

# Water

No.	No.			
1	<b>Industrial Applications of Water and its treatment methods</b>		08	CO1
	1.1	Introduction, Types of Hardness, Equivalence of $\text{CaCO}_3$ , Experimental determination of hardness.		
	1.2	Emerging Technology for Sustainable Water Treatment: Lime soda method Zeolite method, Ion Exchange process.		
	1.3	Methods to determine extent of water pollution, BOD, COD, Treatment of industrial wastewater.		

# Introduction

- 1). Like air, water is one of the few basic materials which is of prime importance for the preservation of life on this earth.
- 2). All are aware of the uses of water for drinking, cooking, bathing & for farming etc.
- 3). But few know the importance of water as an engineering material.
- 4). As an engineering material water is used for producing steam, in boilers to generate hydro-electric power, furnishing steam for engines, for construction of concrete structures for manufacturing purposes & as a solvent in chemical process.

## **Sources of Water:**

The Main Sources Of Water Are:

- 1). Rain water
- 2). River water
- 3). Spring or well water
- 4). Sea water

## Types of impurities in water:

The impurities present in water are classified as:

1). Dissolved impurities: dissolved impurities may be organic or inorganic.

**Inorganic impurities:** the carbonates, bicarbonates, sulphates, chlorides of calcium, magnesium, iron, potassium and aluminium.

**Organic impurities:** Organic water products, amino acids, proteins, etc.

**Gases:**  $O_2$ ,  $CO_2$ , Oxides of nitrogen and sulphur,  $H_2S$  etc.

2). **Suspended impurities:** It is of two types:

1. **Inorganic-** sand & clay;

2. **Organic-** vegetable and animal matter.

3) **Biological Impurities:** Micro-organisms like pathogenic bacteria, fungi, algae, etc.

## DISADVANTAGES OF HARDWATER/ CAUSES OF HARDNESS:

The following are the disadvantages when hard water is used for various purpose:

### (i) DOMESTIC USE:

(a) Washing and Bathing: Hard water does not form lather easily with soap, so soap is wasted

(b) Drinking: Hard water causes bad effects on our digestive system. Sometimes, stone formation takes place in kidneys.

(c) Cooking: The boiling point of water is increased due to the presence of salts. Hence, more fuel and time are required for cooking.

(ii) **INDUSTRIAL USE:**

(a) Textile Industry: Hard water causes wastage of soap. Precipitates of calcium and magnesium soap adhere to the fabrics and cause problem such difference in color shades, dull shades, patches, etc.

(b) Paper Industry: Calcium and Magnesium salts in water may affect the quality of paper.

(c) Sugar Industry: Water containing sulphates, carbonates, nitrates affects the crystallisation of sugar.

(d) Pharmaceutical Industry: Hard water may form some undesirable products while preparation of pharmaceutical products.



(iii) **STEAM GENERATION IN BOILERS:** For steam generation, boilers are employed. If hard water is used in boilers, It may lead to the following troubles-

(a) Boiler Corrosion

(b) Scale and Sludge formation.

(c) Priming and Foaming

(d) Caustic embrittlement Pharmaceutical industry

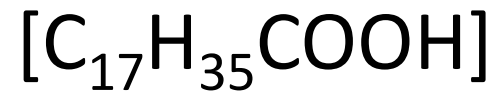
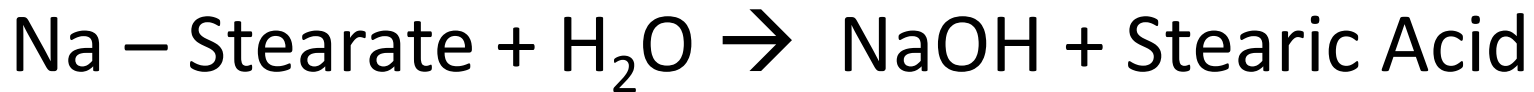
# **HARDNESS OF WATER (OR) HARDWATER AND SOFT WATER:**

**Hard Water:** The water which does not produce lather (or) very little lather with soap is called Hard Water.

**Soft Water:** Soft water readily produces a lot of lather when mixed with little soap.

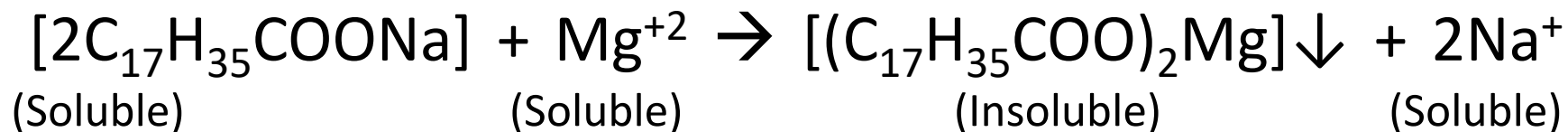
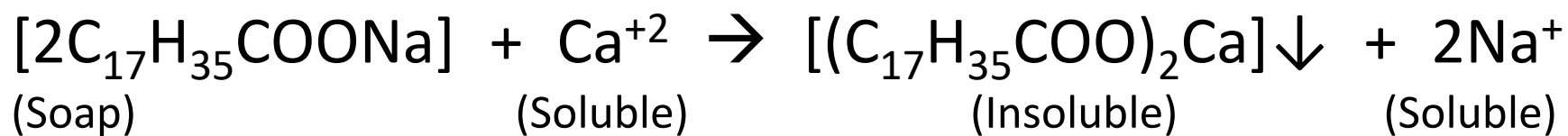
The Hardness of water is caused by the presence of dissolved salts such as Bicarbonates, Sulphates, Chlorides and Nitrates of bivalent metal ions like  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$ .

Soap is sodium/ potassium salt of higher fatty acids like stearic, oleic and palmitic acids. When soap is mixed with soft water lather is produced due to stearic acid and sodium stearate.



Stearic Acid + Na-Stearate  $\rightarrow$  Formation of lather.

When soap comes in contact with HARD WATER, Sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate.

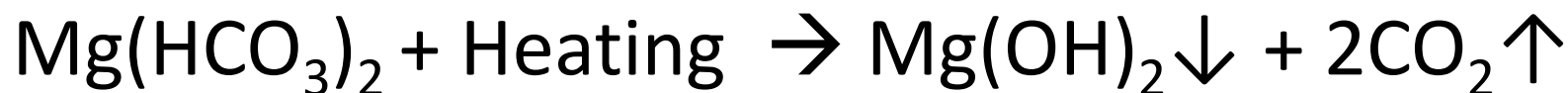
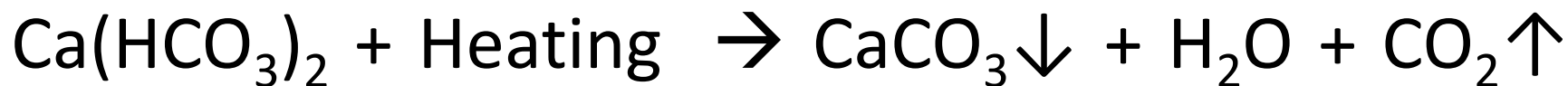


# TYPES OF HARDNESS

The hardness of water is of two types-

- (1) Temporary hardness (or) Carbonate hardness
- (2) Permanent hardness (or) Non-Carbonate hardness

**(1) Temporary Hardness:** Temporary hardness is caused by two dissolved bicarbonate salts  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{Mg}(\text{HCO}_3)_2$ . The hardness is called “Temporary Hardness” because it can be removed easily by means of **boiling**.



(2) **Permanent Hardness:** Permanent hardness of water is due to the dissolved chlorides, sulphates and nitrates of calcium and magnesium. These salts are  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ . These hardness cannot be removed easily by boiling. Hence it is called “Permanent Hardness”. Only **chemical treatment** can remove this hardness.

**Total Hardness Of Water = Temporary Hardness + Permanent Hardness**

## DEGREE OF HARDNESS:

- The Concentration of hardness as well as non-hardness constituting ions are, usually expressed in the term of “Equivalent amount of  $\text{CaCO}_3$ ”
- Since this mode permits the multiplication and division concentration, when required.
- The choice of  $\text{CaCO}_3$  in particular is due to its molecular weight (m.wt.) is “100” (Equivalent wt. = 50), and
- Moreover, it is insoluble salt that can be precipitated in water treatment.

Therefore, 100 parts by weight of  $\text{CaCO}_3$  hardness must be equivalent to-

- 162 parts by weight of  $\text{Ca}(\text{HCO}_3)_2$  hardness
- 146 parts by weight of  $\text{Mg}(\text{HCO}_3)_2$  hardness
- 136 parts by weight of  $\text{CaSO}_4$  hardness
- 111 parts by weight of  $\text{CaCl}_2$  hardness
- 164 parts by weight of  $\text{Ca}(\text{NO}_3)_2$  hardness
- 120 parts by weight of  $\text{MgSO}_4$  hardness
- 95 parts by weight of  $\text{MgCl}_2$  hardness
- 148 parts by weight of  $\text{Mg}(\text{NO}_3)_2$  hardness



Salt	Molar Mass	Chemical Equivalent	Multiplication Factor
$\text{Ca}(\text{HCO}_3)_2$	162	81	100/ 162
$\text{Mg}(\text{HCO}_3)_2$	142	73	100/ 142
$\text{CaSO}_4$	136	68	100/ 136
$\text{FeCl}_2$	127	63.5	100/ 127
$\text{CaCl}_2$	111	55.5	100/ 111
$\text{MgSO}_4$	120	60	100/ 120
$\text{MgCl}_2$	95	47.5	100/ 95
$\text{CaCO}_3$	100	50	100/ 100
$\text{MgCO}_3$	84	42	100/ 84
$\text{CO}_2$	44	22	100/ 44
$\text{Ca}(\text{NO}_3)_2$	164	82	100/164
$\text{Mg}(\text{NO}_3)_2$	148	74	100/ 148
$\text{HCO}_3^-$	61	61	100/ 122
$\text{OH}^-$	17	17	100/ 34
$\text{CO}_3^{2-}$	60	30	100/ 60

Salt	Molar Mass	Chemical Equivalent	Multiplication Factor
NaAlO <sub>2</sub>	82	82	100/ 164
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	342	57	100/ 114
FeSO <sub>4</sub> .7H <sub>2</sub> O	278	139	100/ 278
H <sup>+</sup>	1	1	100/ 2
HCl	36.5	36.5	100/ 73

The method of calculating degree of hardness is given by the following formula

• **Hardness causing salt in terms of equivalent of CaCO<sub>3</sub> = (Amount (Mass) of the hardness causing salt x 100)/ Molecular weight of hardness causing salt**

## UNITS OF HARDNESS:

The 5 different units in which the hardness of water is expressed as given below-

(1) **Parts per million (PPM)**: PPM is the number of parts of  $\text{CaCO}_3$  equivalent hardness per  $10^6$  parts of water.

i.e., 1 PPM = 1 part of  $\text{CaCO}_3$  equivalent hardness in  $10^6$  parts of water.

(2) **Milli grams Per Litre (mg/litre):** mg/L is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per litre of water.

i.e.,  $1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness in 1L of water.}$

But 1 L water weighs = 1 kg of water

$1 \text{ kg} = 1000 \text{ gms} = 1000 \times 1000 \text{ mg} = 10^6 \text{ mg}$

$\therefore 1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ mg of water}$   
 $= 1 \text{ part of } \text{CaCO}_3 \text{ equivalent per } 10^6 \text{ parts of water}$

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

(3) **Degree Of Clarke ( $^{\circ}\text{Cl}$ )**: It is number of grains (1/7000 lb) of  $\text{CaCO}_3$  equivalent hardness per gallon (10 lb) of water.

(or) It is defined as the number of parts of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

$\therefore 1^{\circ}\text{Cl} = 1$  grain of  $\text{CaCO}_3$  eq. hardness per gallon of water.

(or)  $1^{\circ}\text{Cl} = 1$  part of  $\text{CaCO}_3$  eq. hardness per 70,000 parts of water

$\therefore 1 \text{ ppm} = 0.07^{\circ}\text{Cl}$

(4) **Degree Of French ( $^{\circ}\text{Fr}$ ):** It is the number of parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

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

$\therefore 0.1^{\circ}\text{Fr} = 1 \text{ ppm}$

Note: The hardness of water can be converted into all the four units by making use of the following interconversion formula-

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

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

(5) **Milliequivalent per Litre (meq/L)**: It is the number of milliequivalent of hardness present per litre of water.

1 meq/L = 1 meq of  $\text{CaCO}_3$  per litre of water  
=  $10^{-3} \times 50$  g of  $\text{CaCO}_3$  eq. of hardness per litre of water

= 50 mg of  $\text{CaCO}_3$  eq. of hardness per litre of water

= 50 mg/L of  $\text{CaCO}_3$  eq.

= 50 ppm

**$\therefore 1 \text{ meq/L} = 50 \text{ ppm}$**

## PROBLEM:

(1) A sample of water gives an analysis 13.6 mg/L of  $\text{CaSO}_4$  , 7.3 mg/L of  $\text{Mg}(\text{HCO}_3)_2$  . Calculate the total hardness and permanent hardness.

Sol:

Salt	Quantity (mg/L)	M. Wt.	Multiplication Factor	Eq. of $\text{CaCO}_3$	Hardness
$\text{CaSO}_4$	13.6	136	100/ 136	$13.6 \times (100/ 136) = 10$	P
$\text{Mg}(\text{HCO}_3)_2$	7.3	146	100/ 146	$7.3 \times (100/ 146) = 5$	T

Total hardness= Temporary hardness + Permanent

Hardness = 5 + 10 = 15 mg/L = 15 ppm

Permanent hardness = 10 ppm

Temporary hardness= 5 ppm



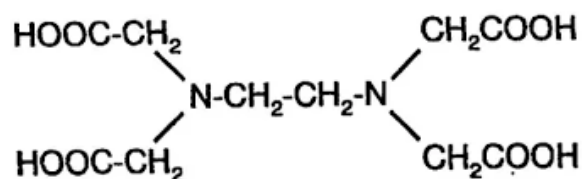
# **DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD:-**

1. This is a Complexometric titration method where Ethylenediamine tetraacetic acid (EDTA) is used.
2. EDTA forms complexes with different metal ions at different pH.
3. Calcium & Magnesium ions form complexes with EDTA at pH 9- 10.

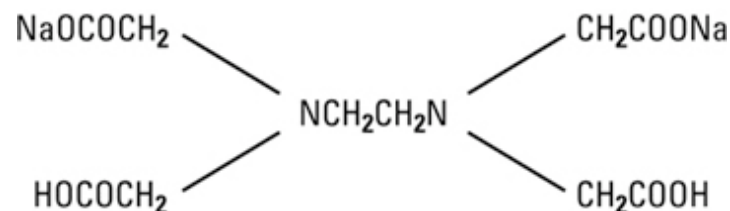
To maintain the pH 9- 10  $\text{NH}_4\text{Cl}, \text{NH}_4\text{OH}$  buffer solution is used.

4. The disodium salt of EDTA is used for complexation.

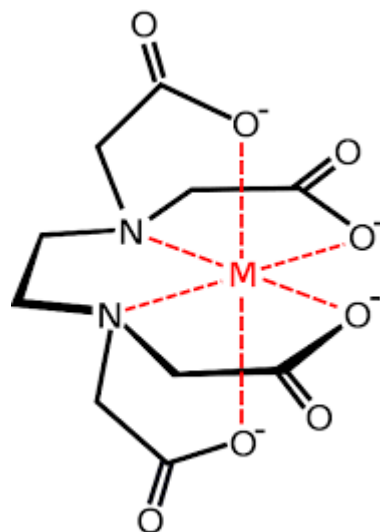
5. An alcoholic solution of Eriochrome Black-T (EBT) is used as an indicator.



EDTA



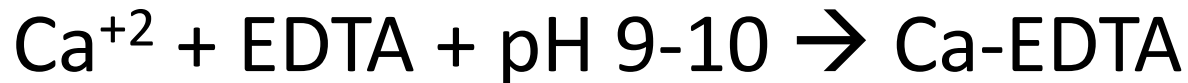
EDTA disodium salt



Metal-EDTA complex

## BASIC PRINCIPLE:

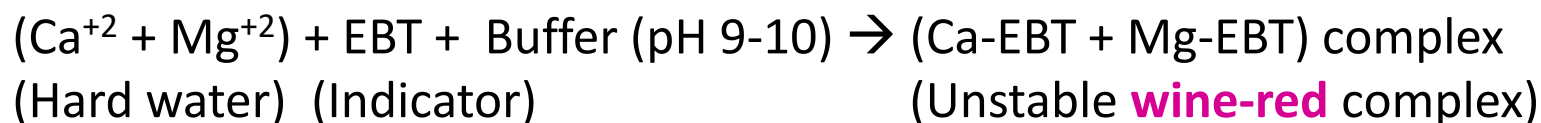
When hard water comes in contact with EDTA, at pH 9- 10, the  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$  forms stable, colourless complex with EDTA.



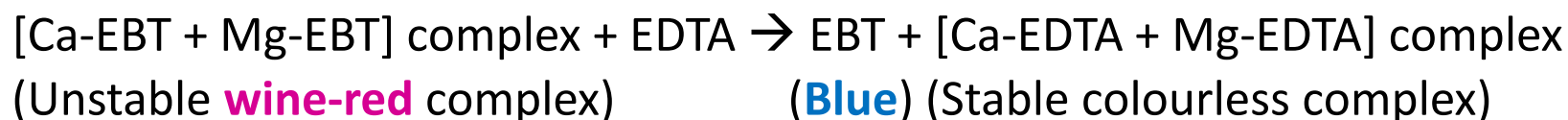
## Working:-

To the hard water sample, the alcoholic blue coloured EBT indicator is added along with the  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$  buffer (pH 9-10) solution.

EBT forms an unstable wine-red complex with  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$ .



This wine-red coloured  $[\text{Ca-EBT} \text{ \& } \text{Mg-EBT}]$  complex is then titrated against EDTA; when EDTA replaces EBT from  $\text{Ca-EBT}$  &  $\text{Mg-EBT}$  complex and forms stable colourless  $[\text{Ca-EDTA}]$  &  $[\text{Mg-EDTA}]$  complex releasing the blue coloured indicator EBT into  $\text{H}_2\text{O}$ .



Hence the colour change at the end point is wine-red to blue colour.

The titration is carried out in the following steps

1. **PREPARATION OF STANDARD HARD WATER:**

Dissolve 1gm of pure, dry  $\text{CaCO}_3$  in minimum quantity of dilute  $\text{HCl}$  and evaporate the solution to dryness on a water-bath. Dissolve the residue in distilled water to make 1 litre in a standard flask and shake well.

Molarity of standard hard water solution =

$$\frac{\text{wt. of CaCO}_3}{\text{M.wt. of CaCO}_3} = \frac{1}{100} = 0.01\text{M}$$

(2) **PREPARATION OF EDTA SOLUTION:**

Dissolve 4 gms of pure EDTA-disodium salt crystals along with 0.1 gm of  $\text{MgCl}_2$  in one litre of distilled water.

(3) **PREPARATION OF INDICATOR (EBT):**

Dissolve 0.5 gms of Erichrome Black-T in 100 ml of alcohol.

(4) **PREPARATION OF BUFFER SOLUTION:** Add 67.5 gm of  $\text{NH}_4\text{Cl}$  to 570 ml of concentrated ammonia solution and dilute with distilled water to one litre

## (5) STANDARDISATION OF EDTA SOLUTION:

Pipette out 20 ml of standard hard water solution into a conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured complex with EDTA taken in a burette after rinsing it with EDTA solution till the wine red colour changes to clear blue.

Note the burette reading and let the volume be “x”ml. Repeat the titration to get concurrent values.

## (6) TITRATION OF SAMPLE HARD WATER (Total) :

Pipette out 20 ml of the water sample into a 250ml conical flask, add 2- 3 ml of buffer (pH 9-10) solution and 2- 3 drops of EBT indicator. Titrate the wine-red coloured solution with EDTA taken in the burette till a clear blue coloured end point is obtained.

Let the volume of EDTA be “y” ml. Repeat the titration to get concurrent values



## (7) TITRATION FOR PERMANENT HARDNESS:

Pipette out 100 ml of hard water sample in a beaker and boil till the volume reduces to 20 ml. All the bicarbonates of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  decomposes to  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ . Cool the solution and filter the water into a flask, wash the beaker and precipitate with distilled water and add the washing to conical flask. Add 2- 3 ml of buffer (pH 9- 10) solution and 2- 3 drops of EBT indicator and titrate with EDTA solution taken in the burette till a clear blue colour end point is obtained.

Note the burette reading. Let the volume be “z” ml.

## CALCULATIONS:

Molarity of standard hard water solution = 0.01 M.

(Calculated in the preparation of standard hard water)

Molarity of EDTA solution ( $M_2$ ):  $\frac{V_1 M_1}{n_1} = \frac{V_2 M_2}{n_2}$

$n_1$  &  $n_2$  are no. of moles of  $\text{Ca}^{+2}$  and EDTA = 1 each

i.e.,  $n_1=1$ ,  $n_2=1$

$V_1$  = volume of standard hard water

$M_1$  = Molarity of standard hard water

$V_2$  = volume of EDTA

$M_2$  = molarity of EDTA

$$M_2 = \frac{V_1 M_1}{V_2} = \frac{20 \times 0.01}{\text{x (titre value)}}$$

**Molarity of sample hard water ( $M_3$ ):**

$$\frac{V_2 M_2}{n_2} = \frac{V_3 M_3}{n_3}$$

$V_2$  = volume of EDTA

$M_2$  = molarity of EDTA

$V_3$  = volume of sample hard water

$M_3$  = Molarity of sample hard water

$$M_3 = \frac{V_2 M_2}{V_3} = \frac{M_2 \times y \text{ (titre value)}}{20} = \frac{y \times 0.01}{x}$$

**Total Hardness Of Water**

=  $M_3 \times 100$  gms/1 litre

=  $M_3 \times 100 \times 1000$  mg/L or ppm =  $(y/x) \times 1000$  ppm

## Permanent Hardness Of Water:

$$\frac{V_2 M_2}{n_2} = \frac{V_4 M_4}{n_4} \quad M_4 = \frac{V_2 M_2}{V_4} = \frac{z M_2}{20} = \frac{z}{x} \times 0.01$$

$V_2$  = volume of EDTA

$M_2$  = molarity of EDTA

$V_4$  = volume of water sample containing permanent hardness (100 ml)

$M_4$  = Molarity of water sample containing permanent hardness

## Permanent Hardness Of The Water Sample

$$= M_4 \times 100 \times 1000 \text{ ppm}$$

$$= \frac{z}{x} \times 1000 \text{ ppm}$$

**Temporary Hardness** Of The Water Sample

= (Total Hardness – Permanent Hardness)

= ( $M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000$ ) ppm

= ( $M_3 - M_4$ )  $\times 100 \times 1000$  ppm

= (y-z)  $\times 1000$  ppm

x

## **Problem:**

1 gm of  $\text{CaCO}_3$  was dissolved in HCl and the solution was made upto 1 Lit with distilled water. 50 ml of the above solution required 30 ml of EDTA solution for titration. 50 ml of hard water sample required 40 ml of the same solution of EDTA for titration. 50 ml of the hard water after boiling, filtering, etc. required 30 ml of the same EDTA solution for titration. Calculate the temporary hardness of the water.

Soln:

**Molarity of  $\text{CaCO}_3$  (SHW) solution** ( $M_1$ ) =  $1/100 = 0.01 \text{ M}$

**Molarity of EDTA solution** ( $M_2$ ) =  $V_1 M_1 / V_2$

$V_1$  = volume of  $\text{CaCO}_3$  solution = 50 ml

$M_1$  = Molarity of  $\text{CaCO}_3$  solution = 0.01 M

$V_2$  = volume of EDTA = 30 ml

$M_2 = 50 \times 0.01 / 30 = 0.016 \text{ M}$

**Molarity of Hard Water Sample Sol.** ( $M_3$ ) =  $V_2 M_2 / V_3$

$V_2$  = volume of EDTA = 40 ml

$M_2$  = Molarity of EDTA = 0.016 M

$V_3$  = volume of hard water sample = 50 ml

$M_3 = 40 \times 0.016 / 50 = 0.0128 \text{ M}$

**Total Hardness** of water

$$= 0.0128 \times 100 \times 1000$$

$$= 1280 \text{ ppm}$$

**Permanent hardness** of water:  $= \frac{V_4 M_4}{n_4} = \frac{V_2 M_2}{n_2}$

$$M_4 = V_2 M_2 / V_4$$

$$n_4 = 1; V_2 = \text{volume of EDTA} = 30 \text{ ml}$$

$$n_2 = 1; M_2 = \text{molarity of EDTA} = 0.016$$

$$V_4 = \text{volume of permanent hardness containing water} = 50$$

$$M_4 = 30 \times 0.016 / 50 = 0.0096 \text{ M}$$



Permanent hardness of water  
 $= 0.0096 \times 100 \times 1000 = 960 \text{ ppm}$

### Temporary hardness

$= \text{Total hardness} - \text{Permanent hardness}$   
 $= 1280 - 960 = 320 \text{ ppm}$

20ml of SHW containing 1.2gm  $\text{CaCO}_3$  per litre required 35ml of EDTA. 50ml of hard water sample required 30ml of same EDTA. 100ml of hard water sample after boiling, cooling required 25ml of same EDTA. Calculate the hardness.

**Solution:** Strength of SHW =  $1.2\text{gm/lit} = 1200\text{mg}/1000\text{ml} = 1.2\text{mg/ml}$

Volume of SHW = 20ml =  $20 \times 1.2 = 24\text{mg}$  of  $\text{CaCO}_3$  eq hardness

Now, 20ml SHW = 35ml EDTA; i.e. 35ml EDTA = 24mg of  $\text{CaCO}_3$  eq hardness

So,  $1\text{ ml EDTA} = 24/35\text{ mg}$   $\text{CaCO}_3$  hardness

50ml WS = 30ml EDTA =  $30 \times 24/35\text{ mg}$   $\text{CaCO}_3$  hardness = 20.57mg

Thus, 1 lit WS = 1000ml =  $1000 \times 20.57/50 = 411.4\text{mg}$

So, **Total hardness = 411.40ppm**

100ml of boiled sample = 25ml EDTA =  $25 \times 24/35 = 17.14\text{mg}$   $\text{CaCO}_3$  hardness

Thus, 1 lit BWS = 1000ml =  $1000 \times 17.14/100 = 171.4\text{mg}$

So, **Permanent hardness = 171.40ppm**

**Temporary Hardness** = Total hardness – Permanent hardness

$$411.40 - 171.40 = 240.00\text{ppm}$$

## **BOILER TROUBLES:**

Water finds a great use in various industries for generation of steam in boilers. When water is continuously evaporated to generate steam, the concentration of the dissolved salts increase progressively causing bad effects for steam boilers. The following are the boiler troubles that arise:

- (1) Priming and foaming
- (2) Caustic embrittlement
- (3) Boiler corrosion
- (4) Scale and sludge formation

## PRIMING & FOAMING:

Priming: When a boiler is steaming rapidly, some particles of the liquid water are carried along with the steam. This process of “WET STEAM” formation is called ‘PRIMING’. Priming is caused by:

- (1) Presence of large amount of dissolved solids
- (2) High steam velocities
- (3) Sudden boiling
- (4) Improper boiler design
- (5) Sudden increase in steam production rate

It can be avoided by: (Preventions)

- (1) Maintaining low water level
- (2) Using softened water
- (3) Fitting mechanical steam purifiers
- (4) Using a well-designed boiler
- (5) Avoiding rapid change in steam rate
- (6) Blow-down of the boiler

Figure 3.12

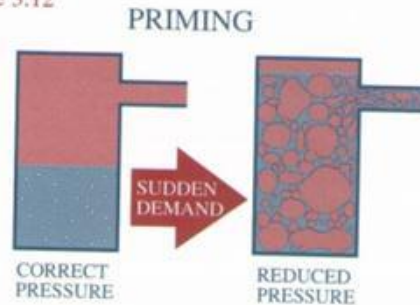
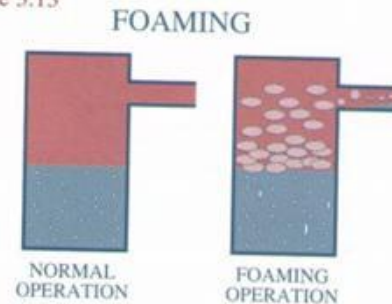


Figure 3.13



## FOAMING:

Foaming is phenomenon of formation of foam or bubbles on the surface of water inside the boiler with the result that the foam may pass along with the steam.

Causes: The presence of large quantity of suspended impurities and oils lowers the surface tension producing foam.

Preventions: Foaming can be avoided by-

- (1) Adding anti foaming chemicals like castor oil
- (2) Removing oil from boiler water by adding compounds like " $\text{NaAlO}_2$ "
- (3) Blow down of the boiler can prevent the foaming

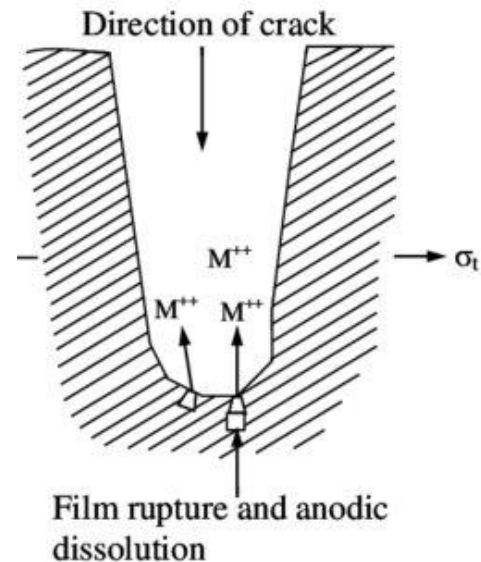
## Disadvantages Of Priming & Foaming:

Priming & Foaming may cause the following boiler troubles:-

- (1) The actual height of the water in boiler is not judged
- (2) Wastage of heat with the result that it becomes difficult to keep up steam pressure and efficiency of the boiler is lowered

## CAUSTIC EMBRITTLEMENT:

Caustic embrittlement is a term used for the appearance of cracks inside the boiler particularly at those places which are under stress such as rivetted joints due to the high concentration of alkali leading to the failure of the boiler. The cracks have appearance of brittle fracture. Hence, the failure is called “Caustic Embrittlement”





### Reasons for the formation of Caustic Embrittlement:

The boiler feed water containing carbonates and bicarbonates of alkali metals, sodium hydroxide (NaOH) and a small quantity of silica or sodium silicate; it is purified by Lime-Soda Process.

During the softening process by lime soda process, free  $\text{Na}_2\text{CO}_3$  is usually present in small portion in the soft water which decomposes to give NaOH and  $\text{CO}_2$  at high pressure of the boilers.



The precipitation of NaOH makes the boiler water **“Caustic”**

The NaOH containing water flows into the small pits and minute haircracks present on the inner walls of the boiler.

As the water evaporates, the concentration of caustic soda (NaOH) increases progressively, creating a **“Concentration Cell”**

Thus, dissolving the iron of the boiler as Sodium Ferrate.



The cracking of the boiler occurs particularly at stressed parts like bends, joints, rivets, etc. causing the failure of the boiler.

The **iron** at plane surfaces **surrounded by dilute NaOH** becomes **Cathodic**; while the **Iron** at bends, rivets and joints is surrounded by **highly concentrated NaOH** becomes **Anodic** which consequently decayed or corroded

(Anodic site) Conc NaOH || dil NaOH (Cathodic site)  
Iron at Joints & bends    Iron at Plane surface

### Prevention Of Caustic Embrittlement:

- (1) By adding  $\text{Na}_2\text{SO}_4$  , tannin, etc. to the boiler water which blocks hair cracks. There by preventing infiltration of caustic soda solution
- (2) By using sodium phosphate as the softening agent instead of sodium carbonate

## DISADVANTAGES OF CAUSTIC EMBRITLLEMENT:

The cracking or weakening of the boiler metal causes failure of the boiler

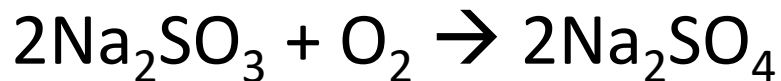
(3) **BOILER CORROSION:** The decay of boiler material by chemical/ electro- chemical attack by its environment is called “Boiler Corrosion”. Reasons for boiler corrosion are: (a) Dissolved oxygen (b) Dissolved  $\text{CO}_2$  (c) Acids from dissolved salts.

(a) Dissolved Oxygen: Water usually contains about 8 mg/L of dissolved oxygen at room temperature. Dissolved O<sub>2</sub> at high temperature attacks boiler material.



Removal of dissolved O<sub>2</sub>:

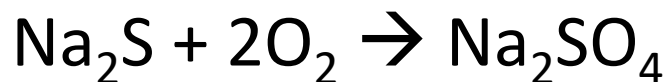
By adding calculated quantity of sodium sulphate (or) hydrazine (or) sodium sulphide



Sodium Sulphite



Hydrazine



(b) Dissolved CO<sub>2</sub>:

Dissolved CO<sub>2</sub> has slow corrosive effect on the materials of boiler plate. Source of CO<sub>2</sub> into water is the boiler feed water which contains bicarbonates. Under the high temperature and pressure, maintained in the boiler the bicarbonates decompose to produce CO<sub>2</sub>.

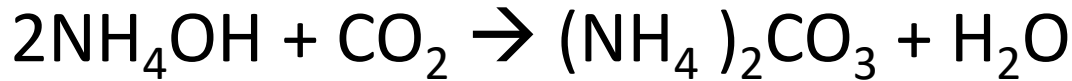


The disadvantage of the CO<sub>2</sub> is slow corrosive effect on boiler plates by producing **carbonic acid**



### Removal of CO<sub>2</sub>:

By the addition of calculated quantity of ammonia.



### (c) Acids from dissolved salts:

Water containing dissolved Mg-salts liberate acids on hydrolysis



Disadvantages of the acid production is that the acids react with Iron of the boiler plate in a chain reaction to produce decay of the metal.



Consequently even a small amount of  $\text{MgCl}_2$  can cause corrosion to a large extent.

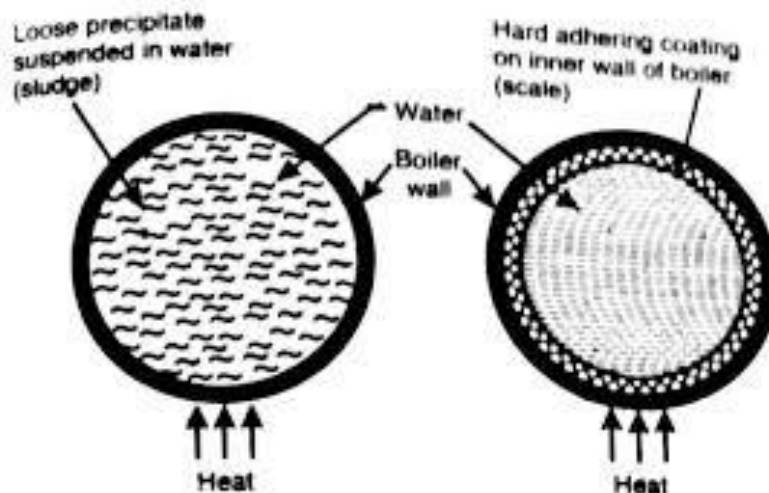
Preventions:

- (1) Softening of boiler water to remove  $\text{MgCl}_2$  from the water
- (2) Addition of corrosion inhibitors like sodium silicates, sodium phosphate & sodium chromate
- (3) By frequent **blow-down operation** i.e., removal of water, concentrated with dissolved salts and feeding the boiler with fresh soft water.
- (4) Sludges and Scales formation: In boiler, water evaporates continuously and the concentration reaches saturation point, they form precipitates (scale or sludge) on the inner wall of the boiler

**SLUDGE:** “Sludge is a soft, loose and slimy precipitate formed within the boiler”. Sludge are formed by substances which have greater solubility in hot water than in cold water. Salts like  $\text{MgCO}_3$  ,  $\text{MgSO}_4$  ,  $\text{MgCl}_2$  ,  $\text{CaCl}_2$  etc., are responsible for sludge formation in boilers.

Disadvantages:

- (a) Sludge is a bad conductor of heat, hence it wastes a portion of heat generated.
- (b) Excessive sludge formation reduces the efficiency of the boiler.





Prevention:

(a) Frequent blow-down operation should be carried out.

(b) Use well-softened water.

**SCALES:** “Scales are the hard, adhering ppt formed on the inner wall of the boiler”. Very difficult to remove once they are deposited on Inner wall of the boiler.

They formed due to decomposition of Calcium bicarbonate, Calcium sulphate etc.,



Boiler scale on water side

## REMOVAL OF SCALES:

- (1) Frequent blow-down operation can remove the scales which are loosely adhering.
- (2) By chemical treatment eg:  $\text{CaCO}_3$  scale removed by washing with 5-10% of HCl.
- (3) By giving thermal shocks.

Prevention: Use soft water.

## **SOFTENING OF WATER:**

The removal of hardness causing salts from water is called “Softening of water”.

The 3 Industrial methods employed for softening of water are:

(1) Lime-Soda Process

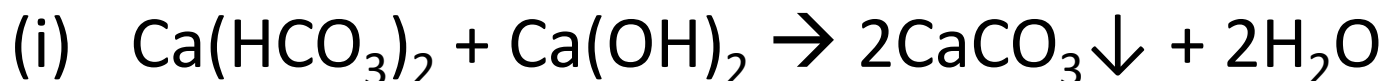
(2) Zeolite (or) Permutite Process

(3) Ion-Exchange (or) Demineralization process

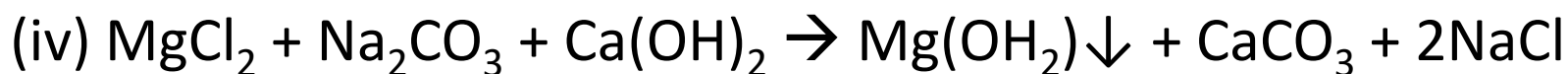
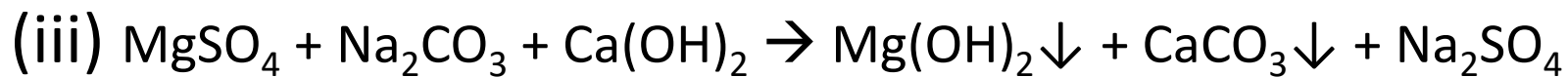
## **(1) LIME-SODA PROCESS:**

This process is based on converting the soluble calcium and magnesium salts into Insoluble calcium carbonate and magnesium hydroxide precipitates by addition of calculated amount of **lime** ( $\text{Ca(OH)}_2$ ) and **Soda** ( $\text{Na}_2\text{CO}_3$ ). The precipitate are removed by filtration. Any free dissolved  $\text{CO}_2$  and acids are also removed by this process. The various chemical reactions involved in this process are:

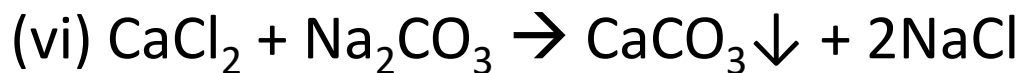
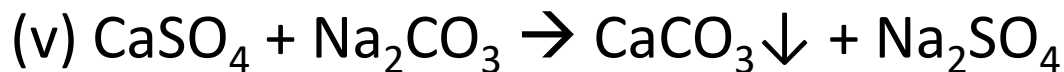
(a) For Calcium and Magnesium bicarbonates, only lime is required



(b) For  $\text{MgSO}_4$  &  $\text{MgCl}_2$ , both lime & soda are required



(c) For  $\text{CaSO}_4$  &  $\text{CaCl}_2$ , only Soda is required



(d) Other Reactions: Free acids, CO<sub>2</sub> , H<sub>2</sub>S dissolved iron and aluminium salts etc are also removed in this process



Constituent	Reaction	Requirement
Ca <sup>+2</sup> (Permanent)	(i) $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3\downarrow + \text{Na}_2\text{SO}_4$ (ii) $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3\downarrow + 2\text{NaCl}$	S
Mg <sup>+2</sup> (Permanent)	(iii) $\text{MgSO}_4 + \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2\downarrow + \text{CaCO}_3\downarrow + \text{Na}_2\text{SO}_4$ (iv) $\text{MgCl}_2 + \text{Na}_2\text{CO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Mg(OH)}_2\downarrow + \text{CaCO}_3 + 2\text{NaCl}$	L + S
HCO <sub>3</sub> <sup>-</sup>	(v) $2\text{NaHCO}_3 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{Na}_2\text{CO}_3$	L - S
Ca(HCO <sub>3</sub> ) <sub>2</sub> (Temporary)	(vi) $\text{Ca(HCO}_3)_2 + \text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3\downarrow + 2\text{H}_2\text{O}$	L
Mg(HCO <sub>3</sub> ) <sub>2</sub> (Temporary)	(vii) $\text{Mg(HCO}_3)_2 + 2\text{Ca(OH)}_2 \rightarrow 2\text{CaCO}_3\downarrow + \text{Mg(OH)}_2\downarrow + 2\text{H}_2\text{O}$	2L
CO <sub>2</sub>	(viii) $\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3\downarrow + \text{H}_2\text{O}$	L
H <sup>+</sup>	(ix) $2\text{HCl} + \text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl} + \text{H}_2\text{O}$	L + S
Coagulants FeSO <sub>4</sub>	(x) $\text{FeSO}_4 + \text{Ca(OH)}_2 \rightarrow \text{Fe(OH)}_2 + \text{CaSO}_4$ $2\text{Fe(OH)}_2 + \text{H}_2\text{O} + \text{O}_2 \rightarrow 2\text{Fe(OH)}_3$ $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$	L + S
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	(xi) $\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca(OH)}_2 \rightarrow 2\text{Al(OH)}_3\downarrow + 3\text{CaSO}_4 + \text{H}_2\text{O}$ $3\text{CaSO}_4 + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 3\text{Na}_2\text{SO}_4$	L + S
NaAlO <sub>2</sub>	(xii) $\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NaOH}$	-L

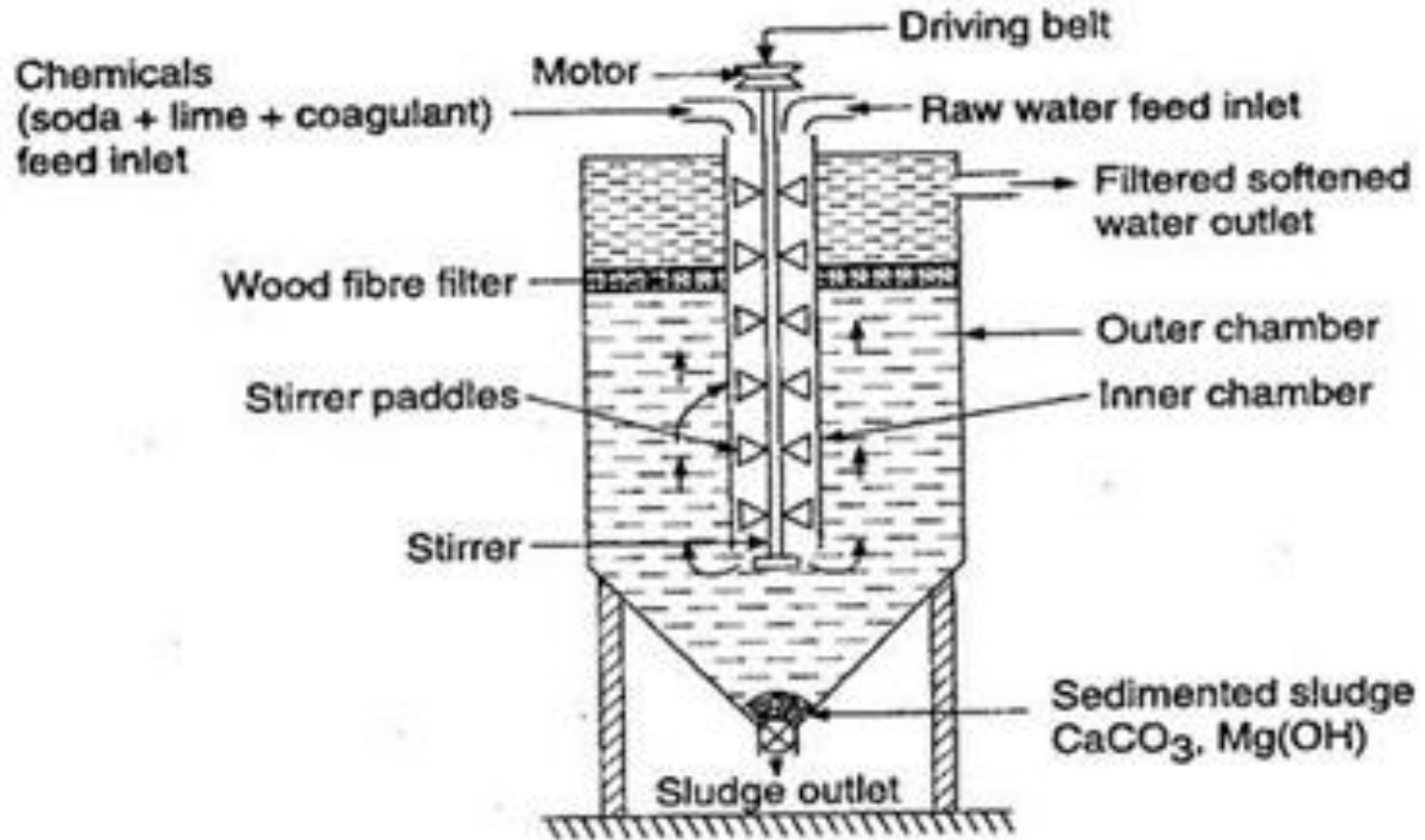
## Calculation:

100 parts by mass of  $\text{CaCO}_3$  are equivalent to 74 parts of  $\text{Ca(OH)}_2$  and 106 parts of  $\text{Na}_2\text{CO}_3$ .

- (a) Amount of **lime** required for softening =  $\frac{74}{100} (\text{Temp Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{+2} + \text{Fe}^{+2} + \text{Al}^{3+}) + \text{CO}_2 + \text{H}^+ (\text{HCl/H}_2\text{SO}_4) + \text{HCO}_3 - \text{all in terms of CaCO}_3 \text{ equivalent})$
- (b) Amount of **soda** required for softening =  $\frac{106}{100} (\text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{+2} + \text{Al}^{3+}) + \text{H}^+ (\text{HCl/H}_2\text{SO}_4) + \text{HCO}_3 - \text{all in terms of CaCO}_3 \text{ eq.})$

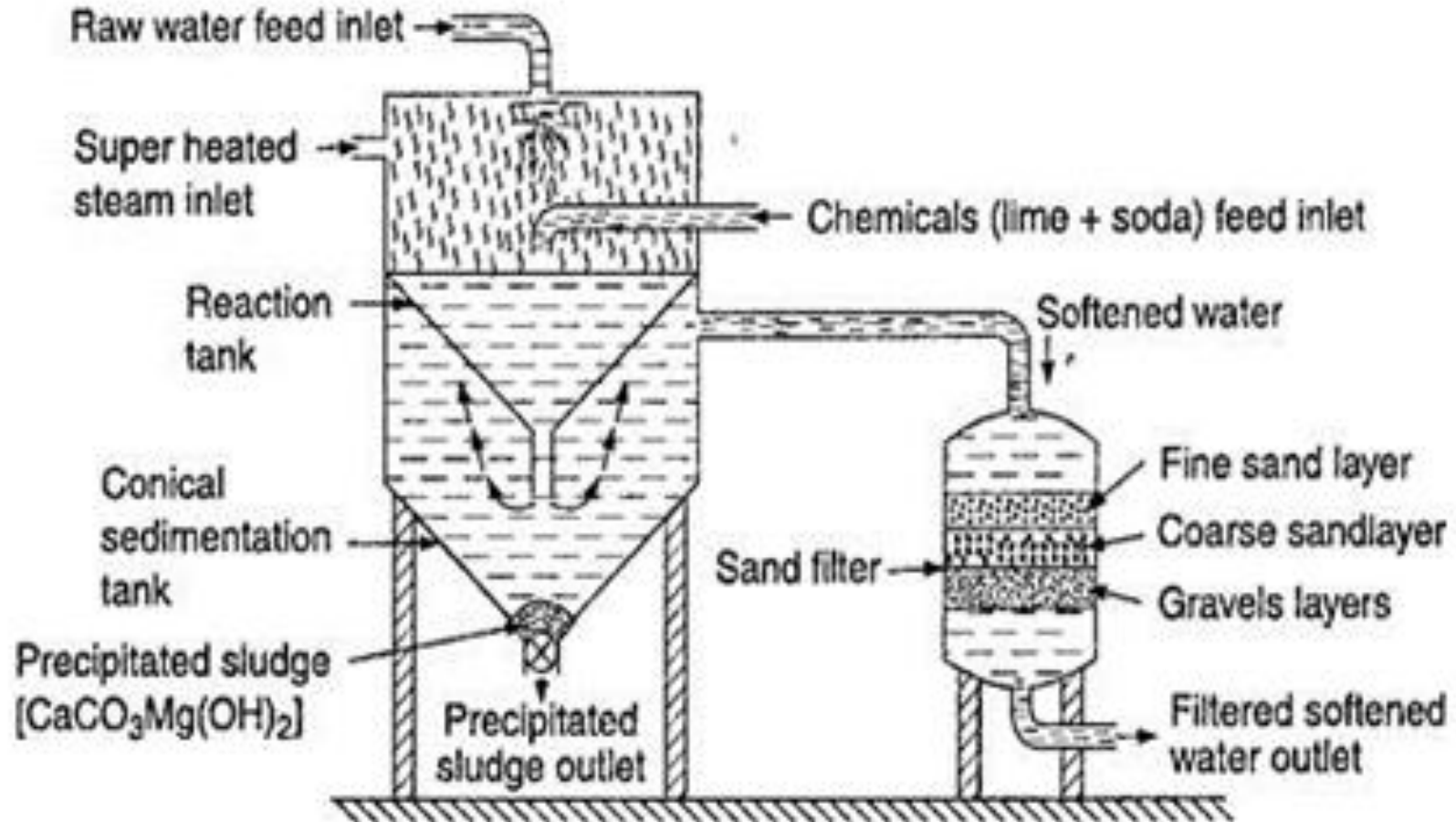


# COLD-LIME-SODA PROCESS:



- In this method the lime & soda are mixed with hard water at room temperature with constant stirring.
- Generally the precipitates formed by this process are finely divided and in order to settle the precipitates, coagulants like alum, ferrous sulphate, etc. are added.
- The hard water to be softened is mixed with calculated quantity of chemicals (Lime + Soda + Coagulant) from the top into the inner chamber on vigorous stirring. The chemical reactions takes place and the hardness producing salts get converted into insoluble precipitates.
- The sludge is removed from the bottom of the outer chamber while the softened water passes through a wood fibre filter to ensure the complete removal of any residual sludge particles.
- The clear softened water is withdrawn from the top of the outer chamber.
- The softened water from this process contains a residual hardness of 50-60ppm

# HOT-LIME-SODA PROCESS:



- This process is similar to the cold lime-soda process, but no coagulant is needed.
- Here the process is carried at a temperature of 80° to 150°C. Since the reaction carried out at high temperature.
  - (a) The reaction takes place faster
  - (b) The sludge settles rapidly
  - (c) Viscosity of soft water is lower, hence filtered easily
  - (d) The dissolved gases such as CO<sub>2</sub>, air, etc. driven out of the water
  - (e) The residual hardness is low, compared to cold lime- soda process.

Hot lime soda process consists of three parts-

- “REACTION TANK” in which complete mixing of water, chemicals and steam takes place and water gets softened.
- “Conical Sedimentation Vessel” where the sludge settle down.
- “SAND FILTER” where sludge is completely removed.

The softened water from this process contains a residual hardness of 15-30 ppm.

## ADVANTAGES OF LIME-SODA PROCESS:

- I. This process is economical.
- II. Mineral content of the water is reduced.
- III. The process increases the pH value of water, which reduces the content of pathogenic bacteria.
- IV. Manganese and Iron salts are also removed by this process.
- V. The process improves the corrosion resistance of the water.

## DISADVANTAGES OF LIME-SODA PROCESS:

- 1) Due to residual hardness, water is not useful for high pressure boilers.
- 2) Large amount of sludge is formed which create disposal problem.

## PROBLEMS:

- 1) Calculate the quantities of Lime & Soda required to soften 5000 litres of water containing the following salts:  $\text{MgCl}_2 = 15.5 \text{ ppm}$ ;  $\text{Ca}(\text{HCO}_3)_2 = 32.5 \text{ ppm}$ ,  $\text{CaSO}_4 = 22.4 \text{ ppm}$ ;  $\text{Mg}(\text{HCO}_3)_2 = 14.6 \text{ ppm}$ ;  $\text{NaCl} = 50 \text{ ppm}$

**Soln:** Calculation of Calcium Carbonate Equivalents:

Impurity mg/L	M. Wt.	$\text{CaCO}_3$ eq.	Requirement
$\text{MgCl}_2 = 15.5$	95	$15.5 \times 100 \div 95 = 16.31$	L + S
$\text{Ca}(\text{HCO}_3)_2 = 32.5$	162	$32.5 \times 100 \div 162 = 20.06$	L
$\text{CaSO}_4 = 22.4$	136	$22.4 \times 100 \div 136 = 16.47$	S
$\text{Mg}(\text{HCO}_3)_2 = 14.6$	146	$14.6 \times 100 \div 146 = 10$	2L
$\text{NaCl} = 50$	-		

Lime =  $74/100$  (Temp  $\text{Ca}^{2+}$  + 2 x Temp.  $\text{Mg}^{2+}$  + Perm. ( $\text{Mg}^{+2}$  +  $\text{Fe}^{+2}$  +  $\text{Al}^{3+}$ ) +  $\text{CO}_2$  +  $\text{H}^+$  ( $\text{HCl}/\text{H}_2\text{SO}_4$ ) +  $\text{HCO}_3^-$  - all in terms of  $\text{CaCO}_3$  equivalent) x (Vol of water/ 1000) x (100/ %P)

Lime required for litre of water:

=  $74/100$  ( $\text{Ca}(\text{HCO}_3)_2$  + 2 x  $\text{Mg}(\text{HCO}_3)_2$  +  $\text{MgCl}_2$ ) as  $\text{CaCO}_3$  eq.

=  $74/100$  (20.06 + 2x10 + 16.31)

=  $74/100$  x 56.37

= 41.71 mg

Lime req'd for 5000 litres of water

= 41.71 x 5000 ÷ 1000 = 208.55 g = 0.208 kg

$$\text{Soda} = 106/100 (\text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Fe}^{+2} + \text{Al}^{3+}) + \text{H}^+ (\text{HCl/H}_2\text{SO}_4) + \text{HCO}_3^- \text{ - all in terms of CaCO}_3 \text{ eq.)} \times (\text{Vol of water/ 1000}) \times (100/ \%P)$$

$$\begin{aligned} \text{Soda req'd for litre of water} \\ &= 106/100 [\text{MgCl}_2 + \text{CaSO}_4] \text{ as CaCO}_3 \text{ eq.} \\ &= 106/100 [16.31 + 16.47] \\ &= 106/100 [32.78] \\ &= 34.74 \text{ mg} \end{aligned}$$

$$\begin{aligned} \text{Soda req'd for 5000 litres of water:} \\ &= 34.74 \times 5000 \div 1000 = 173.70 \text{ gm} = 0.173 \text{ kg} \end{aligned}$$