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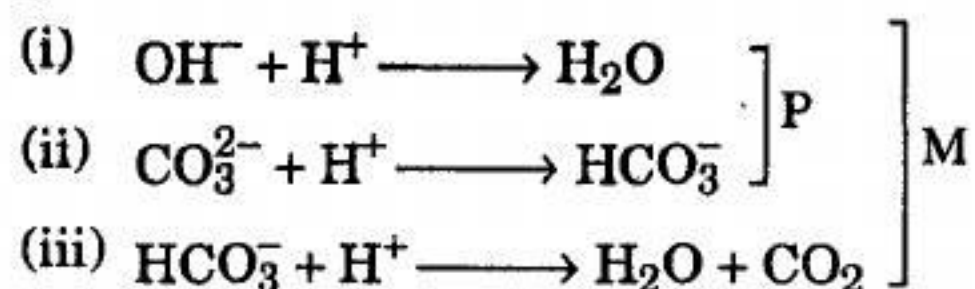
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- (i) Bicarbonate alkalinity
- (ii) Carbonate alkalinity
- (iii) Hydroxide alkalinity

3.3.1. Determination of Alkalinity

The type and extent of alkalinity of a sample of water can be determined easily by titrimetric method. The procedure is as follows.

An aliquot of the sample is titrated against a standard acid using phenolphthalein and methyl orange as indicators. The reactions involved are as follows.



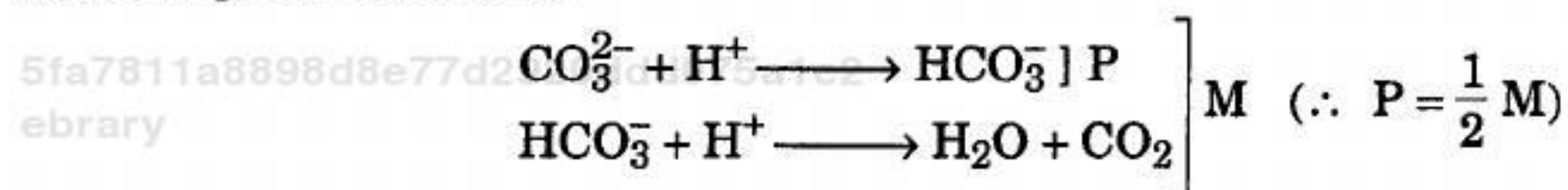
The volume of the standard acid used upto **phenolphthalein end point P** marks the completion of reactions (i) and (ii), whereas the total volume of the standard acid used from the beginning upto the **methyl orange end point M** corresponds to the completion of reactions (i), (ii) and (iii).

From the above, following conclusions may be drawn :

1. When $P = 0$, both OH^- and CO_3^{2-} are absent. In such a case, the alkalinity is due to the presence of bicarbonates only. Thus, alkalinity due to $\text{HCO}_3^- = M$.

2. When $P = M$, the sample consists of only OH^- ions. Thus, alkalinity due to $\text{OH}^- = P = M$.

3. When $P = \frac{1}{2} M$, the sample consists of only CO_3^{2-} ions. This is because, the reaction will take place as follows.



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

4. When $P > \frac{1}{2} M$, the sample consists of OH^- ions in addition to CO_3^{2-} ions. Obviously in this case,

Alkalinity due to $\text{CO}_3^{2-} = 2(P - \frac{1}{2}M)$

Alkalinity due to $\text{OH}^- = M - 2(P - \frac{1}{2}M) = 2P - M$.

5. When $P < \frac{1}{2} M$, the sample consists of HCO_3^- in addition to CO_3^{2-} ions. Obviously,

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

Alkalinity due to $\text{HCO}_3^- = M - 2P$.

These conclusions have been summarised in Table 3.2.

$$\begin{aligned} &= \frac{1}{50} \times 4 \\ &= \frac{4}{1000} = 8 \times 10^{-5} \text{ gram equivalents of H}_2\text{SO}_4 \\ &\equiv 8 \times 10^{-5} \text{ gram equivalents of CaCO}_3 \\ &= 8 \times 10^{-5} \times 50 \times 10^3 = 4 \text{ mg of CaCO}_3 \end{aligned}$$

$$\begin{aligned} \therefore \text{Alkalinity due to HCO}_3^- \text{ per litre of the sample} &= \frac{4 \times 1000}{100} = 40 \text{ mg of CaCO}_3 \\ &= 40 \text{ ppm} \end{aligned}$$

Ans.

Hence, total alkalinity of the sample = 320 + 40 = 360 ppm.

□ 3.4. WATER FOR INDUSTRIAL USE

Water is a very important engineering material and finds a variety of applications in almost all the industries. Each industry requires water of a definite specification. In the forthcoming discussion, we shall study some important aspects related to the industrial use of water.

3.4.1. Quality Criteria of Water for Various Industries

The specifications of water required for some important industries are as follows.

1. Sugar industry : The water used in the manufacture of sugar should be free from dissolved salts and completely devoid of suspended solids. Hard water causes difficulties in the crystallisation of sugar from molasses. It also causes the formation of precipitates which accumulate in the refined sugar. Hence, water containing dissolved salts and suspended solids is of no use for sugar industry. Moreover, water should be free from pathogenic and saprophytic micro-organisms.

2. Paper and pulp industries : The water used in paper and pulp industries should be free from iron and manganese salts and suspended matter as they decrease the brightness, affect colours and interfere with texture and uniformity. Water should also be free from dissolved calcium and magnesium salts as they increase the ash content of the paper. Suspended silica particles in water produce cracks in paper. Turbidity, colour, presence of organic matter and dissolved gases are also not desirable.

3. Textile and dyeing industries : The water used in textile and dyeing industries should be free from suspended matter, turbidity, colour, iron and manganese salts, dissolved calcium and magnesium salts and organic matter. Iron and manganese salts produce coloured spots on fabrics, whereas hard water precipitates basic dyes and decreases the solubility of acidic dyes.

4. Starch industry : The water required for starch industry should be as soft and mineral free as possible. Hard water causes precipitation of salts which accumulate in the starch. Iron and manganese salts provide yellowish colouration to the starch which is not desirable.

5. Rayon and acetate fibre industries : Water should be free from turbidity, colour, hardness, iron and manganese salts, alkalinity and silica.

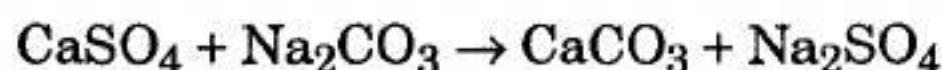
6. Aluminium industry : Water used for washing the hydrate in aluminium industry should be of high quality. Any impurity introduced in the hydrate wash tends to accumulate in NaOH solution and impair its function.

7. Laundries : The water used in laundries should be as much soft as possible. The dissolved calcium and magnesium salts in hard water increase the consumption of soap. Water should also be free from iron and manganese salts which cause stains on the materials being washed. Water should also not contain high bicarbonate alkalinity.

(b) Internal treatment : This method involves the addition of chemicals directly to the water in boilers to remove the scale forming substances which were not completely removed during external treatment. Thus, it is a corrective treatment to remove the slight residual hardness in boiler feed water and is usually used in power stations.

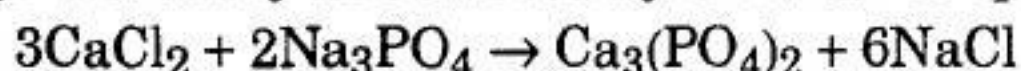
Some important conditioning methods are as follows :

(i) *Carbonate conditioning :* In this method, sodium carbonate is added to boiler water which converts CaSO_4 into calcium carbonate.



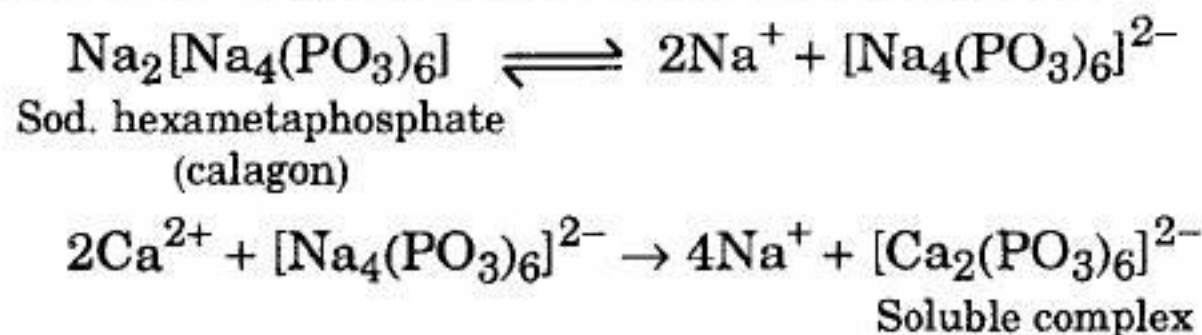
This prevents the deposition of CaSO_4 in the form of scales. Calcium is precipitated as CaCO_3 which can be removed by blow down operation. However, the technique is useful only for low pressure boilers because in high pressure boilers, excess of Na_2CO_3 may get hydrolysed to form NaOH which causes caustic embrittlement.

(ii) *Phosphate conditioning :* Phosphate conditioning is suitable for preventing scale formation in high pressure boilers. In this technique, sodium phosphate is added to boiler water. It reacts with the hardness producing substances to form a soft sludge of calcium and magnesium phosphates. This sludge can easily be removed by blow-down operation.



Instead of sodium phosphate (Na_3PO_4), disodium hydrogen phosphate (Na_2HPO_4) and sodium dihydrogen phosphate (NaH_2PO_4) may also be used. However, the choice depends upon the alkalinity of the boiler feed water.

(iii) *Calgon conditioning :* In this technique, the scale forming salts are converted into soluble complexes by the addition of calgon (sodium hexametaphosphate).



The complexes thus formed do not precipitate under boiler conditions. Thus, scale formation is prevented.

(iv) *Colloidal conditioning :* In low pressure boilers, scale formation can be minimised by adding suitable colloidal conditioning agents such as glue, agaragar, tannin, starch etc. These substances act as protective colloids and prevent precipitation of scale forming substances. Even if they settle out, they form non-sticky and loose deposits which can easily be removed.

(v) *Conditioning with EDTA :* In this technique, the scale forming substances are complexed with EDTA or its sodium salt (Na_2EDTA). The addition of EDTA to boiler water provides a scale-free and sludge-free operation of boiler units.

3.4.4. Boiler Corrosion

The decay of boiler material by its environment is termed as **boiler corrosion**.

Factors causing boiler corrosion : The main factors responsible for boiler corrosion are as follows.

(i) **Presence of dissolved oxygen :** The presence of dissolved oxygen in water is the main cause of boiler corrosion. When water containing dissolved oxygen is heated in the boiler, the dissolved oxygen gets liberated and attacks the boiler material as follows.

(iii) **By the addition of alkali** : Corrosion by acids can be prevented by adding alkalies from outside.

3.4.5. Priming and Foaming

1. Priming

When water is boiled rapidly in a boiler, the steam formed may sometimes be associated with small droplets of water. The steam associated with small water droplets is called **wet steam**. The process of formation of wet steam is called **priming**.

Causes of priming : Priming is caused by the presence of large amounts of dissolved solids such as alkali sulphates and chlorides. It may also be caused by very high water level, high steam velocity and sudden steam demand which leads to sudden boiling. The improper designing of boiler is also responsible for priming.

Prevention of priming : Priming can be prevented by

- (i) using mechanical steam purifiers;
- (ii) keeping the water level lower.
- (iii) avoiding rapid changes in steam rate;
- (iv) efficient softening and filtration of boiler feed water; and
- (v) using a proper boiler design.

2. Foaming

The formation of persistent foam or bubbles in the boiler is called **foaming**.

Causes of foaming : Foaming is caused by the presence of oil and grease in water. These substances greatly reduce the surface tension of water in boiler and cause foaming. The presence of finely divided sludge particles may also cause foaming.

Prevention of foaming : Foaming can be prevented by

- (i) removing oil, grease and finely divided sludge particles from the boiler feed water by the addition of coagulants such as ferrous sulphate, sodium aluminate etc; and
- (ii) adding antifoaming chemicals such as castor oil.

3.4.6. Caustic Embrittlement

Caustic embrittlement is a particular type of boiler corrosion caused by the use of highly alkaline water in the boiler. It may be defined as follows.

The formation of irregular intergranular cracks on the boiler metal particularly at points of high local stress by the use of highly alkaline water in the boiler is called **caustic embrittlement**.

Cause of caustic embrittlement : Caustic embrittlement is more common when boilers operate at high pressures and boiler feed water contains dissolved Na_2CO_3 as impurity. At high pressures, sodium carbonate undergoes hydrolysis to form sodium hydroxide as shown below.



The formation of NaOH makes the boiler water caustic. The caustic water (i.e. water containing NaOH) flows into the minute hair cracks usually present on the boiler material by capillary action. Here, water evaporates and the concentration of dissolved NaOH increases progressively. This highly concentrated NaOH solution attacks the surrounding area by dissolving the iron of boiler as sodium ferroate. This causes the formation of irregular intergranular cracks on the boiler metal particularly at places of high local stress such as bends, joints, rivets etc.

$$= 1.44 \times 10^{-3} \text{ gram equivalent of HCl}$$

$$= 1.44 \times 10^{-3} \text{ gram equivalent of CaCO}_3$$

$$= 1.44 \times 10^{-3} \times 50 \text{ grams of CaCO}_3$$

$$(\because \text{Eq. wt. of CaCO}_3 = 50)$$

$$= 1.44 \times 10^{-3} \times 50 \times 10^3 \text{ mg of CaCO}_3$$

$$= 72 \text{ mg of CaCO}_3$$

$$\therefore \text{Hardness (alkalinity) due to HCO}_3^- \text{ per litre of the sample} = \frac{72 \times 1000}{100}$$

$$= 720 \text{ mg of CaCO}_3$$

$$= 720 \text{ ppm of CaCO}_3 \quad \text{Ans.]}$$

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4.3.1. Lime-Soda Process

Lime-Soda process is a very important method used for the softening of water.

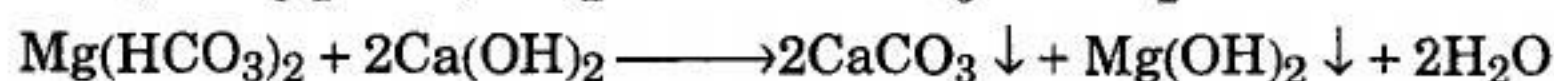
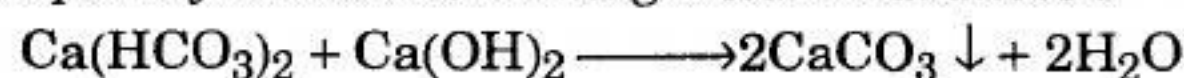
[A] Principle

The lime-soda process involves the chemical conversion of all the soluble hardness-causing salts by the addition of soda and lime into insoluble precipitates which could easily be removed by settling and filtration.

In this process, water to be softened is treated with calculated amounts of lime $[\text{Ca}(\text{OH})_2]$ and soda (Na_2CO_3). For quick completion of reactions, the reagents may be used in 10% excess. The functions of lime and soda are as follows.

Functions of lime : Lime removes temporary hardness, permanent magnesium hardness, dissolved iron and aluminium salts, dissolved CO_2 and H_2S gases and free mineral acids present in water. The reactions involved are as follows.

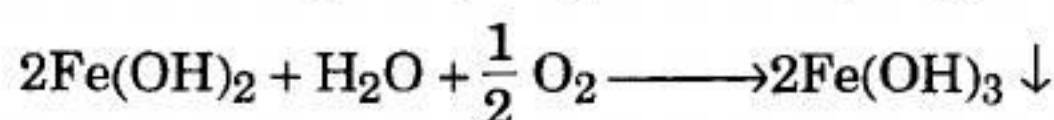
(a) *Removal of temporary calcium and magnesium hardness :*



(b) *Removal of permanent magnesium hardness :*



(c) *Removal of dissolved iron and magnesium salts :*



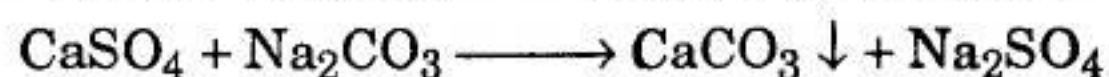
(d) *Removal of dissolved CO_2 and H_2S :*



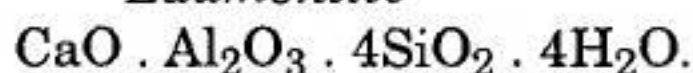
(e) *Removal of free mineral acid :*



Functions of soda : During the removal of Mg^{2+} , Fe^{2+} , Al^{3+} , HCl and H_2SO_4 by lime, permanent calcium hardness is introduced in the water due to formation of calcium salts. The permanent calcium hardness thus introduced on account of the treatment of water with lime and the permanent calcium hardness already present in water before lime treatment are removed by soda. The reactions involved are as follows.



The chemical reactions involved in the lime-soda process are quite slow. Moreover, the precipitates formed [particularly of CaCO_3 and $\text{Mg}(\text{OH})_2$] are fine and have a tendency to form supersaturated solutions. This results in *after deposition* of these precipitates later in the pipes

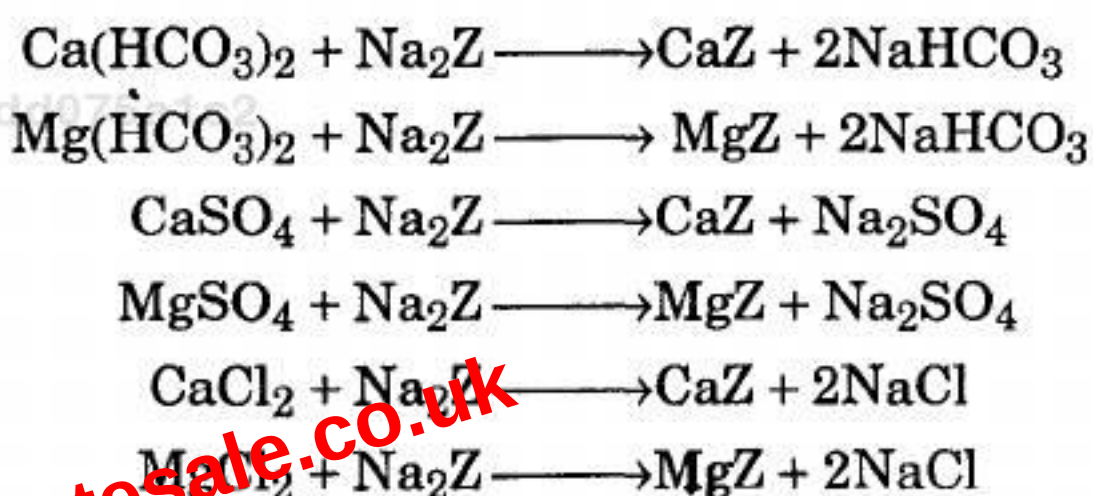
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(ii) **Synthetic zeolites** : These are porous and possess a gel structure. They are usually prepared by heating together china clay, feldspar and soda ash. Synthetic zeolites possess higher exchange capacity as compared to natural zeolites.

Sodium zeolites, $(\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O})$, where $x = 2 - 10$ and $y = 2 - 6$ are important synthetic zeolites and are commonly known as **permutits**. They are widely used for the softening of hard water. They exchange the hardness producing ions (Ca^{2+} , Mg^{2+} etc.) with Na^+ ions which do not cause hardness. Sodium zeolites may simplistically be represented as Na_2Z , where Z stands for the insoluble zeolite radical framework.

The process : The zeolite (permutit) is loosely packed over a layer of coarse sand in a tank as shown in Fig. 4.8. Hard water is allowed to percolate through it.

As the hard water percolates through the permutit, the Ca^{2+} and Mg^{2+} present in hard water get replaced by the action of sodium zeolite. The various reactions that take place are as follows.



The sodium salts formed in the above reactions remain dissolved in the softened water and do not cause any hardness.

Regeneration of the zeolite : As the process continues, sodium zeolite gets exhausted due to its conversion into calcium and magnesium zeolites. It takes about 12 hours for the zeolites to get completely exhausted. Therefore, after a continuous use of 12 hours, it must be regenerated.

The regeneration of the zeolite is done by percolating a 10% brine solution (NaCl solution) through the exhausted zeolite. This operation converts calcium and magnesium zeolites back into sodium zeolite as shown below.

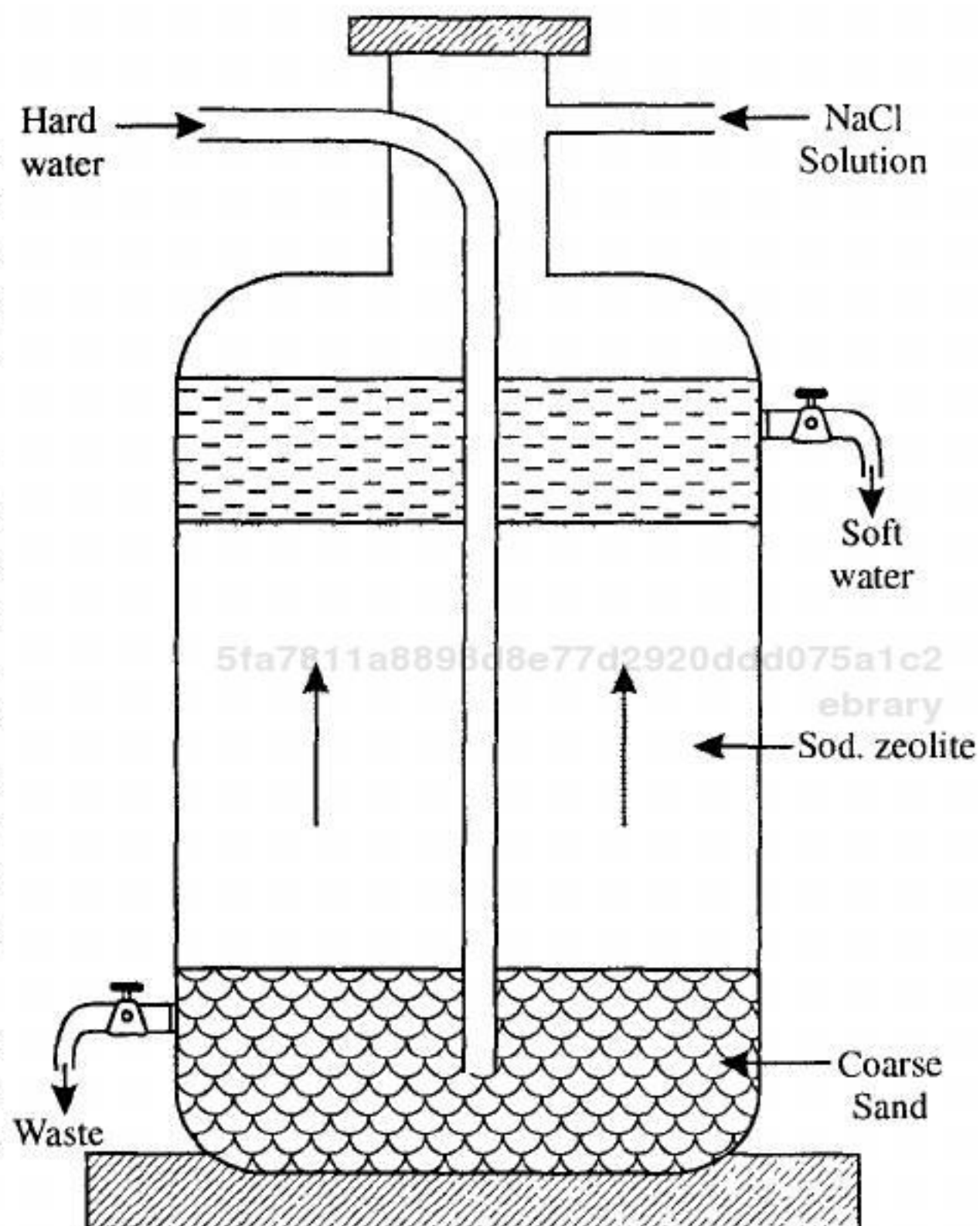
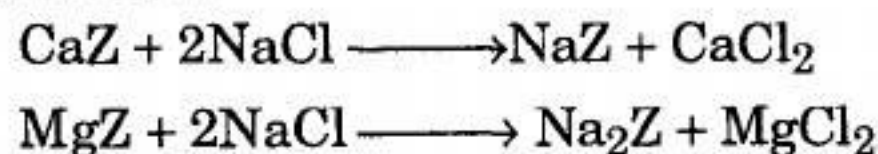


Fig. 4.8.

7. Explain the following terms :
(a) Chlorination (b) Super chlorination
(c) Dechlorination (d) Break-point chlorination.
8. What is break-point chlorination and what are its advantages ?
9. What do you understand by desalination and how is it carried out ?
10. What is the principle involved in reverse osmosis process of desalination of water ? Describe the process and discuss its advantages.
11. What is electrodialysis and how is it carried out ? Discuss the process, its advantages and limitations.
12. What is mixed bed demineralisation ? Explain the process.

[C] Numerical Problems

1. Calculate the amount of lime and soda required for softening of 15,000 litres of water, which analysed as follows : Temporary hardness = 20 ppm, permanent hardness = 15 ppm, permanent Mg hardness = 10 ppm. [Ans. 330g, 238.5 g]
2. A water sample on analysis gives the following data : Ca^{2+} = 20 ppm, Mg^{2+} = 25 ppm, CO_2 = 30 ppm, HCO_3^- = 150 ppm, K^+ = 10 ppm. Calculate the lime (87% pure) and soda (91% pure) required to soften 1 million litres of water sample. [Ans. 218.9 kg, 33.6 kg]
3. Calculate the quantity of lime and soda required for softening 60,000 litres of water containing : CO_2 = 20 mg/L, $\text{Ca}(\text{HCO}_3)_2$ = 20 mg/L, $\text{Mg}(\text{HCO}_3)_2$ = 25 mg/L, HCl = 8.4 mg/L, $\text{Al}_2(\text{SO}_4)_3$ = 40 mg/L and MgCl_2 = 12 mg/L. [Ans. 6.716 kg, 4.007 kg]
4. Calculate the cost of softening 100,000 cubic metres of water, with the following analysis :
Total hardness = 20° Clarke
Carbonate hardness = 10° Clarke
Magnesium hardness = 5° Clarke
Rate of 90% pure lime is Rs. 54 per tonne, and that of 90% pure soda is Rs. 190 per tonne. [Ans. Rs. 4152.04]
5. Yamuna canal water on analysis gave the following results : CO_2 = 22 ppm, HCO_3^- = 305 ppm, Ca^{2+} = 80 ppm, Mg^{2+} = 48 ppm, total solids = 500 ppm. Calculate carbonate and non-carbonate hardness of the water sample. Also calculate the amount of lime and soda that would be required for softening the above water, if 417 ppm of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is used as coagulant. [K.U. Kurukshetra, B.E.I. Dec. 1997]
[Ans. 250 ppm, 150 ppm; 629 mg/L, 318 mg/L]
6. An exhausted zeolite softener was regenerated by passing 150 litres of NaCl solution having a strength of 150 g/L of NaCl. If the hardness of water is 600 ppm, calculate the total volume of water that is softened by this softener. [Ans. 3.219×10^4 L]
[Hint : 150 L of NaCl = 22500 g of NaCl = 1.932×10^7 mg CaCO_3 eq. If the volume of water softened is V litres, we have

$$\frac{1.932 \times 10^7}{V} = 600$$

or

$$V = \frac{1.932 \times 10^7}{600} = 3.219 \times 10^4 \text{ L}$$