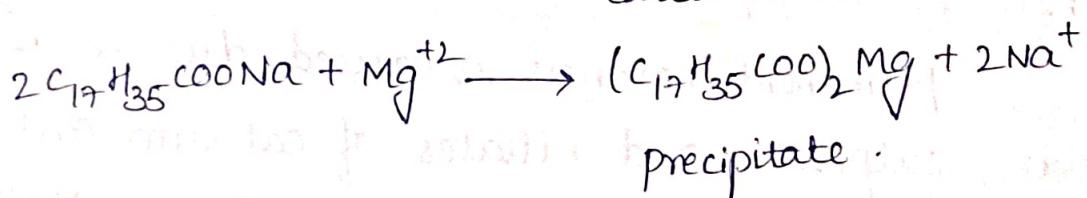
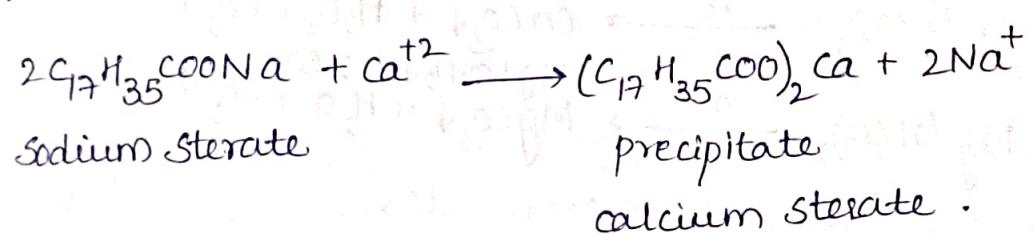


## 2. WATER AND ITS TREATMENTS.

### Hardness of water:

Hard water does not give lather easily with soap, but produce white scum or precipitate with soap. This is due to formation of insoluble soap of calcium and magnesium when  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions react with soap.

→ Soaps are sodium and potassium salts of higher fatty acid such as oleic acid, palmitic acid and stearic acid.



→ Soap can produce lather only after all hardness causing ions are precipitated as insoluble soap. Hence it require large quantity of soap to produce lather.

→ The water which produce lather easily with soap is called soft water.

## Types of Hardness:

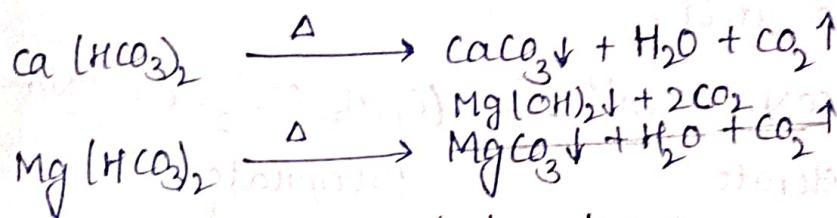
Hardness of water can be classified into.

1. Temporary hardness.
2. Permanent hardness.

### Temporary hardness/carbonate hardness.

Temporary hardness is caused by the presence of dissolved bicarbonates of calcium and magnesium.  
→ This hardness can be removed by boiling of water.

Bicarbonates are converted to insoluble carbonates.



### Permanent Hardness/ Non Carbonates :

Permanent hardness is caused due to dissolved chlorides, sulphates and nitrates of calcium and magnesium salts like  $\text{CaCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{MgCl}_2$ ,  $\text{MgSO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ .  
→ The hardness cannot be removed by boiling. It requires special chemical treatment methods.

The sum of temporary and permanent hardness is referred as total hardness of water.

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

→ Different types of water have different degree of hardness and it is classified as follows.

Hardness	Name of the Water.
0 - 70 mg/lit	soft water.
70 - 150 mg/lit	moderate hard water.
150 - 300 mg/lit	hard water.
300 mg/litre and above	very hard water.

#### EXPRESSION OF HARDNESS:

Hardness is expressed in terms of equivalents of calcium carbonate.

The concentration of hardness as well as non-hardness consisting ion is expressed in terms of equivalents of  $\text{CaCO}_3$ . The choice of  $\text{CaCO}_3$  is particular due to its molecular weight 100. (Equivalent weight = 50)

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of hardness producing salt} \times \text{eq. wt of } \text{CaCO}_3}{\text{eq. wt of hardness producing salt.}}$$

$$\begin{aligned}\therefore 100 \text{ gm of } \text{CaCO}_3 &= 111 \text{ gm of } \text{CaCl}_2 \\ &= 120 \text{ gm of } \text{MgSO}_4 \\ &= 95 \text{ gm of } \text{MgCl}_2 \\ &= 146 \text{ gm of } \text{Mg}(\text{HCO}_3)_2 \\ &= 162 \text{ gm of } \text{Ca}(\text{HCO}_3)_2 \\ &= 136 \text{ gm of } \text{CaSO}_4.\end{aligned}$$

$\therefore$  120 gm of  $MgSO_4$  would react with same amount of soap as 100 gm of  $CaCO_3$ .

111 gm of  $CaCl_2$  would react with the same amount of soap as 100 g of  $CaCO_3$ . If  $x$  is the weight of  $CaCl_2$ , to convert it into  $CaCO_3$  equivalent, it must be multiplied by a factor of  $\frac{100}{111}$ .

$$x \text{ parts of } CaCl_2 = \frac{x \times 100}{111}$$

$Ca(HCO_3)_2$  has the mass of hardness 32.4 mg. calculate its  $CaCO_3$  equivalent.

$$\text{eq. of } CaCO_3 = \frac{32.4 \times 100}{162}$$

$$= 20 \text{ parts of } CaCO_3.$$

### units of Hardness (units and Interconversion of units)

The units normally used to express hardness are parts per million (ppm) or milligram per litre (mg/L) of  $CaCO_3$  equivalents.

1. parts per million (ppm): It is the  $\frac{\text{no. of}}{\text{parts of water}}$  hardness per  $10^6$  parts of water.

i.e. 1 ppm = 1 part of  $CaCO_3$  eq. hardness in  $10^6$  parts of water.

For example, 50 ppm hardness means  $10^6$  parts of water has 50 parts of equivalent  $CaCO_3$ .

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2. Milligram per litre (mg/L) is the number of milligrams of  $\text{CaCO}_3$  equivalent hardness present per litre of water.

$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ eq. hardness into } 10^6 \text{ per 1 litre}$   
But 1 litre weighs 1 kg.

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

$\therefore 1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalents per } 10^6 \text{ mg of water.}$

3. Degree French ( ${}^\circ\text{Fr}$ ): 1 part of  $\text{CaCO}_3$  present in  $10^5$  parts of water.

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

4. Degree Clark ( ${}^\circ\text{Cl}$ ): 1 part of  $\text{CaCO}_3$  present in 1 gallon (70,000) parts of water.

$$1 \text{ gallon} = 70,000 = 7 \times 10^4 \text{ parts.}$$

$${}^\circ\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness in } 70,000 \text{ parts of water.}$$

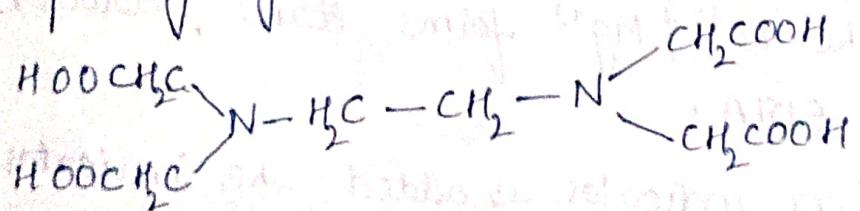
Internal relationship between various units.

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

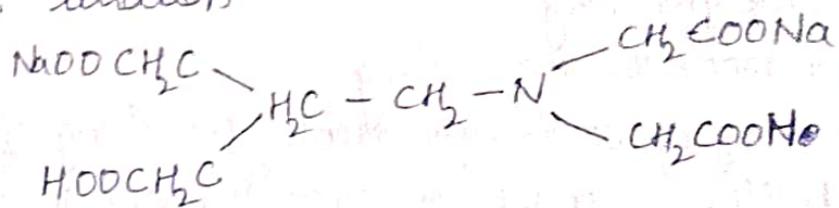
### Determination of Hardness of water:

Hardness of water is mostly commonly determined by complexometric (EDTA) titration because of its high accuracy.

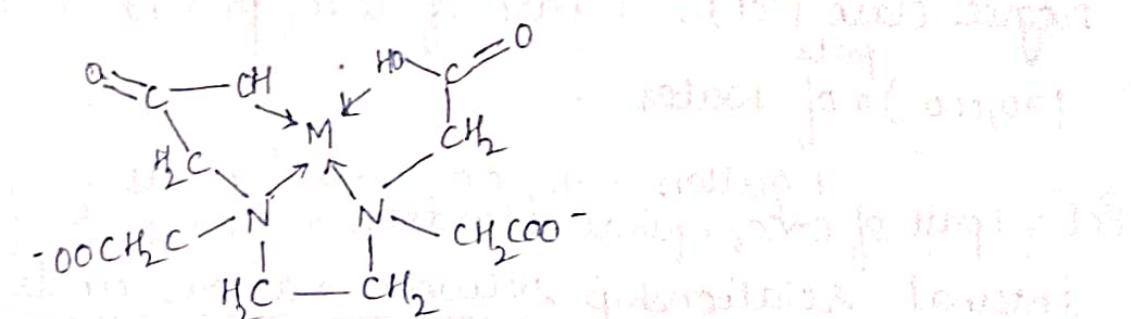
→ Ethylene diamine tetra acetic acid (EDTA) is a strong complexing agent.



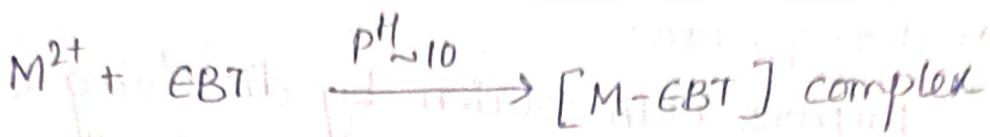
As such it is not soluble in water. Hence EDTA is used in the form of disodium salt in complexometric titration.



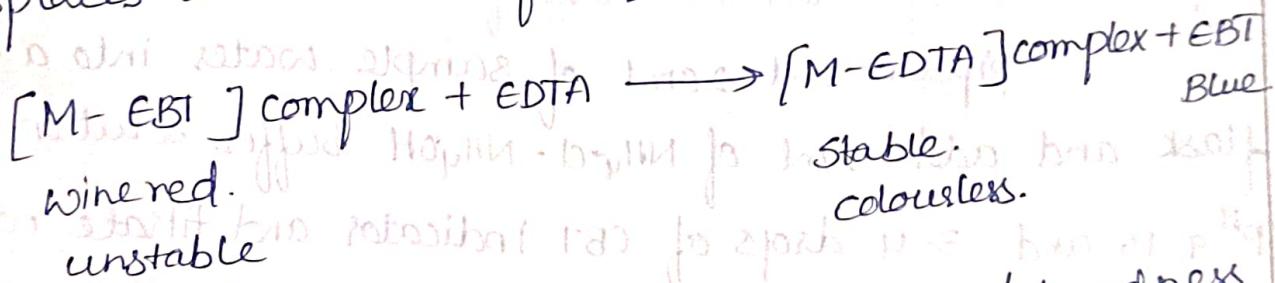
The sodium salt yields anion which forms complex ions with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  (Metal - EDTA complex).



- To determine the equivalence point, indicator Eriochrome black-T (EBT) or solochrome black-T is used. which forms an unstable wine-red complex with  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$
- The indicator is effective at  $\text{pH}=9-10$ . So to maintain  $\text{pH}=9\text{ to }10$ , buffer solution ( $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ ) is used.
- When hard water comes in contact with EDTA solution at  $\text{pH}=9-10$ , the  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$  forms stable, colourless complex with EDTA.
- Few drops of EBT indicator is added. The indicator forms a wine-red unstable complex.



In course of titration, water sample against EDTA, first it combines with free metal ions to give very stable and colourless metal - EDTA complex.  
 $\rightarrow$  After all the free metal ion are reacted upon by EDTA, the next drop of EDTA solution added displaces the indicator from  $[M-EBT]$  complex.



Experimental procedure: The procedure for determination of hardness of water involves the following steps.

1. preparation of standard hard water: weigh accurately about 1.0 g of  $\text{CaCO}_3$  and dissolve it in dil. HCl. Make up the solution up to the mark with distilled water in 1000 ml standard flask.

Molarity of standard = 
$$\frac{\text{Weight of } \text{CaCO}_3}{\text{M. wt. of } \text{CaCO}_3}$$

hard water = 
$$= \frac{1}{100}$$

Molarity of standard = 0.01 M

### ii) Standardisation of EDTA:

- Prepare EDTA solution by dissolving 11g of pure EDTA and 1g of  $MgCl_2$  in 1 litre of distilled water.
- pipette out 20ml of standard hard water into a conical flask, add 2ml of  $NH_4Cl-NH_4OH$  buffer solution of pH 9-10.
- Add 3-4 drops of EBT indicator and titrate with EDTA solution till the wine red colour changes to blue.
- Let the volume of EDTA consumed by standard hard water be  $x$  ml.

### iii) Estimation of total hardness of water:

- Pipette out 20ml of sample water into a conical flask and add 2ml of  $NH_4Cl-NH_4OH$  buffer solution of pH 9-10 and 3-4 drops of EBT indicator and titrate with EDTA solution till the wine red colour of solution changes to blue. Let the volume of EDTA consumed by sample water be  $y$  ml.

### iv) Estimation of permanent hardness of water:

- Take 100ml of water sample in a beaker. Boil the water till the volume is reduced to about 20ml.
- cool the solution and filter the water till into a 100ml standard flask. wash the precipitate with distilled water.
- pipette out 20ml of water into a conical flask, add 2ml of buffer solution and 3-4 drops of EBT indicator and titrate with EDTA until the wine red solution changes

to blue colour. The volume of EDTA consumed will be 2 ml.

### Calculation :

$$\text{Molarity of standard hard water} = \frac{\text{Weight of } \text{CaCO}_3}{\text{M.wt of } \text{CaCO}_3}$$

$$= \frac{1}{100}$$

$$= 0.01 \text{ M.}$$

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

where  $n_1$  and  $n_2$  are the number of moles of  $\text{Ca}^{+2}$ ,  $\text{EDTA} = 1$

$M_1$  = Molarity of standard hard water.

$V_1$  = volume of standard hard water.

$V_2$  = volume of EDTA consumed =  $x$  ml.

$M_2$  = Molarity of EDTA

$$M_2 = \frac{M_1 V_1}{n_1}$$

$$= \frac{20 \times 0.01}{x \text{ ml.}}$$

Molarity of hard water sample =  $M_3$ .

where,

$V_2$  = volume of EDTA

$M_2$  = Molarity of EDTA.

$M_3$  = Molarity of hard water sample.

$V_3$  = volume of hard water sample.

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

$$= \frac{M_2 \times 2\text{ml}}{20}$$

Total hardness of water =  $M_3 \times 100 \text{ g/L}$   
 $= M_3 \times 100 \times 1000 \text{ mg/L}$

Permanent hardness of water is calculated by

$$\frac{M_2 V_2}{n_2} = \frac{M_4 V_4}{n_4}$$

$$n_2 = n_4 = 1$$

where

$V_2$  = Volume of EDTA

$M_2$  = Molarity of EDTA

$M_4$  = Molarity of water sample having permanent hardness.

$$M_4 = \frac{M_2 V_2}{V_4} = M_2 \times 2\text{ml}/100\text{ml.}$$

Permanent hardness of water sample =  $M_4 \times 100 \times 1000 \text{ ppm.}$

Temporary hardness of water sample = Total hardness - permanent hardness

$$= M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000 \text{ ppm}$$

## POTABLE WATER AND ITS SPECIFICATION :

The water which is safe for drinking is called potable water. The essential requirements of of potable water are .

1. Water should be clear and odourless.
2. It should be pleasant to taste.
3. It should be perfectly cool.
4. Its turbidity should not exceed 10 NTU (National turbidity units)
5. It should be free from objectionable minerals such as lead, arsenic, chromium and manganese salt.
6. It should be free from pathogenic bacteria and dissolved gases like  $H_2S$ .
7. The optimum hardness of water must be 125 ppm and pH must be 7.0 to 8.5.
8. The recommended maximum concentration of total dissolved solids in potable water must not exceed 500 ppm.

## TREATMENT OF WATER FOR DOMESTIC PURPOSE:

water treatment for municipal supply or domestic use consists of following stages.

1. screening
2. sedimentation
3. coagulation
4. Filtration
5. Disinfection and sterilization.

### 1. SCREENING:

The water obtained from rivers, reservoirs and lakes is passed through steel screens, having large number of holes. The screening removes solid floating materials such as dead fish and animals, bits of wood, weeds present in water.

### 2. SEDIMENTATION:

Sedimentation is a process of removing suspended impurities by allowing water to remain undisturbed in big tanks.

- Most of the particles settle down due to gravity. The clear supernatant water is drawn from tank with the help of pump.
- In this process, about 75% of the suspended impurities are removed.

### 3. Sedimentation with coagulation:

The suspended and colloidal impurities are allowed to settle under gravitation.

- For setting of fine particles, coagulants like alums, sodium aluminate and salts of iron are added, which produce gelatinous precipitate called floc, process known as flocculation.
- Floc attracts and helps accumulation of the colloidal particles resulting in settling of colloidal particles.
- The following sedimentation tank used for colloidal impurities

In this method certain chemicals, called coagulants like alum  $\text{Al}_2(\text{SO}_4)_3$ , sodium aluminate  $\text{NaAlO}_2$ , Ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  are added to water.

- when  $\text{Al}_2(\text{SO}_4)_3$  is added to water, it gets hydrolysed to form a gelatinous precipitate of  $\text{Al}(\text{OH})_3$ .
- The gelatinous precipitate of  $\text{Al}(\text{OH})_3$  entraps the finely divided and colloidal impurities, settles to the bottom and can be removed easily.

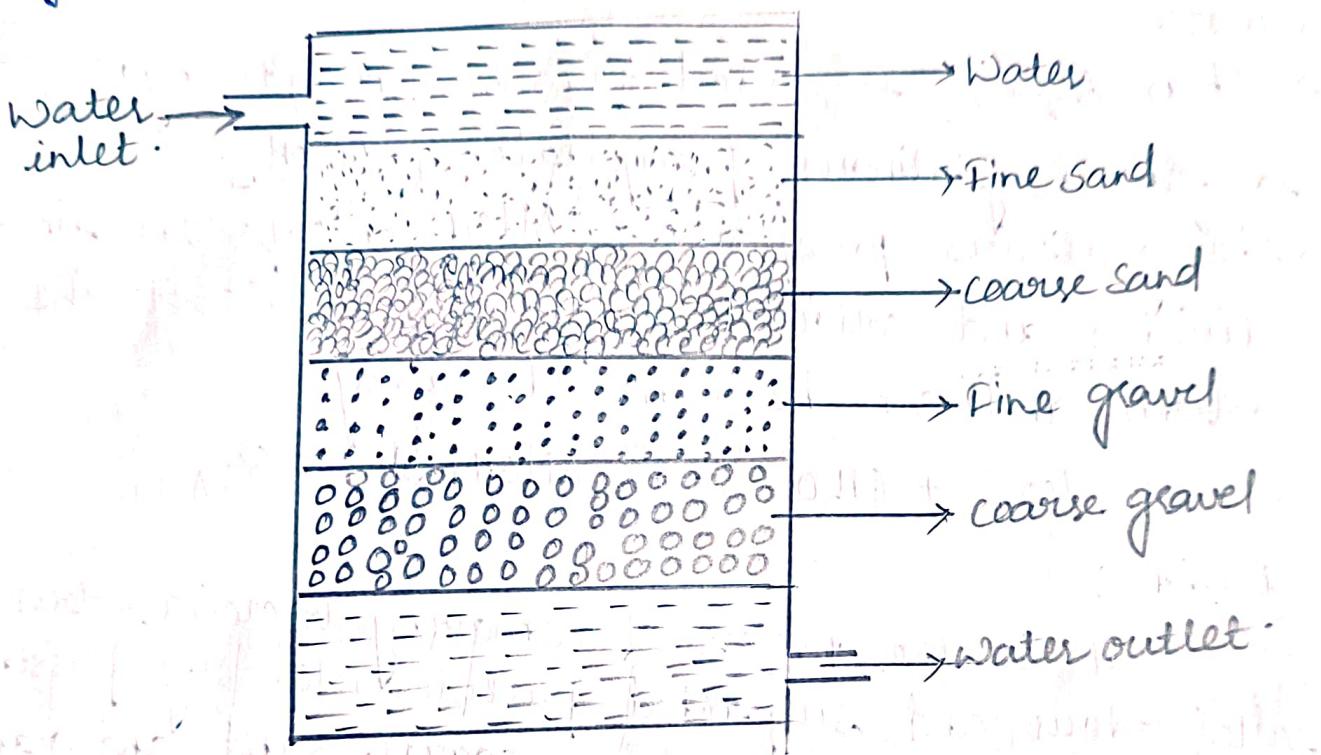


### Filtration:

It is the process of removing bacteria, colour, taste, odour and suspended particles, etc. by passing the water through filter beds, coarse sand and gravel.

- A typical sand filter is shown in figure.
- The sand filter consists of a tank containing a thick top layer of fine sand followed by coarse sand, fine gravel and coarse gravel.
- When the water passes through the filtering medium it flows through the various beds slowly.
- The rate of filtration decreases slowly due to the clogging of impurities in the pores of the sand bed.
- When the rate of filtration becomes very slow, the filtration is stopped and the thick top layer of

fine sand is scrapped off and replaced with clean sand. Bacteria are also partly removed by this process.



### Sterilisation or disinfection:

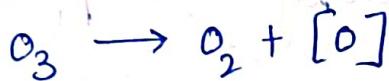
Destruction of harmful pathogenic bacteria from drinking water is carried out by sterilisation. The following are the methods adopted for sterilisation.

#### a. Boiling:

By boiling water for 15-20 minutes, harmful bacteria are killed. This is not possible for the municipal supply of water. It is adopted for domestic purpose.

b. By ozonisation:

ozone is a powerful disinfectant and is readily absorbed by water. ozone is highly unstable and breaks down to give nascent oxygen.



The nascent oxygen is a powerful oxidising agent and kills the bacteria.

Disadvantage:

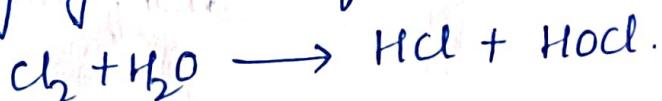
- This process is costly, ozone is unstable and cannot be stored for long time.
- Turbid water cannot be treated.

c. By chlorination:

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

d. By adding chlorine gas:

chlorine gas can be bubbled in water as a very good disinfectant.



2. By adding chloramine:

when chlorine and ammonia are mixed in the ratio of 2:1, a compound com chloramine is formed



disinfectant.

chloroamine compounds decompose slowly to give chlorine.

→ hypochlorous acid ( $HClO$ ) inactivates the enzymes of bacteria and kills bacteria.

→ It gives good taste to the treated water.

→ It is useful for disinfecting swimming pools.

By adding bleaching Powder:

when bleaching powder is added to water, it produces hypochlorous acid ( $HClO$ ).

It is a powerful germicide.



Bleaching

powder.



disinfectant.

→ The long term consumption of such water may damage liver, kidney etc.

d) Break point of chlorination:

The amount of chlorine required to kill bacteria and to remove organic matter is called break point of chlorination.

→ The water sample is treated with chlorine and estimated for the residual chlorine in water and a graph is plotted as shown below

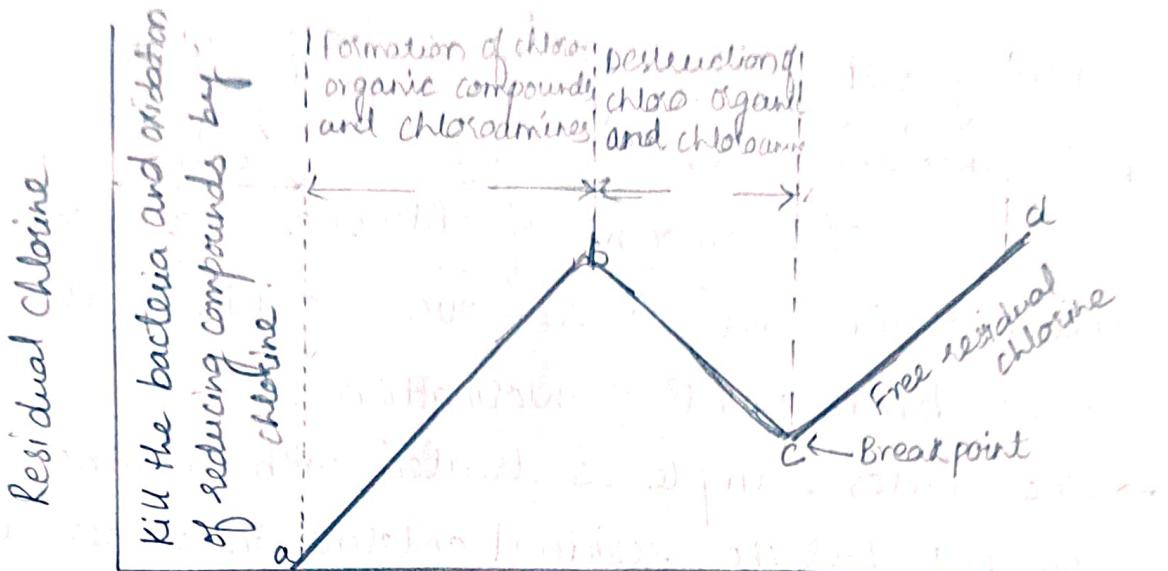
→ Initially all the chlorine is consumed there is no residual chlorine, this is due to complete oxidation of reducing substance present in water.

→ As the amount of chlorine dosage is increased, there is steady increase in amount of residual chlorine and forms chloro-organic compounds without oxidizing

→ Next, when the dosage of chlorine is high enough, oxidation of organic compounds and chloramines take place. Free residual chlorine decrease and reaches a dip when oxidative destruction is complete.

→ Next dosage of chlorine is not used in any reaction and residual chlorine keeps increasing.

→ For effective killing of microorganisms, sufficient chlorine has to be added and this is indicated by dip in the plot. Addition of such dosage is known as break-point or free residual chlorination.



### Advantages:

- 1. It ensures complete destruction of organic compound which give colour, unpleasant taste and bad odour.
- 2. It also ensures complete destruction of disease producing microorganisms.
- 3. It prevents the growth of any weeds in water.

### Dechlorination:

It des over chlorination after the break point produces unpleasant taste and colour in water. Dechlorination of such water can be achieved by either passing water through a bed molecular carbon or by adding activated carbon to water and removed it by filtration after the reaction period.

→ The excess chlorine can also removed by adding small quantities of substances like  $\text{SO}_2$  (or)  $\text{Na}_2\text{SO}_3$ .

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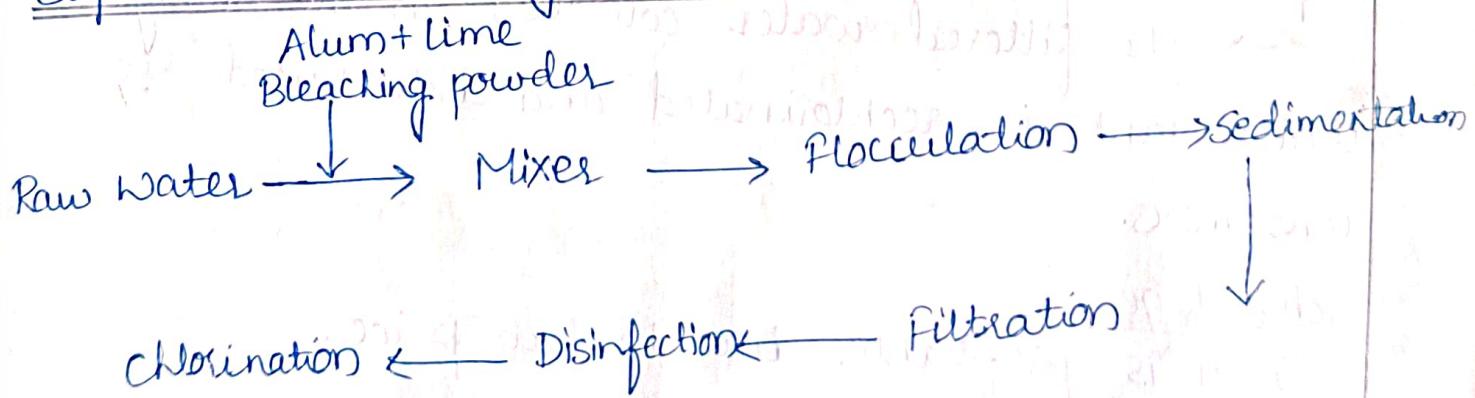
## De-fluoridation :

(10) Applied for water of pH

Fluorine is most active element found in naturally occurring rocks. The limit of fluorine in water is below 1 ppm.

- within the limits it helps to protect teeth enamel and makes it more resistant.
- Above the limit it causes a disease called Fluorosis, the weakening and bending of bones, decay of teeth etc.
- Defluoridation is the removal of excess fluoride from water. An economical and simple method of defluoridation is Nalgonda technique.
- Fluoride is precipitated using 500 mg/lit of alum and 30 mg/lit of lime with small amount of bleaching powder 3 mg/lit for disinfection.

### Steps involved in Nalgonda technique:



### Step 1. Addition of chemical:

→ Raw water is added with alum, lime and bleaching powder.

### Step 2. Mixing:

→ The water is thoroughly mixed with added chemicals for some time using mechanical stirrer.

### Step 3. Flocculation:

→ Flocculation involves subsequent gentle agitation before entry to sedimentation tank.

### Step 4. Sedimentation:

→ It removes settled floc, loaded with fluorides, turbidity, bacteria and other impurities.

### Step 5. Filtration:

→ The treated water, from sedimentation tank, is filtered by gravity sand filter.

### Step 6. Disinfection:

→ The filtered water collected in the storage water tank is rechlorinated and distributed to consumers.

### Advantages:

i) It is preferable due to low price.

ii) ease of handling.

## Determination of F<sup>-</sup> ions by selective electrode method:

Fluoride ions in water can be determined by solid-state membrane electrode.

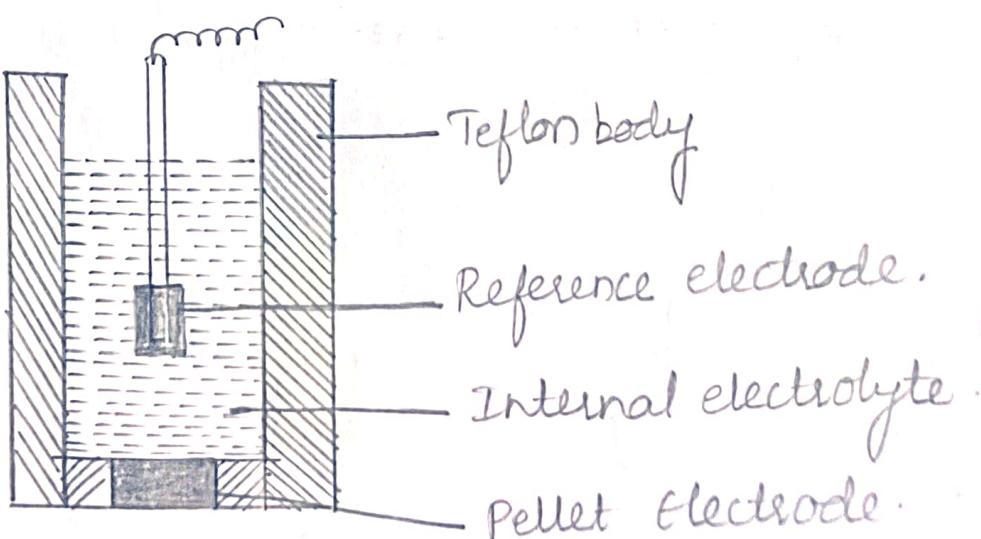
### construction:

- solid-state membrane electrode consists of an internal reference electrode and it contains NaF + NaCl for sensing fluoride ion.
- The body of the electrode is made up of teflon and the pellet, lanthanum trifluoride LaF<sub>3</sub> crystal doped with europium difluoride EuF<sub>2</sub>, is held in position with epoxy resin.
- These electrode will sense only F<sup>-</sup> ions ignoring others.

$$\epsilon = \epsilon^{\circ} - \frac{0.05916}{n} \log [F^-]$$

### uses:

Fluoride ions selective electrode is used in estimation of fluoride ions in water and in toothpaste.



## ION EXCHANGE PROCESS (or) DEMINERALISATION / DEIONISATION

Ion-exchange process includes the exchange of cations and anions of the dissolved salts with  $H^+$  and  $OH^-$  ions respectively.

→ Two types of ion-exchangers are used which are insoluble, cross-linked long chain organic polymer with microporous structure.

### i) Cation Exchange Resin:

They are capable of exchanging  $H^+$  ions with cation of the dissolved salts.

→ The cation exchange resin are represented by general formula  $RH$  where  $R$  is insoluble polymeric matrix.

e.g.: Styrene - divinyl benzene copolymer containing the functional group  $-COOH$  or  $-SO_3H$ . in which  $H^+$  ions are replaced by cation such as  $Mg^{+2}/Ca^{+2}$ .



### ii) Anion Exchange Resin:

They are capable of exchanging their  $OH^-$  ions with anions of the dissolved salts.

→ The anion exchangers are represented by general formula  $R'OH$ . Where  $R'$  represents insoluble organic matrix.

Eg: phenol-formaldehyde (or) Amine-formaldehyde copolymers.

The exchange reactions with their anions can be represented as .



#### PROCESS:

The hard water is passed through cation exchange column where all the cations like  $Ca^{+2}$ ,  $Mg^{+2}$  are removed and an equivalent amount of  $H^+$  ion is released from resin to water.

→ Next water is passed through anion exchange column where all anions like  $Cl^-$ ,  $SO_4^{2-}$  etc are removed and equivalent amount of  $OH^-$  is released from this column to water.

→ The  $H^+$  and  $OH^-$  released respectively from cation exchangers and anion exchangers combine to give water.



Thus, water flowing out of the anion exchange column is free from all cations and anions and becomes ion-free or deionized or demineralized.

## Desalination of water:

The process of removal of dissolved salts (NaCl, KCl) present in water is known as desalination.

water is divided into three categories

- sea water : The salinity is greater than 35000 mg/L
- Brakish water : The salinity is in the range 1000 - 35000 mg/L
- Fresh water : The salinity of water is less than 1000 mg/L

## Reverse osmosis:

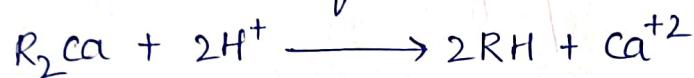
when two solutions of unequal concentrations are separated by a semi permeable membrane / SPM flow of solvent takes place from dilute to concentrated sides, due to osmosis.

- If high a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from solution into pure solvent through SPM.
- Since the flow of solvent is in reverse direction to the observed usual osmosis, the process is called reverse osmosis.
- In reverse osmosis method pure solvent, water is separated from its contaminants rather than removing contaminants from water. The membrane filtration is called as 'super-filtration' or 'hyper-filtration'

## REGENERATION:

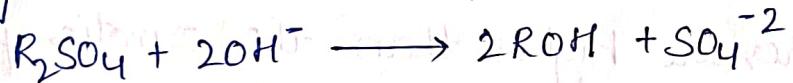
when cation exchangers and anion exchangers are fully saturated by absorption of cations and anions, they lose their exchanging capacity and become exhausted.

→ The cation exchange column is regenerated by passing a solution of dilute HCl or  $H_2SO_4$ .



The column is washed with deionized water and the washing containing  $Na^+$ ,  $Cl^-$  and  $SO_4^{2-}$  are drained.

→ The exhausted anion exchange column is regenerated by passing dilute solution of NaOH.



The regenerated exchangers can be used again.

The residual hardness of water in this process is 0.2 ppm.

### Advantages:

1. The process can be used to soften highly acidic or alkaline water.
2. It produces water of very low hardness. The deionised water is most suitable for high pressure boilers.

### Disadvantages:

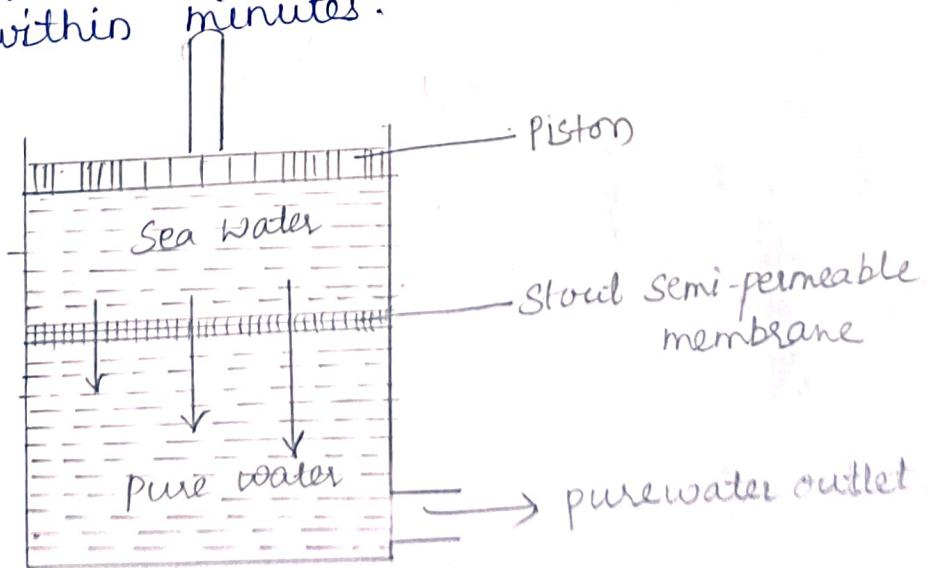
1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, the output is reduced, thus turbidity must be below 10 ppm.

Method: In reverse osmosis process pressure of 15-40 kg/cm<sup>2</sup> is applied to sea water or impure water to force its pure water out through SPM leaving behind the dissolved salts or solids both ionic as well as non-ionic. The membrane consists of very thin films of cellulose acetate, affixed either side of a perforated tube.

→ Recently superior membranes made of polymethyl acrylate and polyamide polymers have come into use.

### Advantages:

1. The process is simple and requires low energy.
2. It deals with the problem of removing colloidal silica which is not removed by demineralization.
3. Life time of SPM is high, 2 years and it can be replaced within minutes.



## BOILER TROUBLES:

The water fed into the boiler for the production of steam is called boiler feed water.

→ As the water is heated continuously to produce steam, the concentration of the dissolved salts in water increases progressively and reaches the saturation point and precipitates out and settle slowly on the inner wall of the boiler plate.

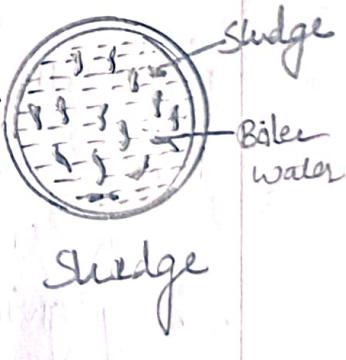
→ If hard water is used the following troubles are seen.

### SLUDGE:

The soft, loose, slimy deposit and non-sticky precipitates are called sludge.

→ Sludges are formed by substances like  $MgCl_2$ ,  $MgSO_4$ ,  $MgCO_3$  and  $CaCl_2$ .

→ They have greater solubility in hot water.



### DISADVANTAGES:

1. Sludges are bad conductor of heat.
2. wastage of heat and fuel.
3. clogging of pipes and plug openings.

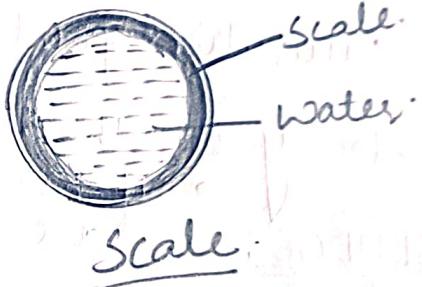
### PREVENTION:

1. By using soft water.
2. By carrying frequent blow-down operation.

## SCALES:

Scales are hard, sticky deposits formed on the inner walls of boiler is called scale.

- Scales are very difficult to remove once they are deposited on the surface of boiler.
- Scales are formed by the substance like:  
 $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{CaSO}_4$ ,  $\text{Mg}(\text{OH})_2$ .



## DISADVANTAGES:

1. wastage of fuel
2. lowering the boiler safety.
3. Decrease in efficiency.
4. Danger of explosion.

## PREVENTION:

1. If the scale is soft, it can be removed by scrapper, wire brush
2. By giving thermal shocks.
3. chemical treatment - By adding 5-10%  $\text{HCl}$  and dil  $\text{H}_2\text{SO}_4$ .
4. Blow down operation.

## CALISTIC EMBRITTLEMENT:

caustic embrittlement is the term used for the appearance of cracks inside the boiler particularly stressed parts like bends, joints, rivets.

→ The cracks have the appearance of brittle fracture hence the failure is called caustic embrittlement

### REASON:

Boiler water usually contains a small portion of  $\text{Na}_2\text{CO}_3$  which decomposes to give sodium hydroxide and carbon dioxide at high pressure.



→ The precipitation of NaOH makes the boiler water caustic. NaOH flows into the minute hair cracks and dissolves the surrounding area of iron as sodium ferroate.



### PREVENTION:

1. By using sodium phosphate as softening reagent.
2. By adding tannin, or lignin to the boiler water, which block the hair cracks.

### DISADVANTAGE:

Cracking of boiler metal causes failure of the boiler.

## INTERNAL TREATMENT:

softening of water carried out inside the boiler is called conditioning or internal treatment of water.

- By complexing the hardness causing salts and by precipitating scale forming substances into sludge which can be removed by blow down operation.
- The important internal conditioning are

### 1. colloidal conditioning

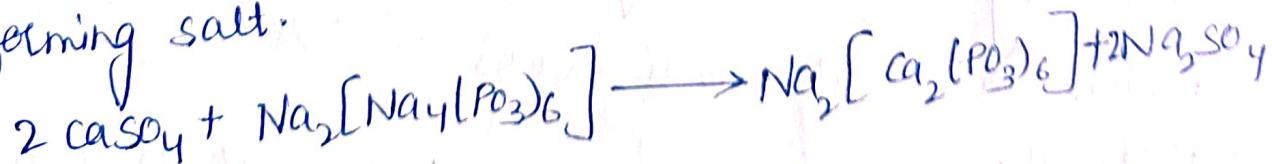
The scale formation in low pressure boiler is prevented by adding kerosene, tannin, agar-agar etc.

- which get coated over the scale forming precipitate They form loose, non sticky deposits that can be removed by blow down.

### 2. colloidal

### 2. Calgon conditioning:

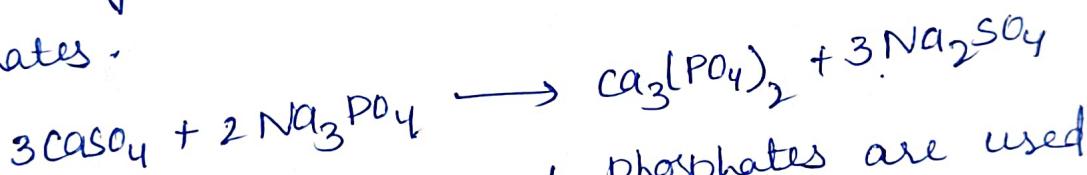
Calgon is sodium hexa meta phosphate  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ . It interacts with  $\text{Ca}^{+2}$  ions and forms water soluble compound; thus prevents the scale forming salt.



The complex is soluble in water and there is no problem of sludge disposal.

### 3. Phosphate conditioning:

Scale formation can be avoided by adding sodium phosphate. It is used in high pressure. The phosphate reacts with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  salts to give soft sludge of calcium and magnesium phosphates.



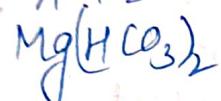
Generally 3 types of phosphates are used

1. Trisodium phosphate:  $\text{Na}_3\text{PO}_4$  (too alkaline) -  
It is used for too acidic water.
2. Disodium hydrogen phosphate:  $\text{Na}_2\text{HPO}_4$  (weakly alkaline)  
used for weakly acidic water
3. Sodium dihydrogen phosphate:  $\text{NaH}_2\text{PO}_4$  (acidic).  
used for alkaline water.

A sample of water contains the following dissolved salts in mg/lit.  $Mg(HCO_3)_2 = 73$ ,  $CaCl_2 = 111$ ,  $Ca(HCO_3)_2 = 81$

$$MgSO_4 = 40$$

Name of  
H.P.S.



Amount in  
mg/lit

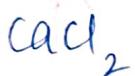
$$73$$

Mol. wt

$$146$$

Amount of equiv.  
to  $CaCO_3$ .

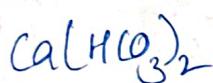
$$\frac{73 \times 100}{146} = 50 \text{ mg/lit}$$



$$111$$

$$111$$

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



$$81$$

$$162$$

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



$$40$$

$$120$$

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

$$\text{Temporary hardness} = Mg(HCO_3)_2 + Ca(HCO_3)_2$$

$$= 50 + 50$$

$$= 100 \text{ mg/lit}$$

$$\text{Permanent hardness} = CaCl_2 + MgSO_4$$

$$= 100 + 33.33$$

$$= 133.33 \text{ mg/lit.}$$

\* A sample of water contains the following salts in mg/lit calculate temporary and permanent hardness of water

$$\rightarrow Mg(HCO_3)_2 = 14.6, MgCl_2 = 9.5, MgSO_4 = 6.0, Ca(HCO_3)_2 = 16.2$$

$$\rightarrow Mg(HCO_3)_2 = 16.8 \text{ mg/lit}, MgCl_2 = 29.6 \text{ mg/lit}, MgSO_4 = 12 \text{ mg/lit}$$

$$\rightarrow Ca(HCO_3)_2 = 121.5 \text{ ppm}, Mg(HCO_3)_2 = 116.8 \text{ ppm}, MgCl_2 = 77.2 \text{ ppm}$$

$$CaSO_4 = 102 \text{ ppm}$$

1. calculate the carbonate and non carbonate hardness of a sample water containing the dissolved salts as given below in mg/lit.  $Mg(HCO_3)_2 = 7.3$ ,  $Ca(HCO_3)_2 = 40.5$ .  
 $CaSO_4 = 13.6$ ,  $MgCl_2 = 21.75$ .

Name of the hardness producing salt	Amount in mg/lit	Molecular weight	Amount equivalent to $CaCO_3$
$Mg(HCO_3)_2$	7.3	146	$\frac{7.3 \times 100}{146} = 5 \text{ mg/lit}$
$Ca(HCO_3)_2$	40.5	162	$\frac{40.5 \times 100}{162} = 25 \text{ mg/lit}$
$CaSO_4$	13.6	136	$\frac{13.6 \times 100}{136} = 10 \text{ mg/lit}$
$MgCl_2$	21.75	95	$\frac{21.75 \times 100}{95} = 22.9 \text{ mg/lit}$

$$\text{carbonate hardness} = Mg(HCO_3)_2 + Ca(HCO_3)_2 \\ = 5 + 25 = 30 \text{ mg/lit}$$

$$\text{Non carbonate hardness} = CaSO_4 + MgCl_2 \\ = 10 + 22.9 = 32.9 \text{ mg/lit}$$

$$\text{Total hardness} = \text{carbonate} + \text{Non-carbonate hardness} \\ = 30 + 32.9 \\ = 62.9 \text{ mg/lit}$$

(14)

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

$$\text{Sol: Molarity of } \text{CaCO}_3 \text{ sol (M}_1) = \frac{1}{100} = 0.01 \text{ M}$$

(M.wt of  $\text{CaCO}_3$ )

$$\text{Molarity of EDTA sol (M}_2) = \frac{M_1 V_1}{V_2}$$

$$V_1 = \text{vol of } \text{CaCO}_3 \text{ sol} = 50 \text{ ml}$$

$$V_2 = \text{vol of EDTA} = 30 \text{ ml}$$

$$M_2 = \text{Molarity of } \text{CaCO}_3 \text{ sol} = 0.01 \text{ M}$$

$$M_2 = \frac{0.01 \times 50}{30}$$

$$= 0.016 \text{ M}$$

$$\text{Molarity of hard water } M_3 = \frac{M_2 V_2}{V_3}$$

$$M_2 = \text{Molar of EDTA} = 0.016 \text{ M}$$

$$V_2 = \text{vol of EDTA} = 40 \text{ ml}$$

$$V_3 = \text{vol of hard water} = 50 \text{ ml}$$

$$M_3 = \frac{40 \times 0.016}{50}$$

$$= 0.0128 \text{ M}$$

$$\text{Total hardness of water} = 0.0128 \times 100 \times 1000 \\ = 1280 \text{ ppm.}$$

Permanent hardness of water :

$$\frac{M_2 V_2}{n_2} = \frac{M_4 V_4}{n_4}$$

$$n_2 = n_4 = 1$$

$$V_2 = \text{vol of EDTA} = 30 \text{ ml}$$

$$M_2 = \text{Molarity of EDTA} = 0.016$$

$$n_4 = \text{vol of permanent hardness containing water} = 50$$

$$M_4 = \frac{30 \times 0.016}{50}$$

$$= 0.0096 \text{ M}$$

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

$$\text{Temporary hardness} = \text{Total hardness} - \text{permanent hardness} \\ = 1280 - 960$$

$$= 320 \text{ ppm}$$

Molarity of Permanent hardness containing water,  $M_4 = \frac{M_2 V_2}{V_4}$  (2D)

$$V_2 = \text{vol of EDTA} = 20 \text{ ml.}$$

$$M_2 = \text{Molar of EDTA} = 0.0025 \text{ M.}$$

$$V_4 = \text{vol of permanent hardness of water} = 20 \text{ ml.}$$

$$M_4 = \frac{20 \times 0.0025}{20}$$

$$= 0.0025 \text{ M.}$$

$$\text{Permanent hardness} = 0.0025 \times 100 \times 1000 \\ = 250 \text{ ppm.}$$

$$250 \text{ ppm} = 25^\circ \text{ Fr} = 250 \times 0.07 = 17.50^\circ \text{ cl.}$$

Temporary hardness of water sample.

Temporary hardness of water sample = Total hardness - Permanent hard.

$$= 375 - 250$$

$$= 125 \text{ ppm.}$$

$$125 \text{ ppm} = 12.5^\circ \text{ Fr} = 12.5 \times 0.07 = 8.75^\circ \text{ cl.}$$

2. calculate temporary, permanent and total hardness of water in ppm, °cl and °Fr from the following determination  
 20 ml of 0.05 solution of standard hard water required  
 40 ml of EDTA for titration - 20 ml of a sample of hard water consumed 30 ml of same EDTA and 20 ml of hard water after boiling, filtering etc. required 20 ml of EDTA for titration.

Sol: Molarity of EDTA  $M_2 = \frac{M_1 V_1}{V_2}$

$$V_1 = \text{vol of standard hard water} = 20 \text{ ml.}$$

$$M_1 = \text{Molarity of SHW.} = 0.05 \text{ M.}$$

$$V_2 = \text{vol of EDTA} = 40 \text{ ml.}$$

$$M_2 = \frac{20 \times 0.05}{40} = 0.025 \text{ M.}$$

$$\text{Molarity of hard water sample } M_3 = \frac{M_2 V_2}{V_3}$$

$$M_2 = \text{Mol of EDTA} = 0.0025 \text{ M}$$

$$V_2 = \text{vol of EDTA} = 30 \text{ ml.}$$

$$V_3 = \text{vol of hard water sample} = 20 \text{ ml}$$

$$M_3 = \frac{0.0025 \times 30}{20} = 0.0375 \text{ M}$$

$$\text{Total hardness of water} = 0.0375 \times 100 \times 1000.$$

$$= 3750 \text{ ppm.}$$

$$= 375 \text{ }^{\circ}\text{Fr}$$

$$= 3750 \times 0.07 = 262.5 \text{ }^{\circ}\text{cl.}$$