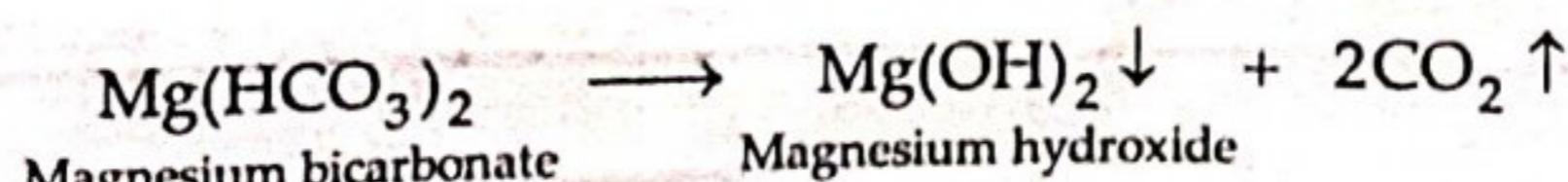
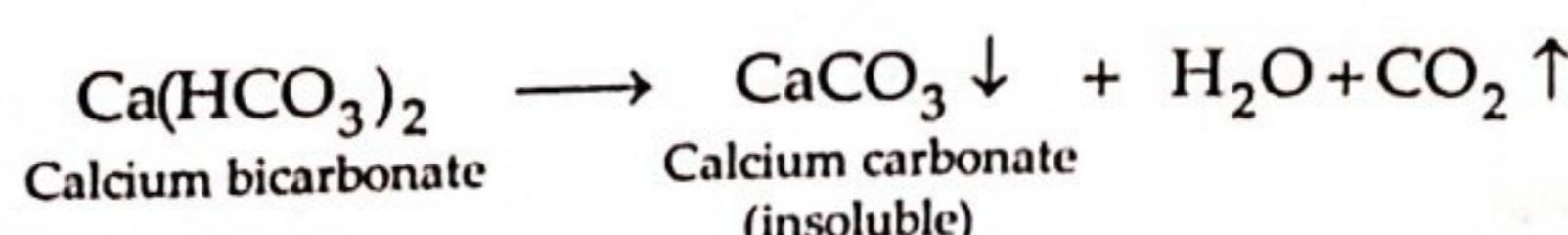
A partial softening leaving a residual total-hardness of about 85 ppm  $\text{CaCO}_3$  equivalents is generally adopted for drinking purposes.

### Types of Hardness

It is of following types :

#### (1) Temporary Hardness

- (a) Temporary hardness is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron. Thus, the salts responsible for temporary hardness are  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ .
- (b) Temporary hardness can be largely removed by mere boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.



- (c) Temporary hardness is also known as carbonate hardness or alkaline hardness.  
 (d) Alkaline hardness is due to the presence of bicarbonate, carbonate and hydroxides of the hardness-producing metal ions. This is determined by titration with HCl using methyl orange as indicator.

## (2) Permanent Hardness

- (a) It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other heavy metals. Hence, the salts responsible for permanent hardness are :  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$  etc. [UPTU, 2000]  
 (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*.



### Important Question

Q. What is carbonate and non-carbonate hardness ?

Ans. Temporary hardness due to the presence of carbonates and bicarbonates is referred to as the Carbonate Hardness (CH) and the amount of hardness in excess of CH (*i.e.*, permanent hardness) is referred to as the non-carbonate hardness (NCH).

$$\therefore \text{Total hardness} = \text{CH} + \text{NCH}$$

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

**Table 2 Advantages and Disadvantages of Hard Water**

S. No.	<i>Hard Water</i>	
	<i>Advantages</i>	<i>Disadvantages</i>
1.	The taste of hard water is usually better than soft water. The label on the bottle of mineral water shows that it contains $\text{Mg}^{2+}$ and $\text{Ca}^{2+}$ 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 $\text{CaCO}_3$ . 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 conventionally expressed in terms of equivalent amount (*equivalents*) of  $\text{CaCO}_3$ .

The reason for choosing  $\text{CaCO}_3$  as the standard for reporting hardness of water [UPTU, 2K] 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.

$$\begin{aligned}\text{Equivalents of } \text{CaCO}_3 &= \frac{\left[ \text{Strength of hardness producing substance (in mg/L)} \right] \times \left[ \text{Chemical equivalent of } \text{CaCO}_3 (= 50) \right] \times 2}{\left[ \text{Chemical equivalent of hardness Producing substance} \right] \times 2} \\ &= \left[ \text{Strength of hardness producing substance in mg/L} \right] \times \left[ \frac{100}{2 \times \text{Chemical equivalents of hardness producing substance}} \right] \\ &= \left[ \text{Strength of hardness producing substance} \right] \times (\text{Multiplication factor}) \text{ in } \frac{\text{mg}}{\text{L}} \text{ or ppm}\end{aligned}$$

### Illustration 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 the multiplication factor for converting into equivalents of  $\text{CaCO}_3$  for  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CO}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{HCO}_3^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NaAlO}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}^+$ .

**Step (i)** Find molar masses by adding together atomic masses.

**Step (ii)** Find *n*-factors for the salts

S.No.	Salt	Ionic Form	<i>n</i> -factor = Least common factor for the valencies on cation and anion
1.	HCl	$\text{H}^+ \text{Cl}^-$	1
2.	$\text{CaCl}_2$	$\text{Ca}^{2+} 2\text{Cl}^-$	2
3.	$\text{MgSO}_4$	$\text{Mg}^{2+} \text{SO}_4^{2-}$	2
4.	$\text{Al}_2(\text{SO}_4)_3$	$2\text{Al}^{3+} 3\text{SO}_4^{2-}$	6

**Step (iii)** Find chemical equivalent of hardness producing substance, by dividing molar mass with *n*-factor.

**Step (iv)** Molar mass of  $\text{CaCO}_3$  is 100.

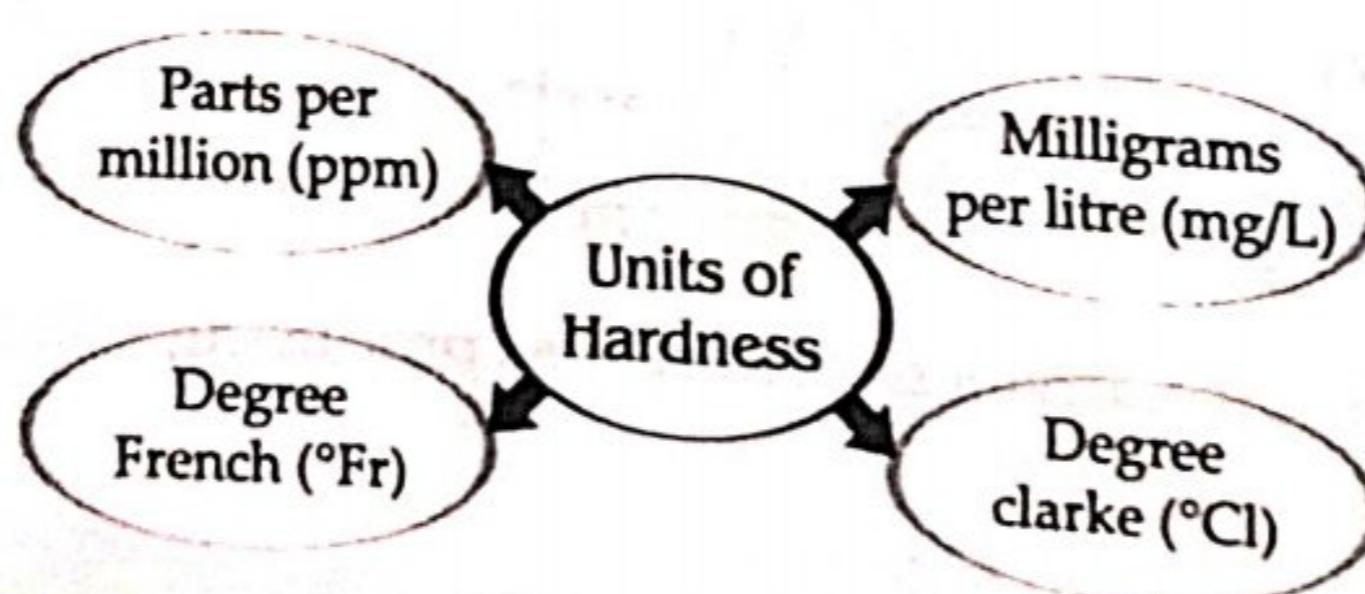
**Step (v)** Multiplication factor = 
$$\frac{100}{2 \times \text{Chemical equivalents of hardness producing substance}}$$

Multiplication factors for different salts are tabulated in Table 3.

**Table 3** Calculations of multiplication factors of different salts

Constituent salt/ion	Molar mass	n-factor	Chemical equivalent = $\frac{\text{Molar mass}}{\text{n - factor}}$	Multiplication factor for converting into equivalents of $\text{CaCO}_3$
$\text{Ca}(\text{HCO}_3)_2$	162	2	$162/2 = 81$	$100/(2 \times 81) = 100/162$
$\text{Mg}(\text{HCO}_3)_2$	146	2	$146/2 = 73$	$100/(2 \times 73) = 100/146$
$\text{CaSO}_4$	136	2	$136/2 = 68$	$100/(2 \times 68) = 100/136$
$\text{MgSO}_4$	120	2	$120/2 = 60$	$100/(2 \times 60) = 100/120$
$\text{CaCl}_2$	111	2	$111/2 = 55.5$	$100/(2 \times 55.5) = 100/111$
$\text{MgCl}_2$	95	2	$95/2 = 47.5$	$100/(2 \times 47.5) = 100/95$
$\text{CaCO}_3$	100	2	$100/2 = 50$	$100/(2 \times 50) = 100/100$
$\text{MgCO}_3$	84	2	$84/2 = 42$	$100/(2 \times 42) = 100/84$
$\text{CO}_2$	44	2	$44/2 = 22$	$100/(2 \times 22) = 100/44$
$\text{Mg}(\text{NO}_3)_2$	148	2	$148/2 = 74$	$100/(2 \times 74) = 100/148$
$\text{HCO}_3^-$	61	1	$61/1 = 61$	$100/(2 \times 61) = 100/122$
$\text{OH}^-$	17	1	$17/1 = 17$	$100/(2 \times 17) = 100/34$
$\text{CO}_3^{2-}$	60	2	$60/2 = 30$	$100/(2 \times 30) = 100/60$
$\text{NaAlO}_2$	82	1	$82/1 = 82$	$100/(2 \times 82) = 100/164$
$\text{Al}_2(\text{SO}_4)_3$	342	6	$342/6 = 57$	$100/(2 \times 57) = 100/114$
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278	2	$278/2 = 139$	$100/(2 \times 139) = 100/278$
$\text{H}^+$	1	1	$1/1 = 1$	$100/(2 \times 1) = 100/2$

Units of Hardness and their inter-relations : [UPTU, 2003]



(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.,  $1 \text{ ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalents hardness in } (10^6) \text{ parts of water.}$

(ii) **Milligrams per litre (mg / L).** It is defined as the number of milligrams of  $\text{CaCO}_3$  present in one litre of water,

i.e.,  $1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3$  equivalent per liter of water. It can be easily proved that  
 $1 \text{ mg/L} = 1 \text{ ppm}$  for water

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

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

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

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

Hence,

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

(iii) **Degree Clarke ( ${}^\circ\text{Cl}$ ).** It is defined as the parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

Or It is number of grains of  $\text{CaCO}_3$  equivalent hardness per gallon of water.

i.e.,  ${}^\circ\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ per 70,000 parts of water.}$

(iv) **Degree French ( ${}^\circ\text{Fr}$ ).** It is defined as the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

i.e.,  ${}^\circ\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness per } 10^5 \text{ parts of water.}$

#### Relationships between various units of hardness

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

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

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

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

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

#### 4.1 Solved Examples based on Hardness of Water

**Example 1** Convert 50 ppm hardness of water in terms of mg/L and degree French.

[UPTU, II Ind Sem., 2011-12]

**Solution.**  $50 \text{ ppm} = 50 \text{ mg/L}$

$$= 50 \times 0.1 {}^\circ\text{Fr}$$

$$= 5 {}^\circ\text{Fr}$$

**Example 2** A sample of hard water has a hardness 500 ppm. Express the hardness in  ${}^\circ\text{French}$  and  ${}^\circ\text{Clark}$ .

[UPTU, II Ind Sem., 2009-10, 2010-11]

**Solution.** Hardness = 500 ppm  
 $= (500 \times 0.1) {}^{\circ}\text{French} = 50 {}^{\circ}\text{Fr}$   
 $= (500 \times 0.07) {}^{\circ}\text{Clark} = 35 {}^{\circ}\text{Cl}$

**Example 3** A water sample contains 408 mg of  $\text{CaSO}_4$  per litre. Calculate the hardness in terms of  $\text{CaCO}_3$  equivalents.

**Solution.** Hardness = (strength of  $\text{CaSO}_4$  in mg / L)  $\times$  multiplication factor

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

**Example 4** How many grams of  $\text{MgCO}_3$  dissolved per litre gives 84 ppm of hardness?

**Solution.**

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

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

Thus,  $70.56 \times 10^{-3}$  gms of  $\text{MgCO}_3$  dissolved per litre gives 84 ppm of hardness.

**Example 5** A sample of water on analysis was found to contain the following impurities:

Impurity	Quantity (mg/L)	Mol. Wt.
$\text{Ca}(\text{HCO}_3)_2$	4	162
$\text{Mg}(\text{HCO}_3)_2$	6	146
$\text{CaSO}_4$	8	136
$\text{MgSO}_4$	10	120

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

[UPTU, 2003, 2011]

**Solution.** Step (i) Conversion into  $\text{CaCO}_3$  equivalents :

Constituent	Amount (mg/L) [A]	Multiplication factor [M]	$\text{CaCO}_3$ equivalent $= [A] \times [M]$
$\text{Ca}(\text{HCO}_3)_2$	4	100 / 162	$4 \times \frac{100}{162} = 2.47 \text{ mg/L}$
$\text{Mg}(\text{HCO}_3)_2$	6	100 / 146	$6 \times \frac{100}{146} = 4.11 \text{ mg/L}$
$\text{CaSO}_4$	8	100 / 136	$8 \times \frac{100}{136} = 5.88 \text{ mg/L}$
$\text{MgSO}_4$	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

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

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

$$\text{Hence, Temporary hardness} = 6.58 \text{ mg/L} = 6.58 \text{ ppm}$$

$$= 6.58 \times 0.1 = 0.658^\circ\text{Fr}$$

$$= 6.58 \times 0.07 = 0.46^\circ\text{Cl.}$$

**Step (iii) Determination of Permanent Hardness.**

As permanent hardness in this case is due to  $\text{CaSO}_4$  and  $\text{MgSO}_4$

$$\therefore \text{Permanent hardness} = 5.88 + 8.33 = 14.21 \text{ mg/L}$$

$$= 14.21 \text{ ppm}$$

$$= 14.21 \times 0.1 = 1.421^\circ\text{Fr}$$

$$= 14.21 \times 0.07 = 0.995^\circ\text{Cl}$$

**Example 6** Calculate the temporary, permanent and total hardness of a sample of water that is analysed as :  $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$ ;  $\text{Ca}(\text{HCO}_3)_2 = 16.2 \text{ mg/L}$ ;  $\text{MgCl}_2 = 9.5 \text{ mg/L}$  and  $\text{CaSO}_4 = 13.6 \text{ mg/L}$ . [UPTU, IIInd Sem., 2010-11]

**Solution.** Temporary hardness =  $\text{CaCO}_3$  equivalents of  $[\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2]$

$$= \left[ 7.3 \times \frac{100}{146} + 16.2 \times \frac{100}{162} \right] = [5 + 10] = 15 \text{ mg/L}$$

Permanent Hardness =  $\text{CaCO}_3$  equivalents of  $[\text{MgCl}_2 + \text{CaSO}_4]$

$$= \left[ 9.5 \times \frac{100}{95} + 13.6 \times \frac{100}{136} \right] = [10 + 10] = 20 \text{ mg/L}$$

Total Hardness = Temporary Hardness + Permanent Hardness  
 $= (15 + 20) = 35 \text{ mg/L}$

**Example 7** A sample of ground water has  $150 \text{ mg/L}$  of  $\text{Ca}^{2+}$  and  $60 \text{ mg/L}$  of  $\text{Mg}^{2+}$ . Find the total hardness expressed in milli-equivalents per liter and  $\text{mg/L}$  in terms of  $\text{CaCO}_3$ . [UPTU, June 2001]

**Solution.** Step (i) conversion into  $\text{CaCO}_3$  equivalents :

Constituent	Amount [A] (mg/L)	Multiplication factor [M]	$\text{CaCO}_3$ equivalent $= [A] \times [M] (\text{mg/L})$
$\text{Ca}^{2+}$	150	100/40	$150 \times \frac{100}{40} = 375$
$\text{Mg}^{2+}$	60	100/24	$60 \times \frac{100}{24} = 250$

Step (ii). Determination of total hardness. As total hardness in this case is due to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions.

$$\therefore \text{Total hardness} = \text{calcium carbonate equivalents of } (\text{Ca}^{2+} + \text{Mg}^{2+})$$

$$= 375 + 250 = 625 \text{ mg/L}$$

Step (iii). Expressing total hardness in milli-equivalents per liter. We know that in terms of  $\text{CaCO}_3$ ,

$$1 \text{ milli-equivalent per liter} = 50 \text{ parts per million}$$

$$\Rightarrow 1 \text{ m eq/L} = 50 \text{ ppm}$$

$$\Rightarrow 1 \text{ m eq/L} = 50 \text{ mg/L}$$

$$\therefore \text{Total hardness} = 625 \text{ mg/L}$$

$$= 625 (\text{mg/L}) \times \frac{1 (\text{m eq/L})}{50 (\text{mg/L})}$$

$$= 12.5 (\text{m eq/L}).$$

**Example 8** 100 mL of water sample has a hardness equivalent of 12.5 mL of 0.08 N  $\text{MgSO}_4$ . What is its hardness in ppm ?

[UPTU, June, 2002]

**Solution.**

$$N_1 V_1 \text{ of water sample} = N_2 V_2 \text{ of } \text{MgSO}_4$$

$$\Rightarrow N_1 \times 100 = 0.08 \times 12.5$$

$$\Rightarrow N_1 = \frac{0.08 \times 12.5}{100} = 0.01 \text{ N}$$

$$\begin{aligned} \text{Now, Hardness of water sample} &= (N_1 \times \text{Eq. wt. of } \text{CaCO}_3) \frac{\text{gms}}{\text{L}} \\ &= (0.01 \times 50) = 0.5 \text{ gms/L} \\ &= (0.5 \times 1000) \text{ mg/L} \\ &= (500) \text{ mg/L} \end{aligned}$$

## 5 BOILER FEED WATER (WATER FOR STEAM GENERATION)

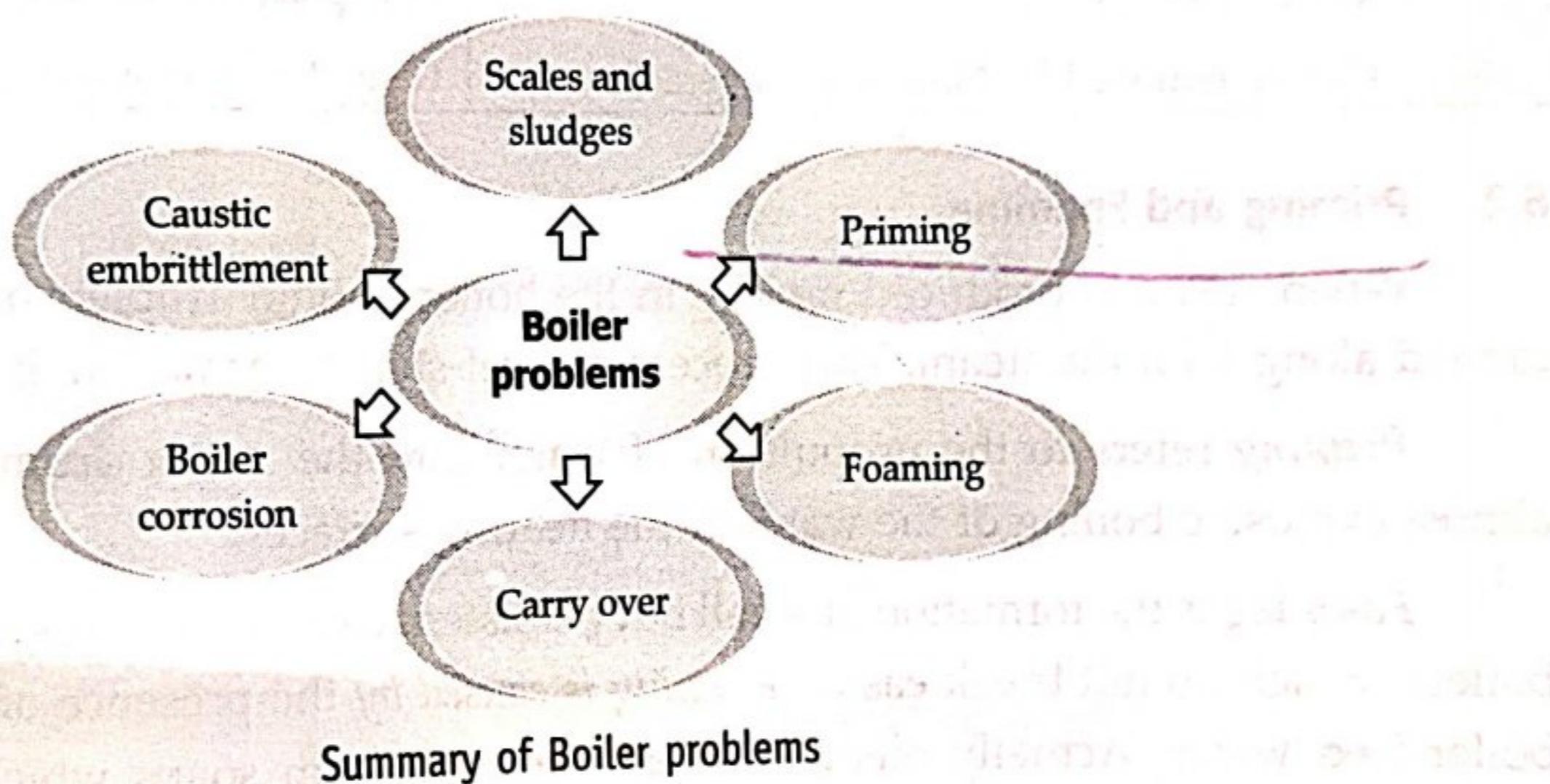
Water is mainly used in boilers for the generation of steam (for industries and power houses). For such water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits. A boiler-feed water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

- (i) Its hardness should be below 0.2 ppm.
- (ii) Its caustic alkalinity (due to  $\text{OH}^-$ ) should lie in between 0.15 and 0.45 ppm.
- (iii) Its soda alkalinity (due to  $\text{Na}_2\text{CO}_3$ ) 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.

## 6 PROBLEMS CREATED BY HARD WATER IN BOILER [UPTU, 2010, 2005]



### 6.1 Sludge and Scale Formation in Boilers [UPTU, 2007]

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.

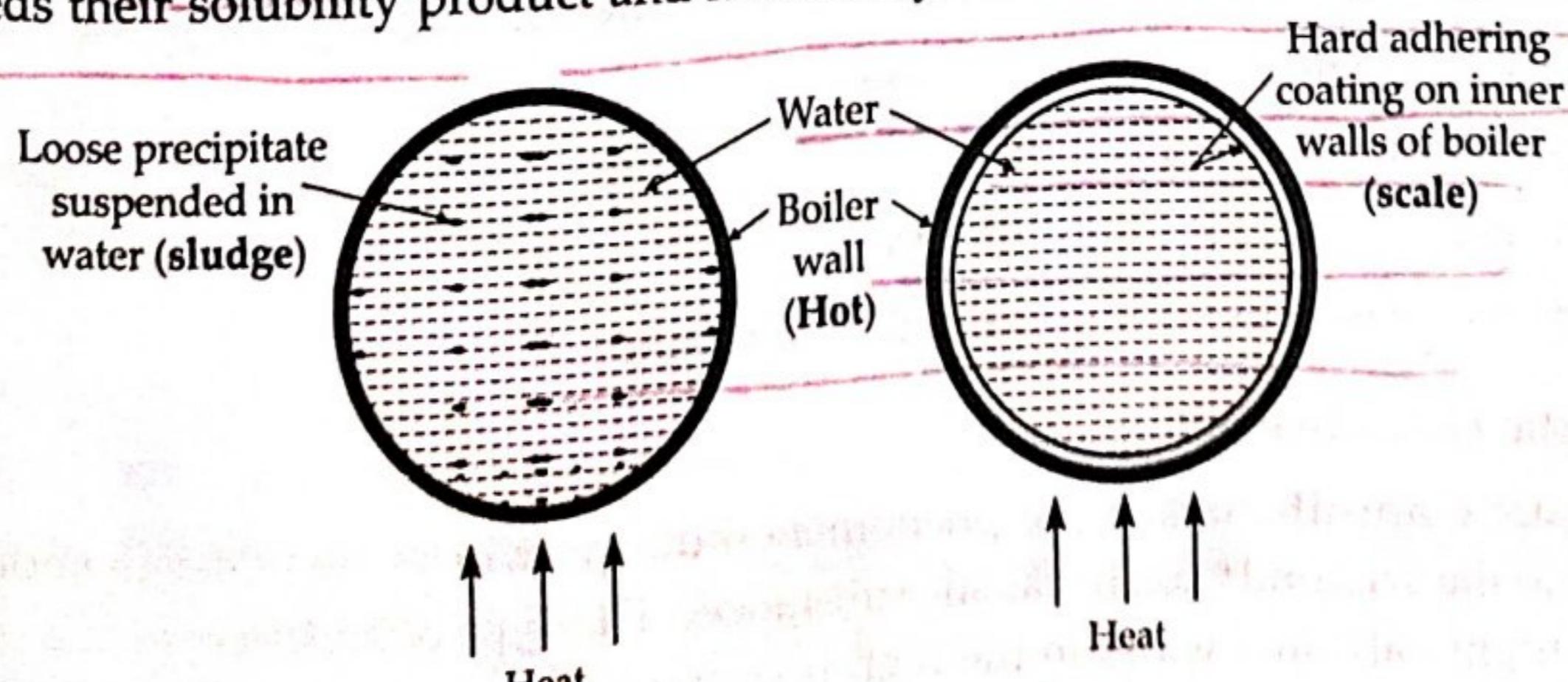


Figure 1 Sludge and scale formation in boilers.

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*.

The essential differences between sludges and scales are summarized in Table 4.

**Table 4** 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 $\text{CaCl}_2$ , $\text{MgCl}_2$ , $\text{MgSO}_4$ , $\text{MgCO}_3$ etc.	Formed by substance like $\text{CaSO}_4$ , $\text{Mg(OH)}_2$ , $\text{CaCO}_3$ , $\text{CaSiO}_3$ 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.

## 6.2 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* refers to the propulsion of water into the steam drum by extremely rapid, almost explosive boiling of the water at the heating surfaces.

*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.

## 6.3 Boiler Corrosion

Boiler corrosion is "decay" or "disintegration" of boiler body material either due to chemical or electrochemical reaction with its environment having  $\text{O}_2$ ,  $\text{CO}_2$  and mineral acids.

The disadvantages of corrosion are :

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

## 6.4 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.

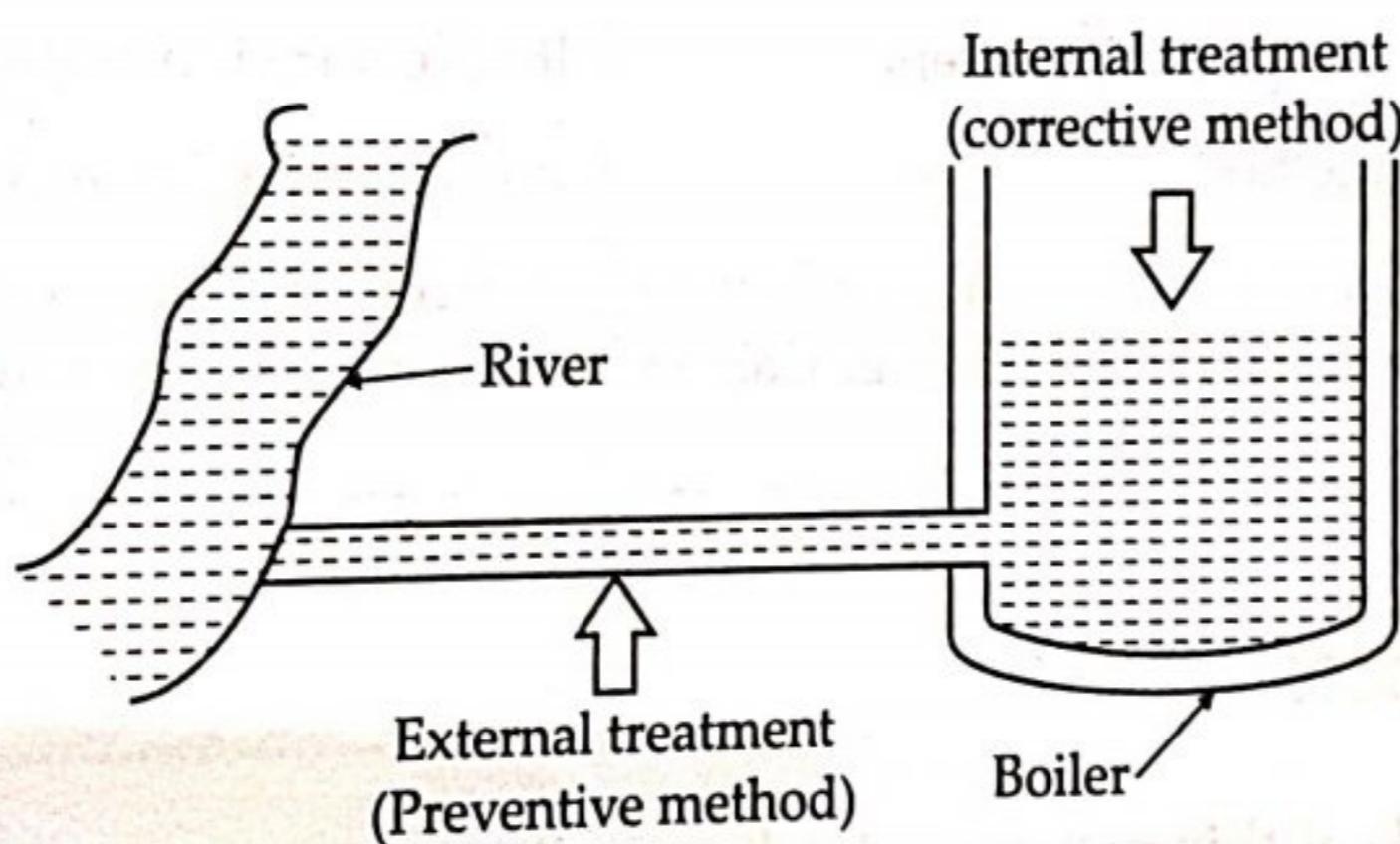
## 7 WATER SOFTENING

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*:

- « External treatment, and
- « 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.

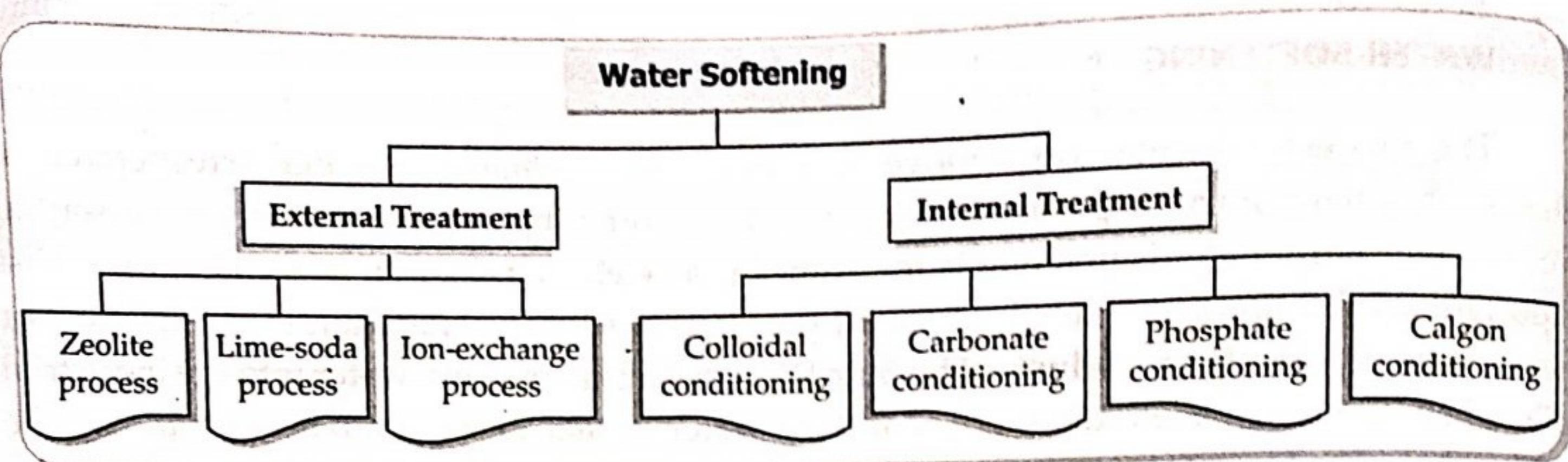


**Figure 2** Illustration of types of water treatment methods and their point of application.

In contrast, *internal treatment* 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. 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 5.

**Table 5** Differences between Internal and External Treatment Methods

S.No.	Internal Treatment (Corrective methods)	External Treatment (Preventive methods)
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.

## 8 LIME-SODA PROCESS [UPTU, 2000]

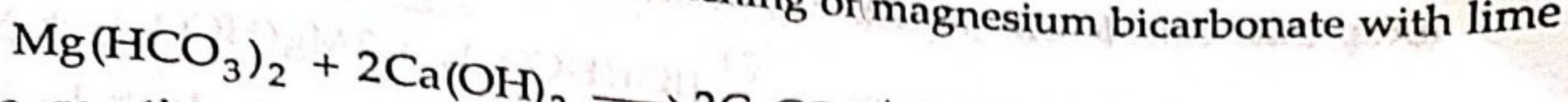
The *basic principle* of this process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates, which may be removed by settling and filtration. For this purpose, a suspension of milk of *lime*,  $\text{Ca}(\text{OH})_2$ , together with a calculated amount of *sodium carbonate*,  $\text{Na}_2\text{CO}_3$ , (*soda*) is added in requisite amount. Proper mixing of the chemicals and water is carried out. Calcium carbonate,  $\text{CaCO}_3$ ; magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ ; ferric hydroxide,  $\text{Fe}(\text{OH})_3$  and aluminium hydroxide,  $\text{Al}(\text{OH})_3$  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 [ $\text{NaAlO}_2$ ] are added, they hydrolyse to precipitate of aluminium hydroxide which entraps the fine precipitate of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . Thus coagulant helps in the formation of coarse precipitates.

**Example 9** Why does magnesium bicarbonate require double amount of lime for softening?

[UPTU, Feb., 2001]

**Solution.** The chemical reaction for the softening of magnesium bicarbonate with lime is written below :



The above reaction suggests that for the softening of one mole of magnesium bicarbonate, two moles of lime are required. Thus, magnesium bicarbonate require double amount of lime for softening.

**Example 10** Calculate the amount of lime and soda required for the treatment of 20,000 litres of water whose analysis is as follows :

$$\begin{aligned}\text{Ca}(\text{HCO}_3)_2 &= 40.5 \text{ ppm}; \text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}; \text{CaSO}_4 = 34.0 \text{ ppm}; \text{MgSO}_4 = 30 \text{ ppm}; \\ \text{CaCl}_2 &= 27.75 \text{ ppm.}\end{aligned}$$

[UPTU, II Ind Sem. Exam. 2010]

**Solution. Step (i).** Identification of lime and soda requirements for different salts. Suppose, L stands for lime  $[\text{Ca}(\text{OH})_2]$  and S stands for soda  $[\text{Na}_2\text{CO}_3]$ . They are added in hard water so as to convert hardness causing calcium and magnesium salts into corresponding insoluble precipitates of  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . For bicarbonate salts, lime must be added as bicarbonate ions and hydroxide ions react together to form carbonate ions.



Constituent	Reactions	Need
$\text{Ca}(\text{HCO}_3)_2$	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	L
$\text{Mg}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + \text{Mg}(\text{OH})_2 \downarrow + 2\text{H}_2\text{O}$	2L
$\text{CaSO}_4$	$\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	S
$\text{MgSO}_4$	$\text{MgSO}_4 + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 \downarrow + \text{CaSO}_4$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + \text{Na}_2\text{SO}_4$	(L + S)
$\text{CaCl}_2$	$\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 \downarrow + 2\text{NaCl}$	S

**Step (ii). Calculations of  $\text{CaCO}_3$  equivalents :**

Constituent	Amount (ppm)	Multiplication factor	$\text{CaCO}_3$ equivalent (ppm)
$\text{Ca}(\text{HCO}_3)_2$	40.5	100/162	$40.5 \times \frac{100}{162} = 25$
$\text{Mg}(\text{HCO}_3)_2$	36.5	100/146	$36.5 \times \frac{100}{146} = 25$
$\text{CaSO}_4$	34.0	100/136	$34.0 \times \frac{100}{136} = 25$
$\text{MgSO}_4$	30.0	100/120	$30.0 \times \frac{100}{120} = 25$
$\text{CaCl}_2$	27.75	100/111	$27.75 \times \frac{100}{111} = 25$

**Step (iii). Calculations for lime requirements :**

$$\begin{aligned}\text{Lime requirement} &= \frac{74}{100} [(\text{Ca}^{2+} + 2\text{Mg}^{2+} + \text{MgSO}_4) \text{ all in} \\ &\quad \text{terms of CaCO}_3 \text{ equivalents}] \times \text{Volume of water} \\ &= \frac{74}{100} [(25 + 2 \times 25 + 25)] \times 20,000 \text{ (mg)} \\ &= 14,80,000 \text{ mg} = 1.48 \text{ kg}\end{aligned}$$

**Step (iv). Calculations for soda requirements :**

$$\begin{aligned}\text{Soda requirement} &= \frac{106}{100} [(\text{CaSO}_4 + \text{MgSO}_4 + \text{CaCl}_2) \text{ all in} \\ &\quad \text{terms of CaCO}_3 \text{ equivalents}] \times \text{Volume of water} \\ &= \frac{106}{100} [(25 + 25 + 25)] \times 20,000 \text{ (mg)} \\ &= 15,90,000 \text{ mg} = 1.59 \text{ kg}\end{aligned}$$

**Example 11** A water sample contains the following impurities :

$$\text{Ca}^{2+} = 20 \text{ ppm}, \text{Mg}^{2+} = 18 \text{ ppm}, \text{HCO}_3^- = 183 \text{ ppm} \text{ and } \text{SO}_4^{2-} = 24 \text{ ppm.}$$

Calculate the Lime and soda needed for softening. ( $\text{Ca} = 40, \text{Mg} = 24$ )

[UPTU, II<sup>nd</sup> Sem., 2007-08]

**Solution.** Step (i) Conversion into  $\text{CaCO}_3$  equivalents :

Constituent	Amount (ppm)	Multiplication factor	$\text{CaCO}_3$ equivalents
$\text{Mg}^{2+}$	18	100/24	$18 \times 100 / 24 = 75 \text{ ppm}$
$\text{Ca}^{2+}$	20	100/40	$20 \times 100 / 40 = 50 \text{ ppm}$
$\text{HCO}_3^-$	183	100/122	$183 \times 100 / 122 = 150 \text{ ppm}$

**Step (ii). Amount of lime required for softening :**

$$\begin{aligned}&= \frac{74}{100} [(\text{Mg}^{2+} + \text{HCO}_3^-) \text{ as CaCO}_3 \text{ equivalents}] \\ &= \frac{74}{100} [(75 + 150)] = 166.5 \text{ ppm}\end{aligned}$$

**Step (iii). Amount of soda required for softening :**

$$\begin{aligned}&= \frac{106}{100} [(\text{Mg}^{2+} + \text{Ca}^{2+} - \text{HCO}_3^-) \text{ as CaCO}_3 \text{ equivalents}] \\ &= \frac{106}{100} [(75 + 50 - 150)] = -26.5 \text{ ppm.}\end{aligned}$$

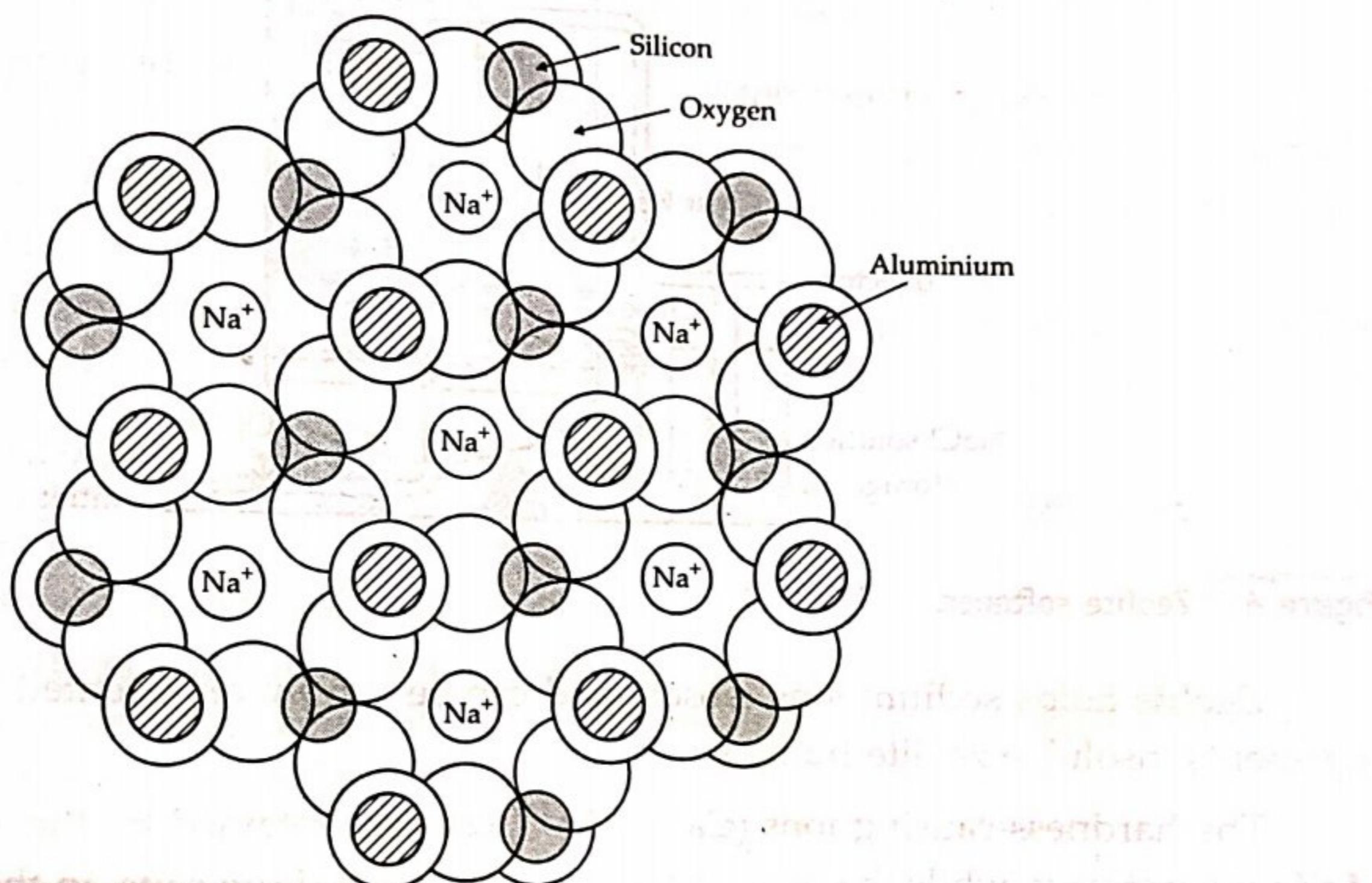
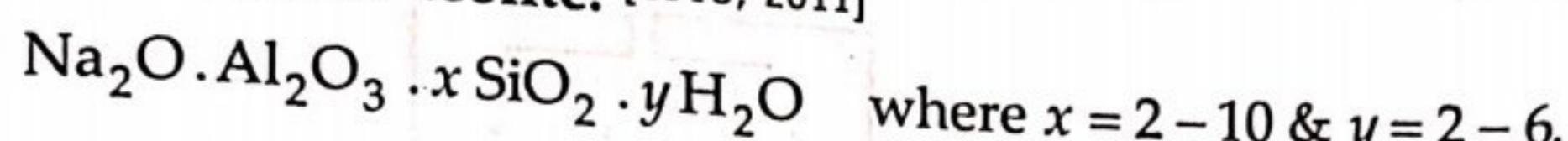
Hence, soda is not required.

## 9 ZEOLITE OR PERMUTIT PROCESS

**Zeolites** are naturally occurring hydrated sodium aluminosilicate minerals capable of exchanging reversibly its sodium ions for hardness-producing ions in water.

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

**The chemical formula of zeolite.** [UPTU, 2011]



**Figure 3** Structure of a naturally occurring zeolite,  $\text{NaAlSiO}_4$ . The sodium ions are loosely held in holes in the lattice.

A zeolite crystal can be considered to result from the linking of several  $\text{SiO}_4$  tetrahedra, each oxygen of a tetrahedron being shared with an adjacent one. The empirical formula is thus  $(\text{SiO}_2)_n$ . However, some of the  $\text{Si}^{4+}$  ions may be isomorphously replaced by  $\text{Al}^{3+}$  ions and in order to balance the charges an extra positive-ion such as  $\text{Na}^+$  and  $\text{K}^+$  must also be incorporated for every  $\text{Al}^{3+}$  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.

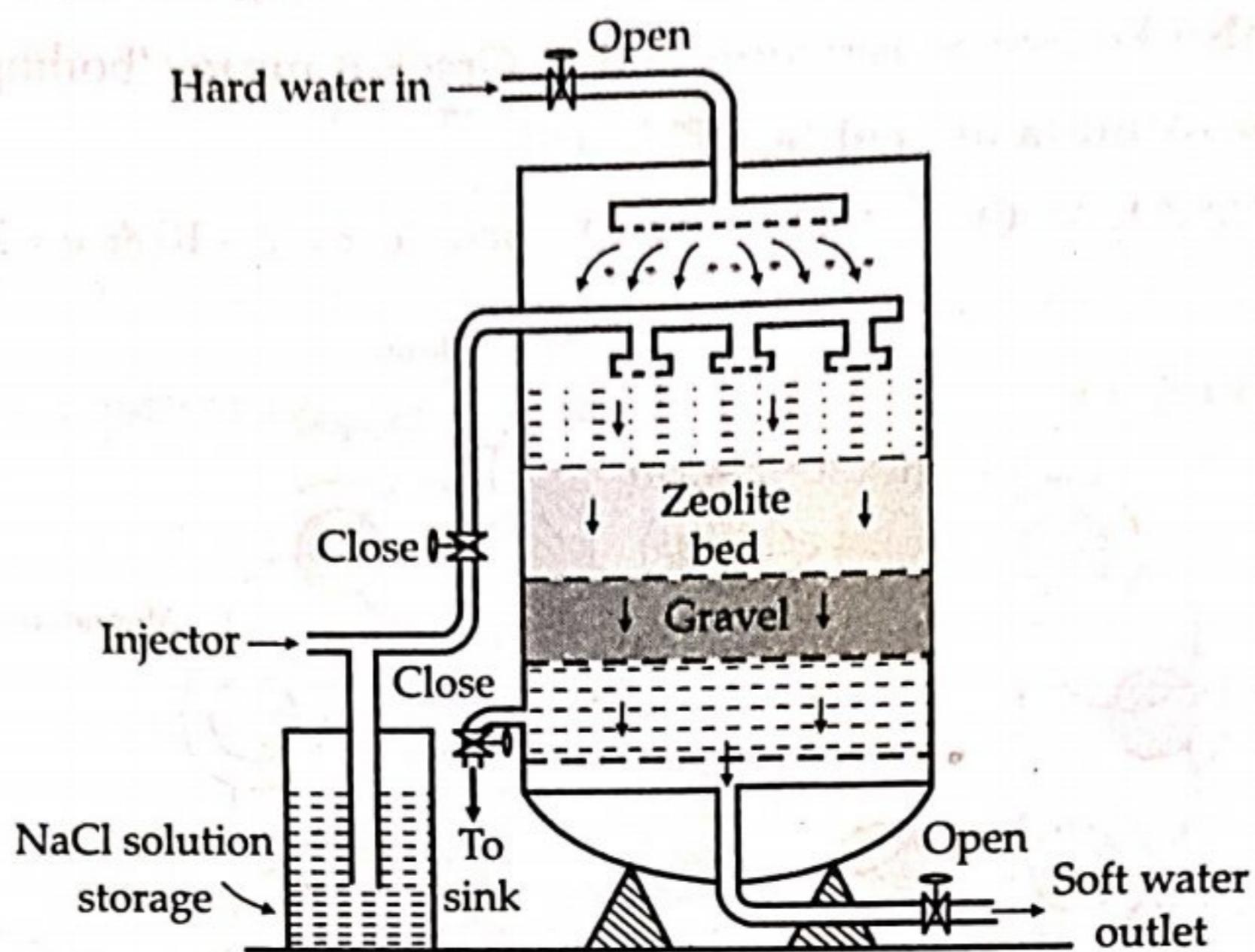
- (i) *Natural zeolites* are non-porous, amorphous and durable for example, natrolite,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ .
- (ii) *Synthetic zeolites* are porous and possess a gel structure. They are prepared by heating together sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and silica ( $\text{SiO}_2$ ).

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

[UPTU, 2001, 03, 04, 07, 09, 11, 12]

**Zeolite Process for the Removal of Hardness of Water**

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. 4.

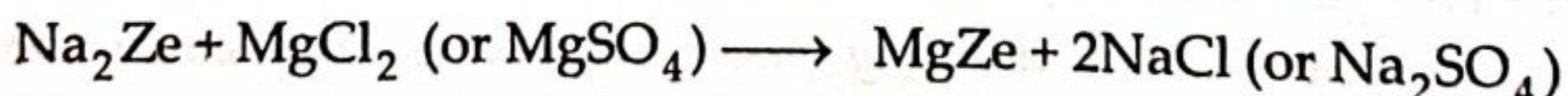
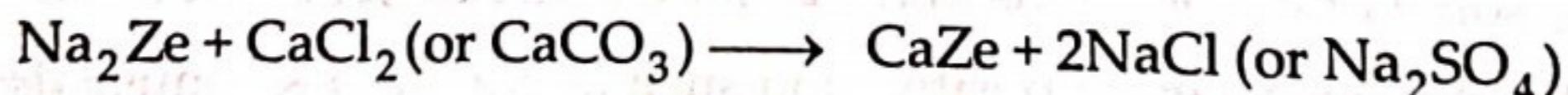
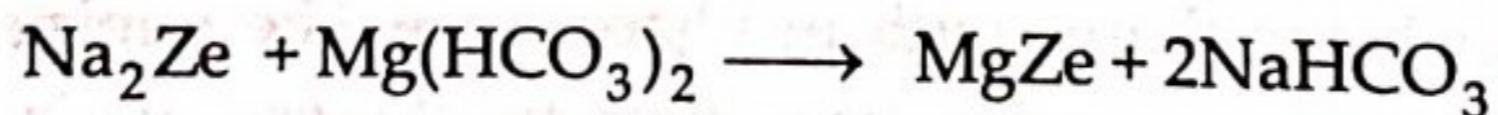
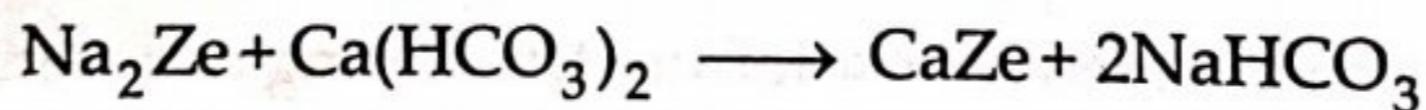


**Figure 4** Zeolite softener.

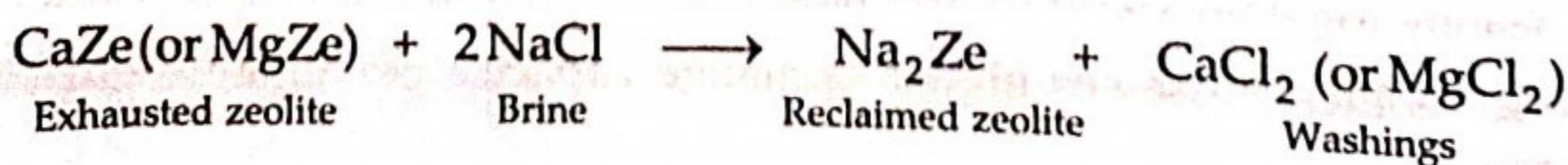
Zeolite holds sodium ions loosely and can be simply represented as  $\text{Na}_2\text{Ze}$  where Ze represents insoluble zeolite frame work.

The hardness-causing ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc.) are retained by the zeolite as  $\text{CaZe}$  and  $\text{MgZe}$  respectively, while the outgoing water contains sodium salts. In the process, the water becomes free from  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$ , 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 reaction takes place :



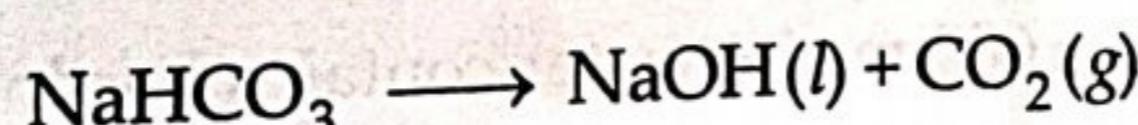
The washings (containing  $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) are led to drain and the regenerated zeolite bed thus obtained is used again for softening purpose.

#### NOTE

Instead of  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$  etc. can also be used for regeneration but  $\text{NaCl}$  is mostly used because of its low cost and the products of regeneration process ( $\text{CaCl}_2$  and  $\text{MgCl}_2$ ) are highly soluble and can be easily rinsed out from the zeolite bed.

#### *Limitations (or demerits) of zeolite process [UPTU, 2009, 2012]*

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  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$ , 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  $\text{NaHCO}_3$  which goes into soft water effluent. If it is used as boiler feed, under the boiler conditions  $\text{NaHCO}_3$  dissociates to



Both the products are not desirable. Since  $\text{NaOH}$  may lead to caustic embrittlement and  $\text{CO}_2$  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 (or merits) of zeolite process [UPTU, 2012]*

- (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.

**Example 12** The hardness of 1,000 litres of a sample of water was removed by passing it through a zeolite softener. The zeolite softener then required 30 litres of sodium chloride solution containing 1.5 gm/litre of NaCl for regeneration. Find the hardness of water sample.

[UPTU, 2nd Sem., 2008-09]

**Solution.** NaCl contained in 30 L of NaCl solution

$$= 1.5 \text{ gm/L} \times 30 \text{ L}$$

$$= 45 \text{ gm of NaCl} = 45 \times \frac{50}{58.5}$$

$$= 38.46 \text{ gm equivalents of CaCO}_3$$

$$\therefore 1,000 \text{ litres of water} = 38.46 \text{ gm equivalents of CaCO}_3$$

$$\Rightarrow 1 \text{ L of water} = \frac{38.46 \times 10^3}{1,000} \text{ mg/L of CaCO}_3 \text{ eq.}$$

Hence, hardness of water is 38.46 ppm.

**Example 13** An exhausted zeolite softener was regenerated by passing 150 litres of NaCl solution, having a strength of 1.5 gm/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 600 ppm.

[UPTU, 2004]

**Solution.** 150 L of NaCl solution contains  $= 150 \text{ L} \times (1.5 \text{ g/L})$  of NaCl

$$= 225 \text{ gm of NaCl} = 225 \text{ gm} \times \left( \frac{100}{117} \right) \text{ CaCO}_3 \text{ eq.}$$

$$= 192.308 \text{ gm CaCO}_3 \text{ eq.} = 192308 \text{ mg CaCO}_3 \text{ eq.}$$

Let  $V$  litres (of 600 ppm = 600 mg/L) water contains hardness

$$= 192308 \text{ mg CaCO}_3 \text{ eq.}$$

$$\therefore \text{The total volume of water that can be softened} = \left( \frac{192308}{600} \right) = 320.5 \text{ L}$$

**Example 14** A zeolite softener was 90% exhausted by removing the hardness completely when 10,000 litres of hard water sample passed through it. The exhausted zeolite bed required 200 litres of 3% sodium chloride solution for its complete regeneration. Calculate the hardness of water solution.

**Solution.** NaCl contained in 200 L of 3% NaCl solution

$$= (30 \text{ gm/L}) \times 200 \text{ L} = 6,000 \text{ g NaCl}$$

$$= 6,000 \times \frac{50}{58.5} = 5,128 \text{ gm equivalents of CaCO}_3$$

$$\therefore 90\% \text{ hardness of } 10,000 \text{ L of water} = 5,128 \text{ gm equivalents CaCO}_3$$

$$\Rightarrow 1 \text{ L of water} = \frac{5,128}{\left( 10,000 \times \frac{90}{100} \right)} = \frac{5,128}{9000} = 0.5698 \text{ gm equivalents of CaCO}_3$$

$$= 0.5698 \times 1000 \text{ mg CaCO}_3 \text{ eq.} = 569.8 \text{ mg CaCO}_3 \text{ eq.}$$

Hence, hardness of water is 569.8 mg/L or 569.8 ppm.

10

## 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*.

### **Ion-exchange method for Water Softening [UPTU, 2008]**

The hard water is first passed through cation exchange column (Fig. 5), when all the cations like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc. are removed (taken up by the resin) from it, and equivalent amount of  $\text{H}^+$  ions are released from this column to water.

Thus

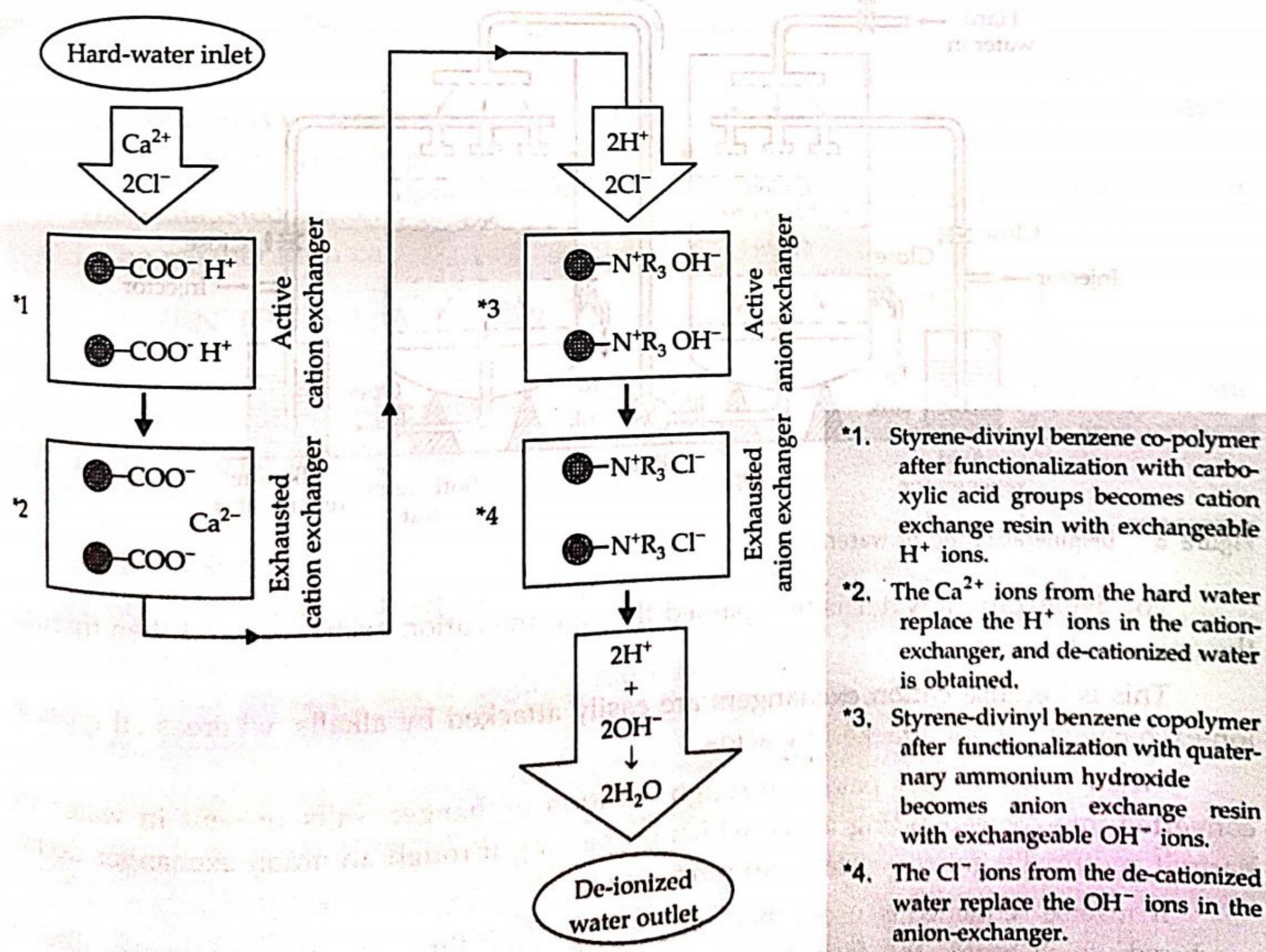
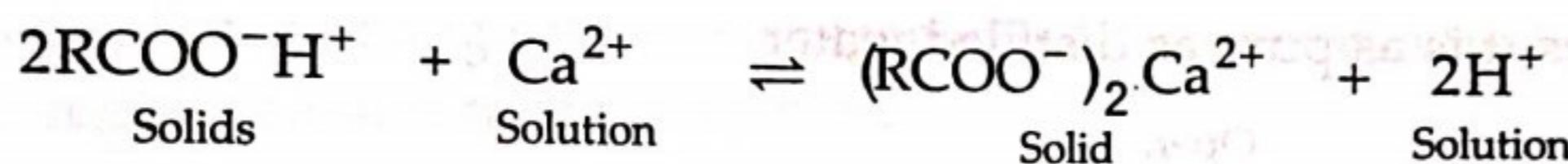
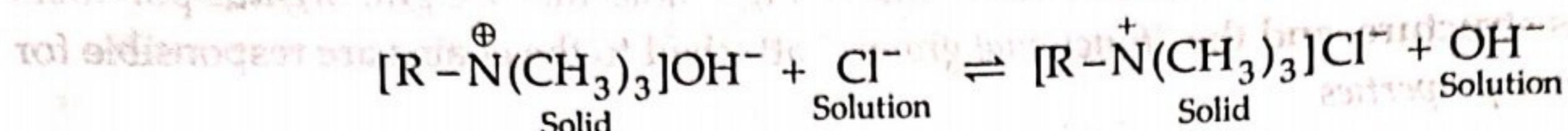


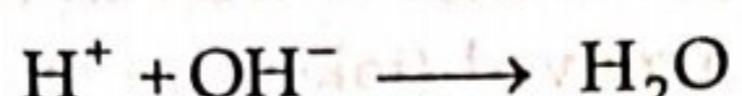
Figure 5 Illustration of the de-ionization process using ion-exchange resins.

After passing through cation exchange column, the hard water is passed through anion exchange column, when all the anions like  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , etc. present in the water are removed (taken up by resin) and equivalent amount of  $\text{OH}^-$  ions are released from this column to water.

Thus :



$\text{H}^+$  and  $\text{OH}^-$  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.

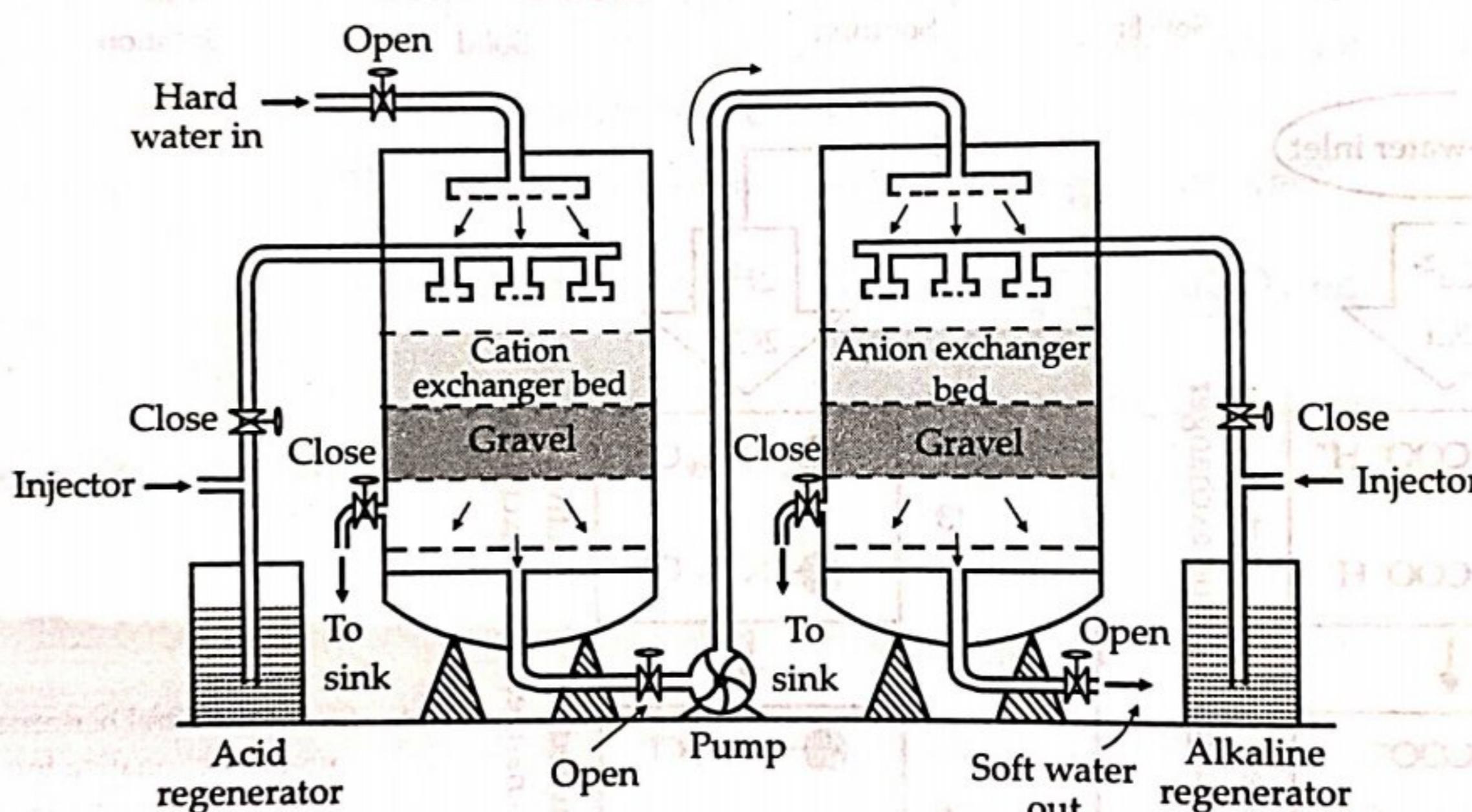


Figure 6 Demineralization of water.

For deionization, water is first passed through the cation exchanger and then through the anion exchanger.

This is because cation exchangers are easily attacked by alkalis, whereas all types of ion-exchangers are not attacked by acids.

When water is first passed through a cation exchanger, salts present in water are converted into corresponding acids, which on passing through an anion exchanger do not harm it and finally get converted into pure water.

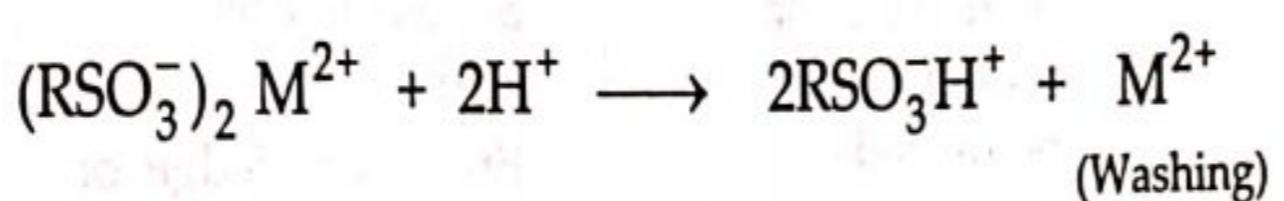
If reverse sequence is used, then on passing water through anion-exchanger, alkali is produced which harms the cation-exchanger in subsequent step. Thus, such a sequence is usually avoided.

### Differences between Soft Water and Demineralised Water

	Soft Water	Demineralised Water
1.	Soft water has hardness $\leq 85$ ppm ( $\text{CaCO}_3$ eq.). Thus, soft water has more hardness than demineralised water.	Demineralised water does not have any salt (or cations & anions) present in it. So, hardness $\ll 2$ ppm.
2.	It is fit for domestic use.	It is not recommended as such for drinking purposes.
3.	It can be made by using either Lime-Soda process or Zeolite process.	It can be made either by distillation or by using cation & anion exchangers.
4.	Soft water is unfit for feeding into boilers.	It is very good for use in high-pressure boilers.

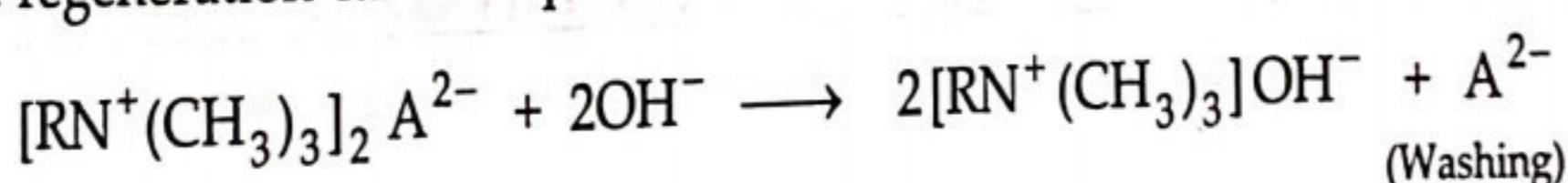
**Regeneration.** When capacities of cation and anion exchangers to exchange  $\text{H}^+$  and  $\text{OH}^-$  ions respectively are lost, they are then said to be *exhausted*.

The exhausted cation exchange column is regenerated by passing a solution of dil.  $\text{HCl}$  or dil.  $\text{H}_2\text{SO}_4$ . The regeneration can be represented as :



The column is washed with deionized water and washing (which contains  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc. and  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  ions) is passed to sink or drain.

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



The column is washed with deionized water and washing (which contains  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$  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.

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  $\text{Na}^+$  form is used. Its operation is reversible and regeneration is carried out using readily available, inexpensive  $\text{NaCl}$  solution (brine).

The Pros and Cons of ion-exchange, zeolite and lime-soda processes are summarized in Table 6.

**Table 6 Comparison of Ion-exchange, Zeolite (or Permutit) and Lime-soda processes**

[UPTU, 2004, 2008, 2011]

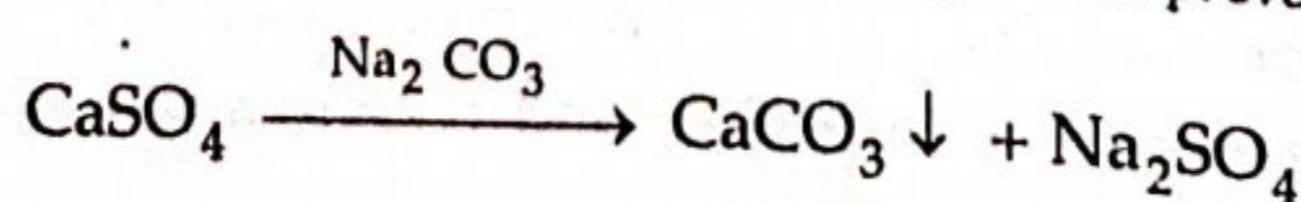
S.No.	Characteristic	Ion-exchange process	Zeolite process	Lime-soda process
1.	Requirements	Cation and anion exchangers	zeolite	Lime, soda and coagulants
2.	Exchange of ions	Exchange of both cations and anions takes place	Exchange of only cations takes place	No exchange of ions.
3.	Capital cost	Very high	High	Low
4.	Operating expenses	High	Low	High
5.	Raw water	<ul style="list-style-type: none"> <li>■ Should be non-turbid</li> <li>■ Both acidic or alkaline water can be treated</li> <li>■ Prior knowledge of hardness not required</li> </ul>	<ul style="list-style-type: none"> <li>■ Should be non-turbid</li> <li>■ Should not be acidic</li> <li>■ Prior knowledge of hardness not required.</li> </ul>	Prior knowledge of hardness is essential
6.	Automation	Possible	Possible	Not possible
7.	Residual hardness	Least (0-2 ppm)	Low (0-15 ppm)	High (15-50 ppm)

#### NOTES

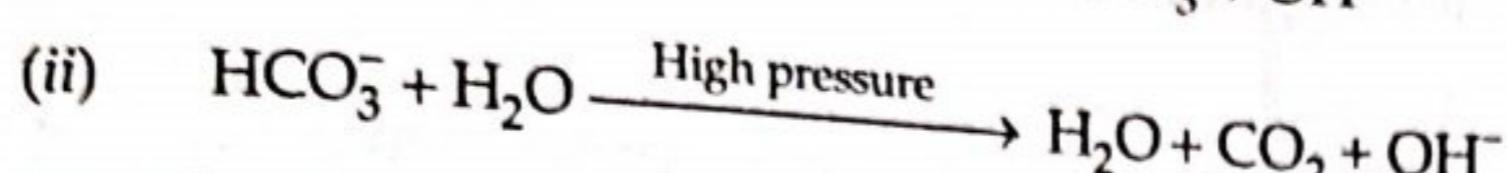
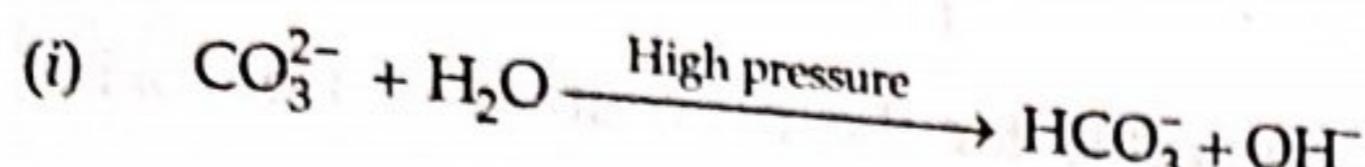
**1. Colloidal conditioning.** Scale formation can be avoided in low pressure boilers by adding substances like kerosene, tannin, agar-agar, etc. which get adsorbed over the scale forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by blow-down operation.

**2. Carbonate conditioning.** For a salt to be precipitated, the ions constituting the salt must be present in sufficient concentration so that the product of their concentrations (i.e., ionic product) exceeds a limiting value known as the solubility product. Thus, for a salt like  $\text{CaCO}_3$  to be precipitated, the product of the concentrations of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  must exceed the solubility product of  $\text{CaCO}_3$ , represented as  $K_{sp}^{\text{CaCO}_3}$ .

When sodium carbonate solution is added to boiler water, the  $[\text{CO}_3^{2-}]$  increases and when it becomes greater than  $K' [\text{SO}_4^{2-}]$ , only  $\text{CaCO}_3$  gets precipitated. Moreover,  $\text{CaSO}_4$  remains in solution so the deposition of scale-forming calcium sulphate is prevented.



In high-pressure boilers, scale formation cannot be avoided by adding sodium carbonate to boiler water. This is because, in high pressure boiler, the  $\text{CO}_3^{2-}$  ions undergo hydrolysis to from  $\text{OH}^-$  ions.



Because of the above two hydrolysis reactions (i) and (ii), the concentration of carbonate ions (i.e.,  $[\text{CO}_3^{2-}]$ ) gets reduced. Thus, it becomes impossible for solution to become saturated w.r.t. calcium or magnesium carbonate. As a consequence, precipitation and subsequent loose sludge formation due to  $\text{CaCO}_3$  or  $\text{MgCO}_3$  becomes impossible.

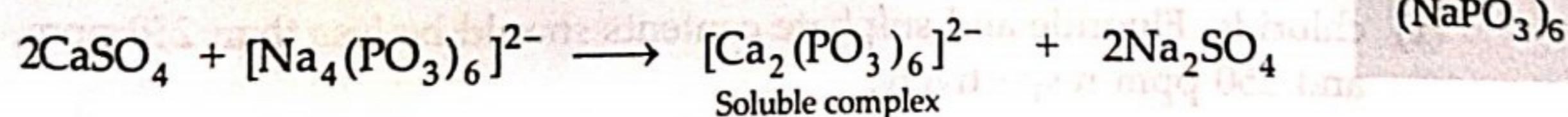
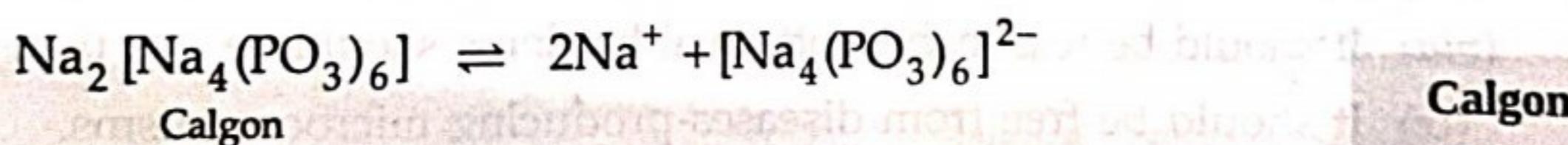
Moreover, due to hydrolysis reactions (i) and (ii), the hydroxide ion concentration (i.e.,  $[\text{OH}^-]$ ) becomes high which can lead to caustic embrittlement.

To sum up,

Carbonate conditioning is not done in high pressure boilers, because (a) it is not applicable, (b) It may lead to caustic embrittlement.

## 11 CALGON CONDITIONING [UPTU, 2007, 08]

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  $\text{CaSO}_4$ ) into soluble complex compound, which are harmless to boiler.

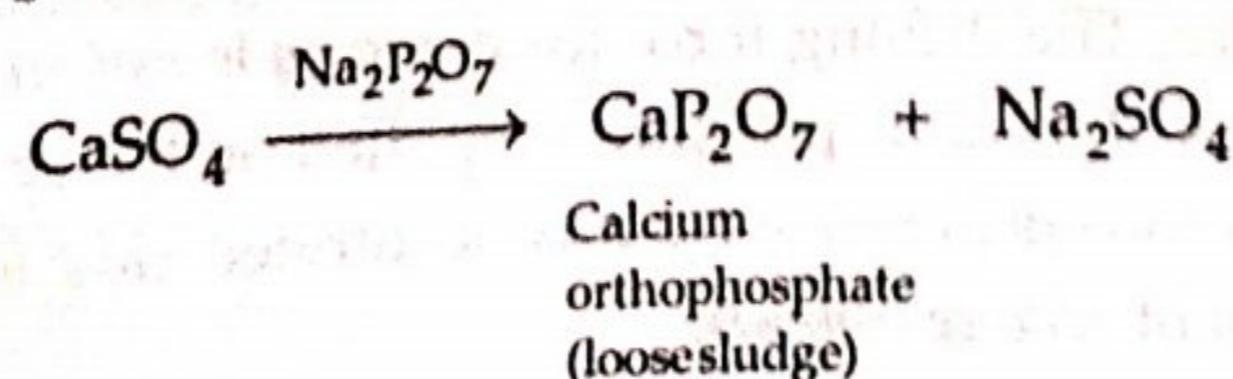
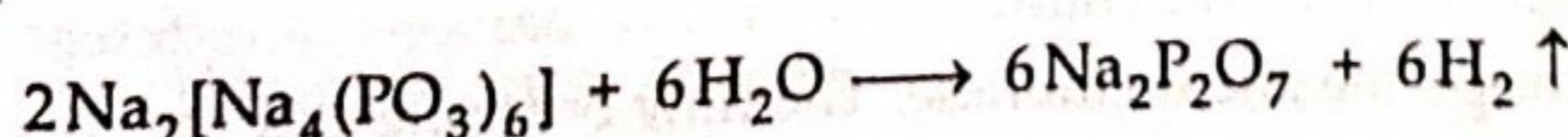


Calgon

$(\text{NaPO}_3)_6$

Addition of 0.5 – 5 ppm of calgon prevents scale formation in one of the following ways :

- (i) At low temperatures and pressures, it forms quite stable and soluble complexes with calcium salts,
- (ii) At high temperatures and pressures, calgon is converted into sodium orthophosphate which reacts with calcium salts to form calcium orthophosphate.



Calcium orthophosphate appears as loose sludge and thus can be removed by blow-down operation.

### Limitations of Calgon Conditioning

Calgon conditioning is not applicable for the prevention of iron oxide and copper depositions.

However, iron oxide and copper depositions can be prevented by adding EDTA or its sodium salt to the boiler water. In this method, the problem causing cations are converted into complexes, which will stay in "dissolved form" in water and thus do not cause any harm.

## 12 POTABLE WATER [UPTU, 2007]

*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.

## 13 REVERSE OSMOSIS

### 13.1 Principle of Reverse Osmosis [UPTU, 2006]

*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. 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*.

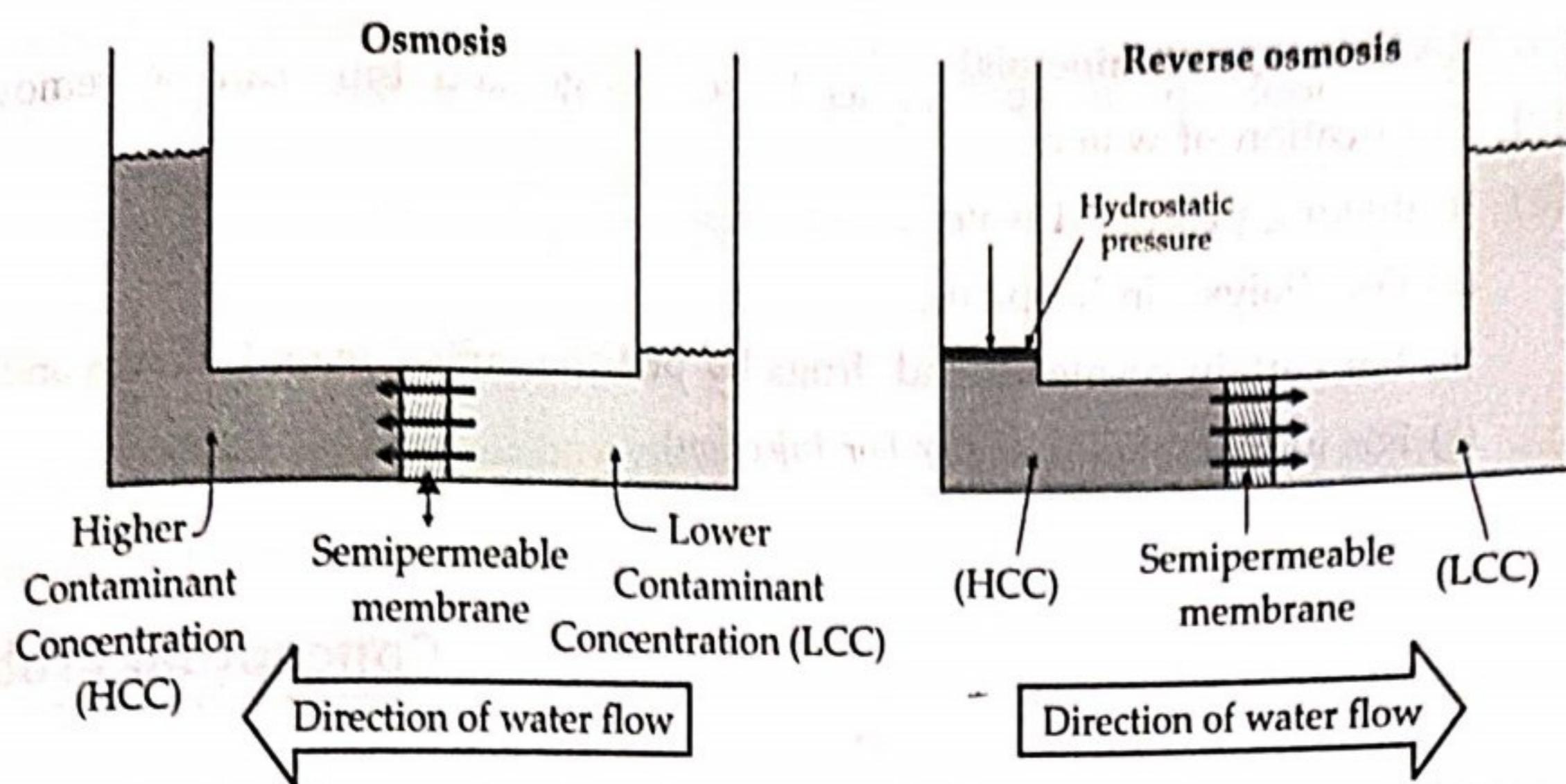


Figure 7 Diagrammatic representation of Osmosis and Reverse Osmosis Processes.

### 13.2 Desalination of Brackish water using Reverse Osmosis [UPTU, 2006]

(Semi-permeable membrane is selective membrane which does not permit the passage of dissolved solute particles.) 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. 8) for separating the water (pure solvent) from its contaminants. The process is also known as *super-or hyper-filtration*.

### 13.3 Advantages

- Colloidal  $\text{SiO}_2$  can be removed by reverse osmosis which even cannot be removed by demineralisation ;
- It is simple and reliable process ;
- Capital and operating expenses are low ;
- 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.
- It operates at a comparatively low temperature.
- It is relatively energy efficient.

### 13.4 Applications

- Treatment of waste water,
- Desalination,

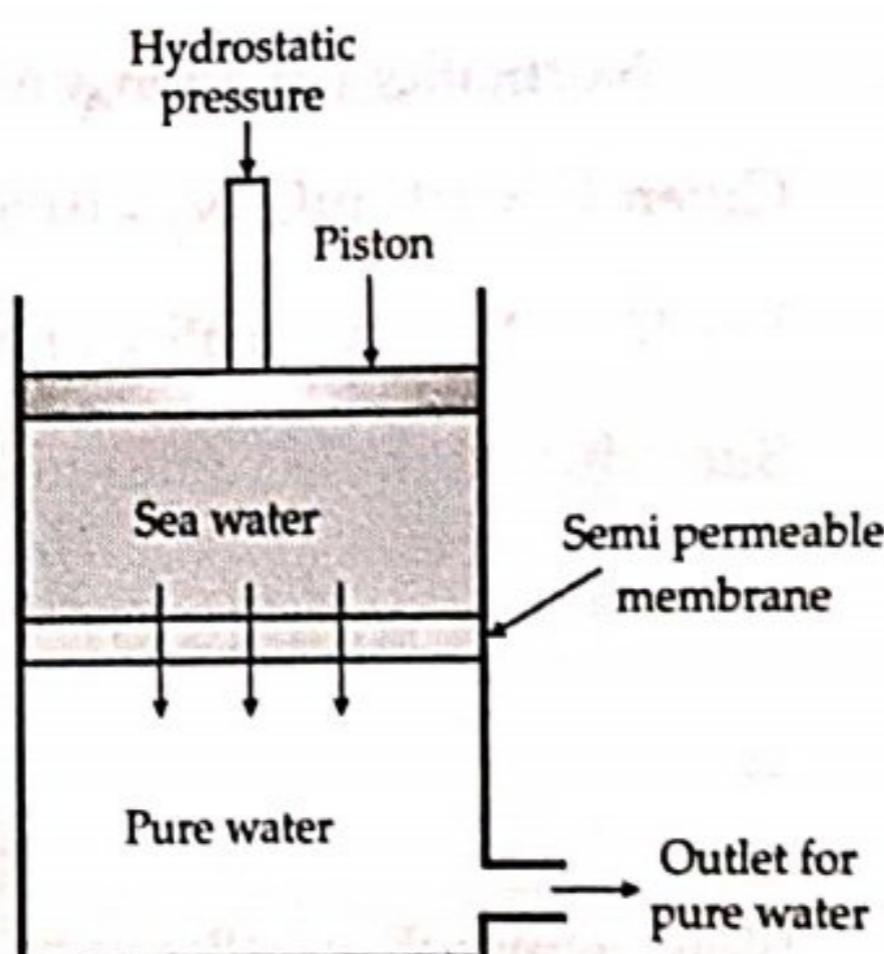


Figure 8 Reverse Osmosis cell

- (iii) Reclamation of minerals,
- (iv) Purification of water,
- (v) In making processed water :
  - (a) For dialysis in hospitals,
  - (b) For certain cosmetics and drugs by pharmaceutical manufacturers and
  - (c) For injection (WFI, Water For Injection).

## Conceptual Problems

1. A 100 mL water sample required 25 mL of 0.05 N sulphuric acid for phenolphthalein end point and another 10 mL for methyl orange end point. Determine the nature and amount of alkalinity present in water.

**Ans. (A)** Titration of 100 mL of water sample against 0.05 N sulphuric acid upto phenol-phthalein end point.

$$\text{Normality equation} \equiv N_1 V_1 \text{ (Alkaline water)} = N_2 V_2 \text{ (Sulphuric acid)} \quad \dots(1)$$

Given  $V_1 = 100 \text{ mL}$ ,  $N_2 = 0.05 \text{ N}$ , and  $V_2 = 25 \text{ mL}$ .

Let  $N_1 = N_P \equiv$  normality of alkaline water sample estimated using phenolphthalein indicator.

Substituting these values in Equation (1), we get

$$\therefore N_P \times 100 = 0.05 \times 25 \quad \dots(2)$$

$$\Rightarrow N_P = \left( \frac{0.05 \times 25}{100} \right) \quad \dots(3)$$

Now, strength of alkalinity of water, in terms of  $\text{CaCO}_3$  equivalents (in ppm), upto phenolphthalein end-point

$$\Rightarrow P = (N_P \times 50 \times 1000) \text{ ppm} \quad \dots(4)$$

$$\Rightarrow P = \left( \frac{0.05 \times 25}{100} \times 50 \times 1000 \right) \text{ ppm}$$

$$\Rightarrow P = 62.5 \text{ ppm} \quad \dots(5)$$

**(B)** Titration of 100 mL of water sample against 0.05 N sulphuric acid upto methyl orange end point.

Here  $V_1 = 100 \text{ mL}$ ,  $N_2 = 0.05 \text{ N}$ ,  $V_2 = (25 + 10) = 35 \text{ mL}$

Let  $N_1 = N_M \equiv$  normality of alkaline water sample estimated using methyl orange indicator.

Substituting these values in equation (1), we get

$$N_M \times 100 = 0.05 \times 35$$

$$\Rightarrow N_M = \left( \frac{0.05 \times 35}{100} \right) \quad \dots(6)$$

$$\dots(7)$$

Now, strength of alkalinity of water, in terms of  $\text{CaCO}_3$  equivalents (in ppm), upto methyl orange  
 end point =  $M = (N_M \times 50 \times 1000)$  ppm ... (8)

$$\Rightarrow M = \left( \frac{0.05 \times 35}{100} \right) \times 50 \times 1000 \text{ ppm}$$

$$\Rightarrow M = 87.5 \text{ ppm} \quad \dots (9)$$

From equations (5) and (9),  $P > \frac{1}{2} M$

Hence  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  ions are present. ... (10)

$$\text{Alkalinity due to } \text{OH}^- = (2P - M) \quad \dots (11)$$

$$= (2 \times 62.5 - 87.5) = 37.5 \text{ ppm} \quad \dots (12)$$

$$\text{and Alkalinity due to } \text{CO}_3^{2-} = 2(M - P) \quad \dots (13)$$

$$= 2(87.5 - 62.5) = 50 \text{ ppm} \quad \dots (14)$$

2. Calculate the amount of lime and soda required for softening 50,000 L of water containing the following salts :

$\text{Ca}(\text{HCO}_3)_2 = 8.1 \text{ mg/L}$ ,  $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/L}$ ,  $\text{CaSO}_4 = 13.6 \text{ mg/L}$ ,  $\text{MgSO}_4 = 12.0 \text{ mg/L}$ ,  
 $\text{MgCl}_2 = 2.0 \text{ mg/L}$ ,  $\text{NaCl} = 4.7 \text{ mg/L}$ . (Atomic weights : Ca = 40, Mg = 24, Na = 23, C = 12, S = 32,  
 O = 16, H = 1, Cl = 35.5)

Ans.

Constituent	Amount $A \left( \frac{\text{mg}}{\text{L}} \right)$	Multiplication Factor $M$	$\text{CaCO}_3$ Equivalents $A \times M \left( \frac{\text{mg}}{\text{L}} \right)$	Need $\text{Lime} = L$ $\text{Soda} = S$
$\text{Ca}(\text{HCO}_3)_2$	8.1	$\frac{100}{162}$	5	L
$\text{Mg}(\text{HCO}_3)_2$	7.3	$\frac{100}{146}$	5	2 L
$\text{CaSO}_4$	13.6	$\frac{100}{136}$	10	S
$\text{MgSO}_4$	12.0	$\frac{100}{120}$	10	$L + S$
$\text{MgCl}_2$	2.0	$\frac{100}{95}$	2.1	$L + S$

$$\text{Lime} = \frac{74}{100} [\text{Ca}(\text{HCO}_3)_2 + 2\text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2 + \text{MgSO}_4] \frac{\text{mg}}{\text{L}} \times \text{volume (L)}$$

$$= \frac{74}{100} [5 + 2 \times 5 + 2.1 + 10] \times 50,000 \text{ mg} = 74.19 \times 10^6 \text{ mg} = 74.19 \text{ kg}$$

$$\text{Soda} = \frac{106}{100} [\text{CaSO}_4 + \text{MgCl}_2 + \text{MgSO}_4] \frac{\text{mg}}{\text{L}} \times \text{volume (L)}$$

$$= \frac{106}{100} [10 + 2.1 + 10] \times 50,000 \text{ mg} = 1.17 \times 10^6 \text{ mg} = 1.17 \text{ kg}$$

## Exercises

1. Calgon treatment prevents scale formation in boilers, explain.
2. What are Zeolites ? How do they function in removing hardness of water ? What are the limitations of this process ?
3. (a) Zeolite softeners are not recommended for obtaining feed water for the modern high pressure boilers. Give reasons.  
(b) Why is calgon conditioning better than phosphate conditioning ?
4. Describe the ion exchange process of water softening.

## Examination Questions

### Based on Hard Water and Hardness

1. Discuss the problems created by hard water in boiler. [UPTU, IIInd Sem., 2009-10]
2. Why does soap not give lather with hard water ? Write chemical reactions in support of your answer. [UPTU, IIInd Sem., 2011-12]
3. (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 ? [U.P. Tech., B.Tech, 1st Sem. 2000-01]
4. A sample of ground water has 150 mg/L of  $\text{Mg}^{2+}$ . Find the total hardness expressed in milli-equivalent per litre and mg/L in terms of  $\text{CaCO}_3$ . [UPTU, 2001, 2004]
5. Why is it conventional to express hardness of water in terms of  $\text{CaCO}_3$  at the International level ? Write other units also. [U.P. Tech., B.Tech, 1st/2nd Sem. 2000-02]
6. (a) What do you understand by Hardness of Water ?  
(b) What are different units of hardness of water ? Write relationship between them. [IUPTU, 2003, 2009, 2011]
7. What are the disadvantages in using hard water ? [U.P. Tech., 1st Sem., 2003]
8. A water sample contains 408 mg of  $\text{CaSO}_4$  per litre. Calculate the harness in terms of  $\text{CaCO}_3$  equivalent. [U.P. Tech., 2nd Sem., 2006-07]