

## WATER AND ITS TREATMENT

Introduction to hardness of water - Estimation of hardness of water by complexometric method and related numerical problems.

Portable water and its specifications - steps involved in the treatment of portable water - Disinfection of portable water by chlorination and break - point chlorination. Defluoridation -

Determination of  $F^-$  ion by ion-selective electrode method.

Boiler troubles: sludges, scales and caustic embrittlement, Internal treatment of Boiler feed water - calgon conditioning - phosphate conditioning - colloidal conditioning, External treatment methods - softening of water by ion-exchange processes.

Desalination of water - Reverse osmosis.

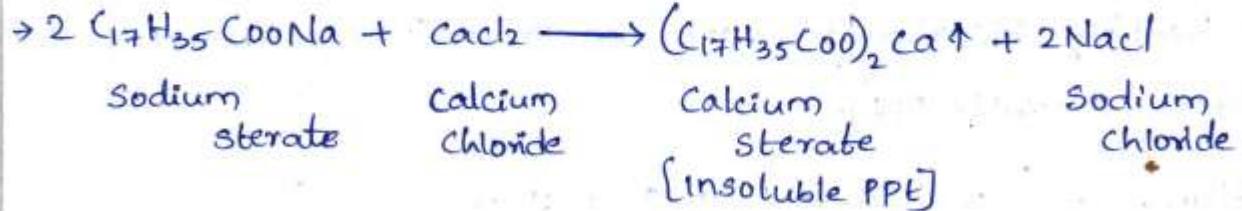
## Types of Water:-

There are two types of water

1. Hard water
2. Soft water

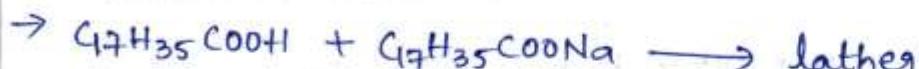
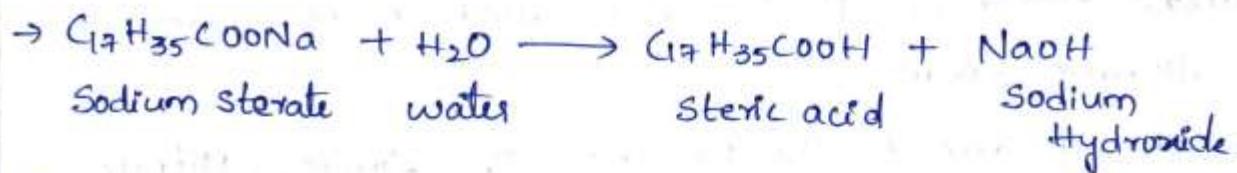
### 1. Hard Water:

- It doesn't produce leathering soap solution.
- It forms insoluble ppt.



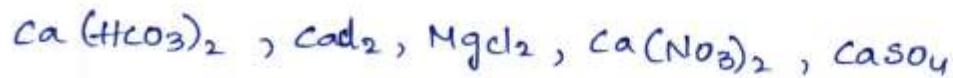
### 2. Soft water:

- Water which produces leathering soap solution



## Hardness of water:-

- It is a characteristic property of water
- The water which prevents the lathering with soap solution
- (or) lather prevention capacity is called hardness of water.
- This is caused due to the presence of Bicarbonates, chlorides, Sulphates, Nitrates of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metal ions.



## Types of Hardness:

1. Temporary Hardness:- It is also called carbonate hardness and alkaline hardness.
  - It is caused due to the presence of bicarbonates of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metal ions.  
i.e.  $\text{Ca}(\text{HCO}_3)_2$ ,  $\text{Mg}(\text{HCO}_3)_2$ .
  - Temporary hardness is removed by simple boiling of water.
  - While heating bicarbonates are converted into carbonates and hydroxides [insoluble ppt].  
$$\text{Ca}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{CaCO}_3 \downarrow + \text{CO}_2 \uparrow + \text{H}_2\text{O}$$
$$\text{Mg}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{Mg}(\text{OH})_2 + 2\text{CO}_2 \uparrow$$
  - this insoluble ppt deposited as a clust at the bottom of the vessel.
2. Permanent Hardness:- It is also called as non-carbonate or non-alkaline hardness.
  - It is caused due to the presence of chlorides, Nitrates, Sulphates of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metal ions.  
i.e  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{CaSO}_4$   
 $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{MgSO}_4$
  - Like temporary hardness; Permanent hardness cannot be removed by simple boiling.

Types of H <sub>2</sub> O	Hardness
Soft H <sub>2</sub> O	0-70 PPM
Hard H <sub>2</sub> O	70-150 PPM
Moderate Hard H <sub>2</sub> O	150-300 PPM
Very hard H <sub>2</sub> O	above-300 ppm

Degree of Hardness or (<sup>expression</sup>experience) of Hardness of Water:-

- The Hardness of water calculated in terms of CaCO<sub>3</sub> equivalence.
- It is expressed in CaCO<sub>3</sub> equivalence because of two reasons.
  - 1. Its molecular weight is 100 easy for calculations.
  - 2. It is most insoluble ppt in water treatment.

Hardness in terms of CaCO<sub>3</sub> equivalence =  $\frac{\text{Amount of hardness}}{\text{Molecular weight of hardness of salt}} \times 100$

Units of Hardness:-

1. PPM
2. mg/l
3. % Clark
4. °French

1. Parts per million:- No. of parts of hardness causing salts in CaCO<sub>3</sub> equivalent present in 10<sup>6</sup> parts [1 million parts] of water.

One PPM = One parts of hardness causing salts in CaCO<sub>3</sub> equivalent present in 10<sup>6</sup> parts of water.

2. Milli gram per litre: It is the no. of parts or milligrams of CaCO<sub>3</sub> equivalent hardness present per one litre of water.

1 mg/lit = 1 mg of  $\text{CaCO}_3$  equivalent hardness present per one litre of water.

3. Degree Clark: It is the no. of parts of  $\text{CaCO}_3$  equivalent hardness present per Gallon [70,000] of water.

1°/clark = 1 grain of  $\text{CaCO}_3$  equivalent hardness per gallon of water or 70,000 parts of water.

4. Degree-french:- It is no. of parts of  $\text{CaCO}_3$  equivalent hardness present per  $10^5$  parts of water.

1°/french = 1 part of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

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

# ESTIMATION OF HARDNESS OF WATER BY COMPLEXOMETRIC METHOD

→ It is a complexometric method in this method EDTA is the reagent.

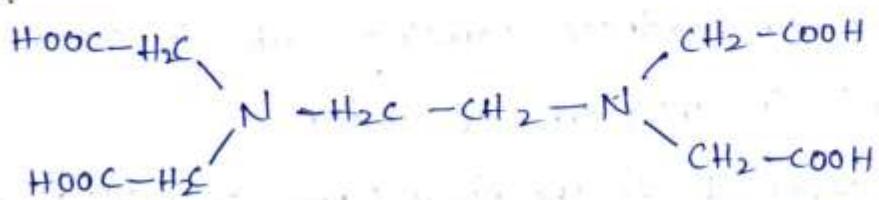
→ EDTA forms the complexes at different pH.

For eg:  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  ions form the complexes with EDTA at pH 9-10

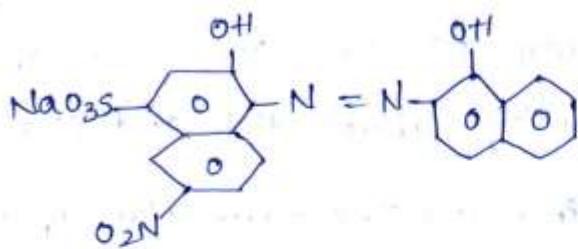
→ To maintain the pH 9-10 buffer solution added  $[NH_4OH + NH_4Cl]$

→ In this method Eriochrome Black-T is used as an indicator.

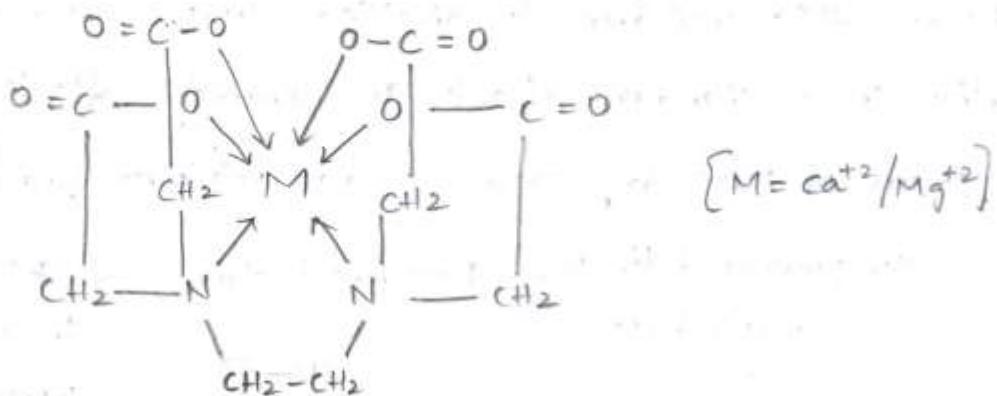
EDTA:



EBT:

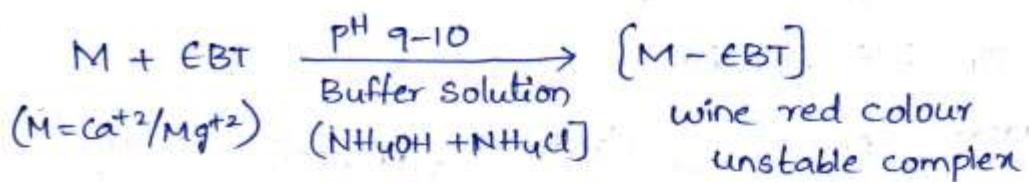


Metal EDTA:-

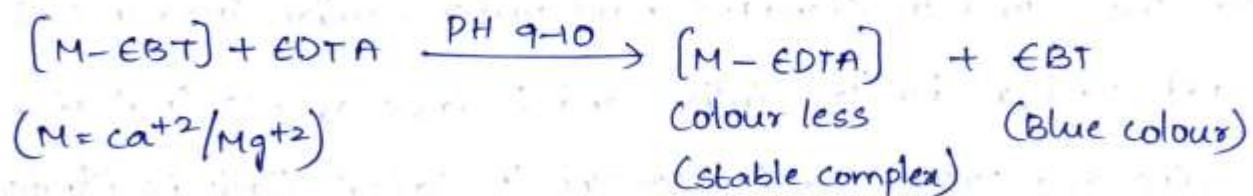


Principle:-

- When hardwater treated with EBT indicator it forms M-EBT complex which is in wine red colour and forms unstable complex.
- To maintain the pH 9-10 the buffer solution is added.



- This wine red colour solution is titrated against with EDTA and it forms (M-EDTA) complex which is colourless and stable complex and it releases the free EBT indicator which is in blue colour.



### Procedure:-

Preparation of standard hardwater:- Dissolve one gram of pure and dry  $\text{CaCO}_3$  in minimum quantity dilute HCl and evaporate the solution to dryness (or) water bath. The formation of residue will takes place.

→ Dissolve this residue in distilled water to make one litre solution in a standard flask or volumetric flask.

→ 1 gram of pure dry  $\text{CaCO}_3$  → add minimum quantity of HCl → evaporated it in → Residue is form → This residue dissolved in 1 lit of distilled water by standard flask

$$\text{Molarity of standard hardwater (M)} = \frac{\text{wt}}{\text{M.wt}} \times \frac{1}{\text{V(lit)}}$$

$$M_1 = \frac{1}{100} \times \frac{1}{1}$$

$$M_1 = 0.01$$

### Standardisation of EDTA solution:-

Take 20ml of standard hardwater in a conical flask + 2ml of buffer solution + 2/3 drops of EBT  $\xrightarrow{[M-EBT]}$  wine red colour  $\xrightarrow{\text{Titrate with EDTA}}$

$[M-EDTA] + EBT$   
colourless      Blue colour

→ Pipette out 20ml of standard hard water solution into a conical flask add 2ml of buffer solution and 3 drops of EBT indicator.  
→ The wine red colour solution present in conical flask is titrated against with EDTA solution [which is taken in a burette] till the wine red colour changes to blue colour.

→ Let the volume of EDTA is 'x' ml

$$M_1 v_1 = M_2 v_2$$

(SHW)                    (EDTA)

$M_1$  = Molarity of standard hard water = 0.01 M

$V_1$  = volume of standard hard water = 20 ml

M<sub>2</sub> = Molarity of EDTA = ?

$$V_2 = \text{Volume of EDTA} = 2 \text{ ml}$$

$$M_2 = \frac{M_1 V_1}{V_2}$$

$$M_2 = \frac{0.01 \times 20}{\pi}$$

### Standardisation of total hardness :-

→ Pipette out 20 ml of the water sample in to a clean conical flask and add 2 ml of buffer solution, add 3 drops of EBT indicator and titrate this against with EDTA solution (which is taken in a burette). Till the wine red colour changes to blue colour.

→ Let the volume of EDTA is 4ml

$$M_2 v_2 = M_3 v_3$$

(EDTA) (Hard water)

$M_2$  = Molarity of EDTA

$$V_2 = \text{volume of EDTA} = 1 \text{ mL}$$

$M_3$  = Molarity of hard water solution = ?

$V_3$  = volume of hard water solution = 20 ml

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

$$\text{Total Hardness of water} = M_3 \times 10^5 \text{ PPM}$$

## Standardisation of permanent hardness:

- Pipette out 100 ml of hard water sample (Tap water) in a beaker and boil it till the volume reduced to 20 ml. cool the solution and filtered the water into a conical flask and add 2 ml of buffer solution and add 3 drops of EBT indicator and titrate with EDTA till a blue colour end point is obtained.
- Take the reading as  $V_2$  ml

$$M_2 V_2 = M_4 V_4$$

(EDTA) (HWS after heating)

$M_2$  = Molarity of EDTA

$V_2$  = Volume of EDTA

$M_4$  = molarity of hard water solution after heating

$V_4$  = volume of hard water solution after heating.

Permanent hardness of water =  $M_4 \times 10^5$  ppm

## Calculation of temporary hardness:-

Total hardness = Temporary hardness + permanent hardness

Temporary hardness = Total hardness - Permanent hardness

## PORABLE WATER

- The water which is used for drinking purpose (or) safe to drink is called as portable water

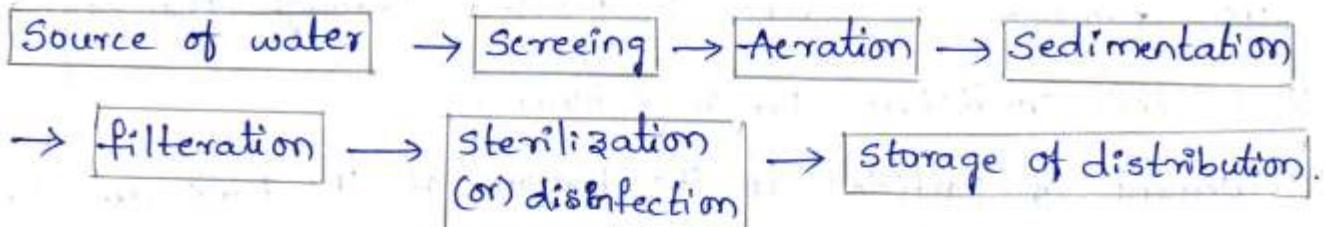
Specifications:-

- It is colourless, odourless.
- It should be good in taste
- The optimum hardness of water must be 125 ppm.

- Turbidity of water must not exceed 25 ppm
- Water must be free from pathogenic bacteria and dissolved gases like  $H_2S$ .
- The total dissolved salts in water must not exceed 500 ppm.
- Water must be free from heavy metals like lead, chromium and manganese.
- The pH of water should be 7-8.5

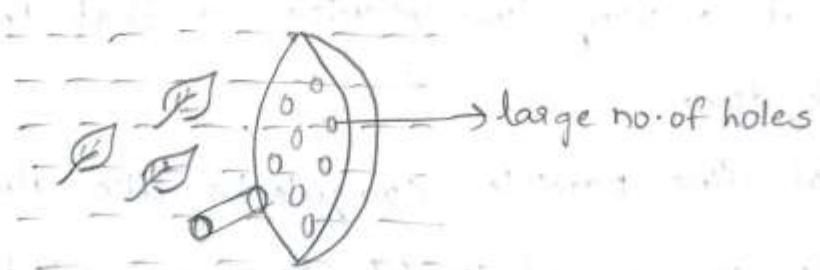
Steps involved in the treatment of portable water:-

- It involves in the removal of colloidal impurities, suspended impurities and pathogenic bacteria in water.
- Treatment of water for domestic supply involves following steps.



Screening:-

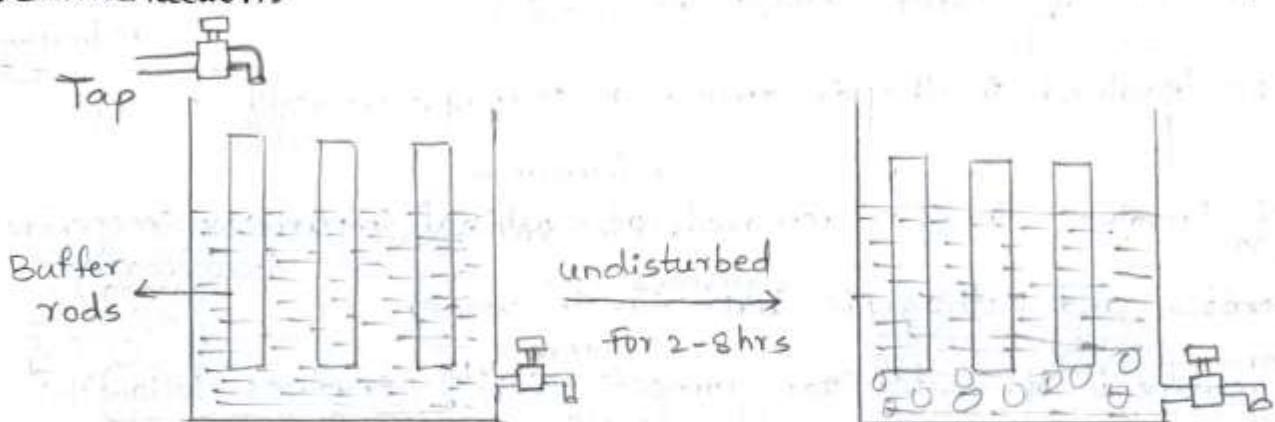
- The water is passed through the screen which is having large no. of holes
- While passing it involves removal of floating materials like leaves, wooden pieces.



### Aeration:-

- The water is then subjected to aeration  
→ which helps in exchange of gases between water and air.  
→ Increases the oxygen (content) content, taste.  
→ It removes impurities like iron, manganese in the form of their hydroxides.

### Sedimentation:-



- In this process the water is passed through the cans.  
→ It is left undisturb for 2-8 hours.  
→ settlement of particles at the bottom of the tank due to gravitational force.

### Sedimentation with coagulation:-

- The suspendend and collidial impurities are allowed to settle under gravitation.  
→ The basic principle of this treatment is to allow water to flow at a very slow velocity so that the heavier particles are settle down.  
→ (For off) fine particle coagulants like alum, sodium aluminate are added which produces gelatinous ppt called

'floc'.

→ It absorbs the colloidal and suspended impurities in water.  $Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$

→ The following sedimentation tank used for the removal colloidal impurities.

Potash alum -  $K_2(SO_4) \cdot Al_2(SO_4)_3 \cdot 24H_2O$

Sodium aluminate -  $NaAlO_2$

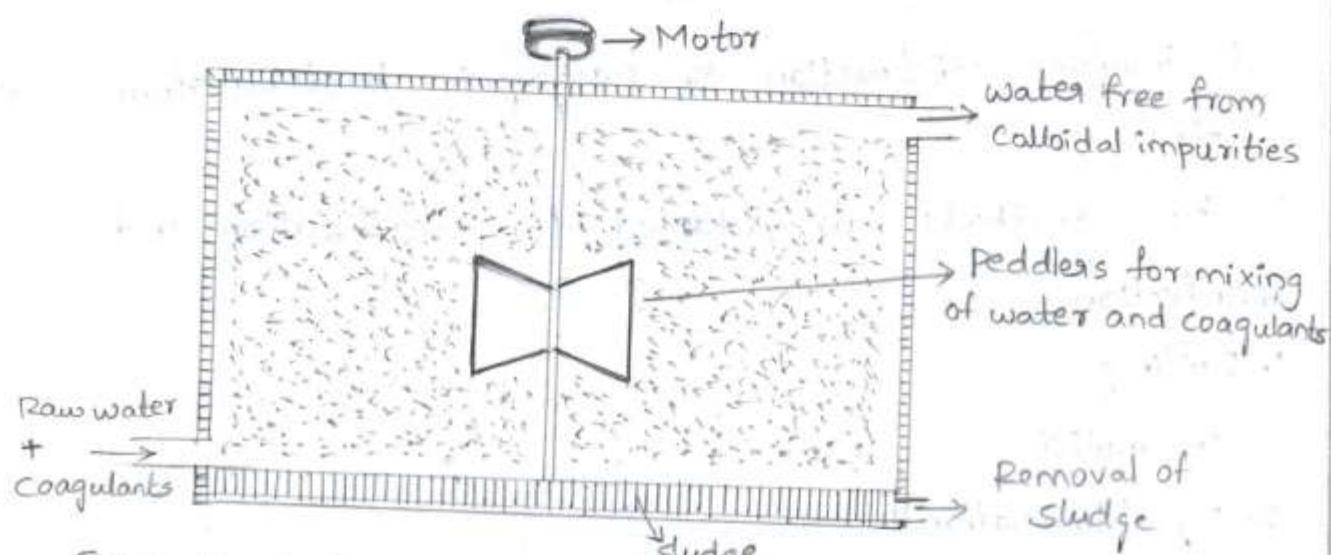


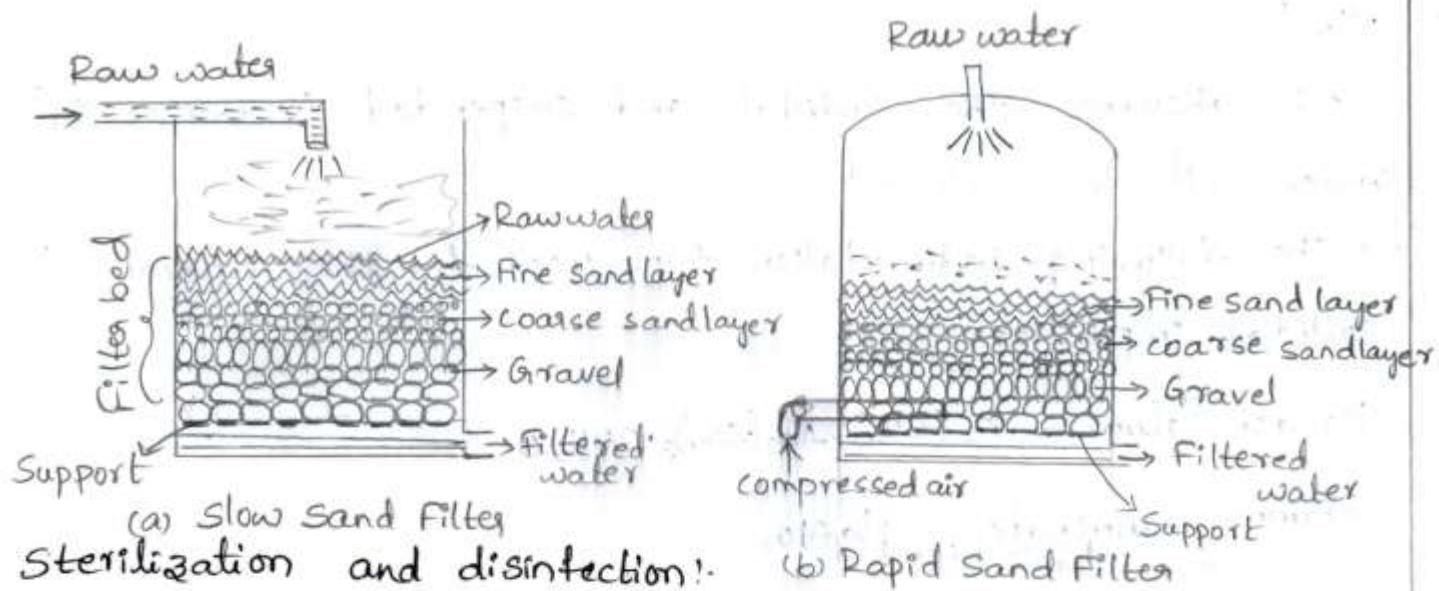
fig: Sedimentation tank for purification of colloidal impurities.

It involves removal of colloidal particles which are not removed in sedimentation process. In these two types of Sand filters are used.

1. Slow sand filter

2. Rapid sand filter

→ In case of rapid sand filter, filtration becomes fast. When compared to slow sand filter due to application of pressure.



→ It involves destruction of pathogenic bacteria from water sample.

→ Three methods are adapted for sterilization and disinfection:-

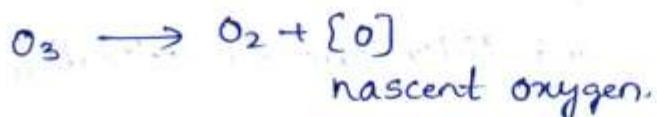
1. Boiling
2. O-zonolysis
3. By chlorination.

1. By boiling:-

By boiling water about 20-30 mins bacteria are killed. This process is adapted for domestic purpose but not for industrial purpose.

2. By adding ozone:-

When ozone is passed into water it decomposes into  $O_2$  and nascent oxygen ( $O$ ).



- Nascent oxygen acts as disinfectant [which kills bacteria]
- $O_3$  is an unstable isotope of oxygen.

## Disadvantage:-

This treatment is costly and ozone is unstable and cannot be stored for a long time.

## 3. Chlorination:

The process of adding chlorine to water to kill bacteria is called chlorination.

→ There are 3 types of chlorinating reagents are used.

1. By (passing) adding chloramine

2. By adding bleaching powder

3. By adding chlorine.

### 1. By Passing chloramine:-



(Chloro amine)



Hypo chlorous acid  
(disinfectant)

→ chlorine is mixed with Ammonia in the ratio 2:1 to form a stable chloro amine further it reacts with water to form Hypo chlorous (HClO) acid and Ammonia (NH<sub>3</sub>).

→ HClO is acts as disinfectant.

### 2. By adding bleaching powder:-



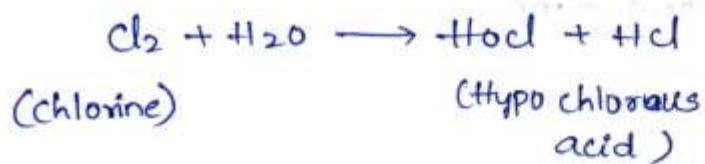
(Bleaching powder)



(Hypo chlorous acid)

→ Here HCl acts as disinfectant [which kills bacteria]

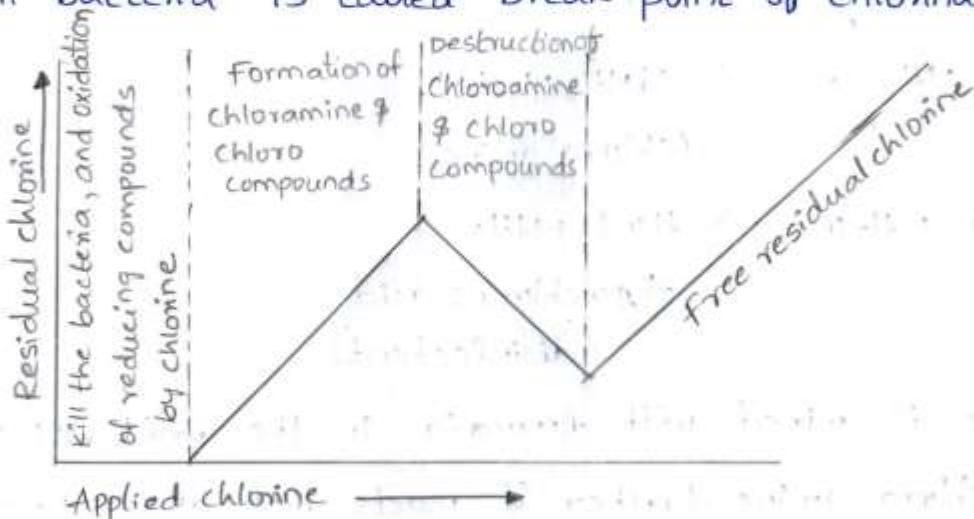
3. By adding chlorine:-



→ chlorine after reacting with bacteria excess amount of chlorine remains in water as residual chlorine which cause bad taste, odour and toxic to human beings.

## BREAK-POINT OF CHLORINATION

→ The process of adding required amount of chlorine to  $\text{H}_2\text{O}$  to kill bacteria is called break point of chlorination.



→ The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as shown above which gives the "Break point of chlorination". From graph it is clear that

- \* 'a' gms of chlorine added oxidises reducing impurities of  $\text{H}_2\text{O}$ .
- \* 'b' gms of 'cl' added forms chloroamines and other chloro compounds.

\* 'c' gms of 'cl' added causes destruction of bacteria.

\* 'd' gms of chlorine is residual chlorine.

\* 'c' gms is the break point for the addition of chlorine to water. This is called "Break point of chlorination".

Advantages:-

- It removes colour taste and organic impurities.
- It destroys all disease causing bacteria in water.
- It prevents growth of weeds in water.

## DEFLUORIDATION

→ Flourine is most active element found in naturally occurring rocks.

→ The limited flourine water is 1 ppm.

→ Above one ppm is causing a disease called fluorosis.

→ Due to this weakening and bending of bones decay of teeth etc.

→ The following are the list of ways to obtain drinking water without flourine.

1. Reverse osmosis filtration
2. Activated Aluminium defluoridation
3. Distilled water.

## DETERMINATION OF $F^-$ ION BY ION-SELECTIVE METHOD

$F^-$  (fluoride ions) in water can be determined by using solid-state membrane electrode.

### Construction

Solid-state membrane electrode consists of an internal reference electrode (Pt) in reference solution containing  $NaF + NaCl$  (for sensing fluoride ions). The body of the electrode is made up of teflon and the pellet, lanthanum trifluoxide ( $LaF_3$ ) crystal doped with europium di fluoride ( $EuF_2$ ), is held in position with epoxy resin. These electrode will sense only  $F^-$  ions ignoring others.

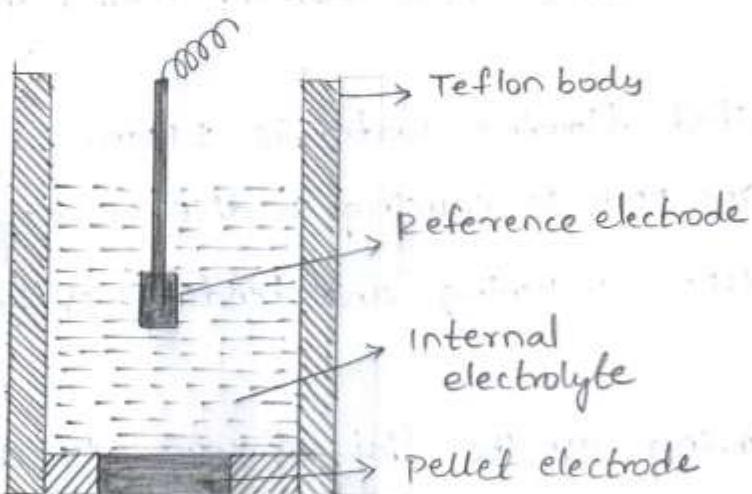


Fig: Solid state membrane electrode

### Uses

Fluoride ions selective electrode is used in the estimation of fluoride ions in water and in tooth pastes.

## BOILER TROUBLES

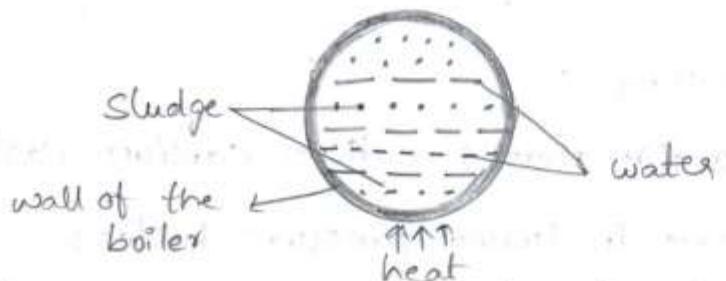
→ It is caused by using hard water.

→ Boiler troubles are

- i. Sludge
- ii. Scale
- iii. Caustic embrittlement.

(i) Sludge :-

→ It is a soft, loose, slimy and non-sticky precipitate form with in the boiler.



Reasons! -

Fig: sludge formation in boilers.

→ Salts which have high solubility in hot water compare to cold water cause formation of sludge.

Disadvantages:-

→ It is a poor conductor of heat and results wastage of fuel like kerosene, L.G.P etc.

→ The efficiency of boiler decreases.

→ Safety of boilers also lowers.

→ explosion of boilers takes place.

Prevention! -

→ Using soft water in boilers

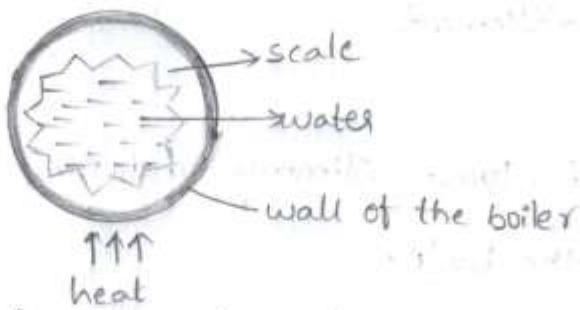
→ By using Blow down operation (removal of high concentrated salts at the bottom of the tank through a tap).

## Removal of sludge!

→ It is formed at colder places of boiler and get collected by using wire brushes.

## (ii) Scale:-

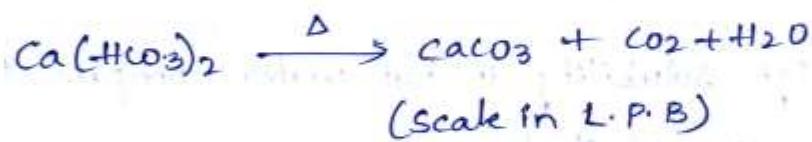
→ It is a hard and sticky ppt formed are inner walls of boilers.



Reasons!- Fig: Scale formation in boilers

### 1. Decomposition of $\text{Ca}(\text{HCO}_3)_2$ :-

→  $\text{Ca}(\text{HCO}_3)_2$  on decomposition forms calcium carbonate ( $\text{CaCO}_3$ ) which forms scale in lower pressure boilers

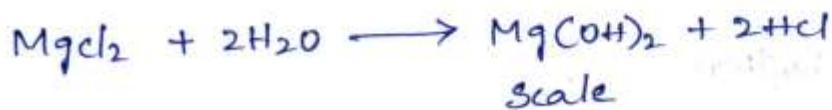


→ Because  $\text{CaCO}_3$  dissolve in H.P.B

### 2. Decomposition of $\text{CaSO}_4$ :-

The solubility of calcium sulphate increases on decreasing temperature. So, in H.P.B and increasing temperature. the solubility of  $\text{CaSO}_4$  will decrease and forms a hard scale on the inner walls of the boilers.

### 3. Hydrolysis of Mg salts:-



### 4. Presence of silica!

If silica is present in  $\text{H}_2\text{O}$  then it precipitates out as calcium silicate and magnesium silicate which form scale in boilers.

### Disadvantages:-

- It is poor conductor of heat and results' wastage of fuel like kerosene, L.P.G etc
- The efficiency of boiler decreases
- Safety of boilers are lower.
- Explosion of boilers takes place.

### Prevention:-

- By using soft water in boilers

### Removal of Scale:

- calcium carbonate scale can be removed by treating with 10% HCl.
- caseous scale can be removed by treated with EDTA method.

### Caustic embrittlement:-

The phenomenon in which boiler material becomes brittle due to accumulation of caustic substances like NaOH.

### Reason:-

The H<sub>2</sub>O purified by lime soda process contains little amount of sodium carbonate which are decomposition form NaOH.



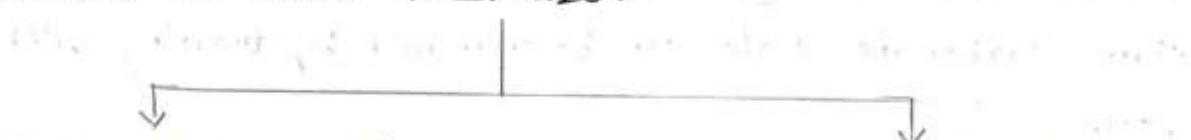
- The formed NaOH flows into cracks are the inner walls of the boiler bends, rivets and joints then water is evaporated. Con. NaOH increases at above areas and forms con. electrolytic cells as follows.

- At anode  $\text{NaOH}$  attacks on iron so, iron undergoes corrosion. so, iron at anode becomes brittle.
- In this process  $\text{NaOH}$  cause brittleness of boiler so, this phenomenon is called 'caustic embrittlement'.

Prevention:-

- By using  $\text{Na}_3\text{PO}_4$  instead of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in lime soda process.

Treatment of boiler feed  $\text{H}_2\text{O}$ :-

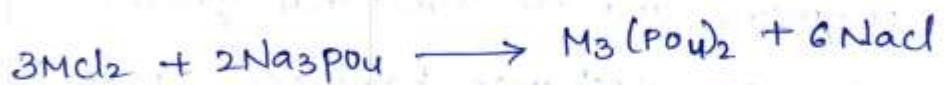


- 1. colloidal conditioning
  - 2. Phosphate conditioning
  - 3. Calgon conditioning.
- 1. Ion exchange process.

### INTERNAL TREATMENT OF BOILER FEED WATER

- Removal of hardness causing salts with in the boiler
- 1. Colloidal conditioning:-
  - In low pressure boilers scale formation can be prevented by adding substances like kerosene and Agaragar.
  - These substances get absorbed over scale forming salts and results formation of soft, loose, non-sticky ppt (sludge)
  - Which can be easily removed by using wire brushes and Blow down operations.
- 2. Phosphate conditioning:-
  - In high pressure boilers, scale formation can be avoided by adding  $\text{Na}_3\text{PO}_4$  which reacts with hardness causing

Salts ( $\text{Ca}^{+2}/\text{Mg}^{+2}$ ) salts forming sludge. Soft, loose and Non-sticky ppt of calcium phosphate, Magnesium phosphate which can be easily removed by wire brushes and Blow down operation.

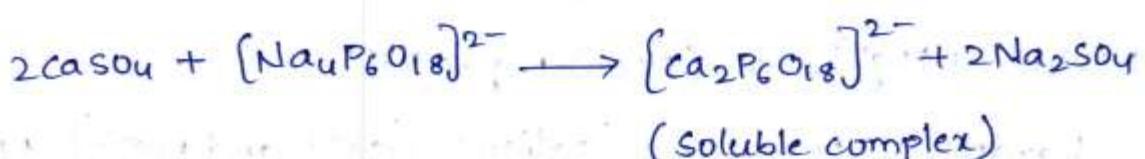
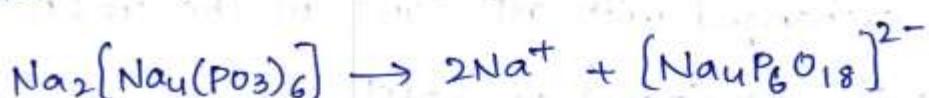


### 3. Calgon conditioning :-

→ It is sodium hexa meta phosphate  $[\text{Na}_2(\text{Na}_5(\text{PO}_3)_6)]$  in this process scale formation can be prevented by adding calgon.

→ 0.5 - 5 ppm calgon prevents scale formation.

→ This forms soluble complex compounds with  $\text{CaSO}_4$  which causes no boiler troubles.



→ The treatment of boiler water with calgon is called calgon conditioning.

## EXTERNAL TREATMENT METHODS

→ Removal of hardness causing salts from the water outside of boiler.

**Ion exchange process (Or) Deionisation (Or) Demineralisation process! -**

It involves exchange in cation of hardness causing salts with  $\text{H}^+$  ions and anions of hardness causing salts with  $\text{OH}^-$  ions, for this two types of ion exchange resins are used.

(i) cation exchange resin

(ii) Anion exchange resin

Principle:-

Ion exchange resins are insoluble, cross-linked, longchain organic polymers and the functional groups attached to the chains can exchange hardness producing cations and anions present in water.

Process:-

This process involves the following steps:

Step-1:- The hard water is passed through a bed of cation exchange resin ( $\text{RCOOH}$  (or)  $\text{SO}_3\text{H}$ ) of tank 'A'. The  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions are exchanged with  $\text{OH}^-$  ions of the resin.



→ Thus hardness producing cations [ $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ] are removed.

→ The water coming out contains  $\text{Cl}^-$ ,  $\text{SO}_4^{+2}$ ,  $\text{HCO}_3^-$ .

→ Styrene divinyl benzene copolymer is used as cation exchanged resin.

Step 2:-

→ The hard water is then passed through a bed of anion exchange resin ( $\text{R-OH}$  (or)  $\text{R-NH}_2$ ) of tank 'B'.

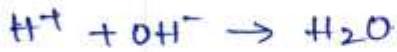
→ The  $\text{Cl}^-$ ,  $\text{SO}_4^{+2}$ ,  $\text{HCO}_3^-$  ions are exchanged with  $\text{OH}^-$  ions of the resin.



→ Thus hardness producing anions  $[Cl^-, SO_4^{2-} \text{ & } HCO_3^-]$  are removed.

Step 3:-

→ The  $H^+$  ions produced in tank 'A' combined with  $OH^-$  produced in tank 'B' to form water.



→ Thus this process removes all types of hardness producing cations and anions present in water.

→ The resulting water is known as "De-mineralised" (or) "De-ionised water".

→ When water sample is completely de-ionised, it has the tendency to absorb gases like  $CO_2, O_2$  etc... from atmosphere which cause boiler corrosion.

→ Hence De-ionisation must be followed by de-gasification.

→ Phenol formaldehyde (or) Amine formaldehyde is used as anion exchange resin.

Regeneration of resins:-

→ With constant use, the resins get exhausted.

→ This can be regenerated as follows.

1. The exhausted cation exchange resin can be regenerated by passing dil. HCl

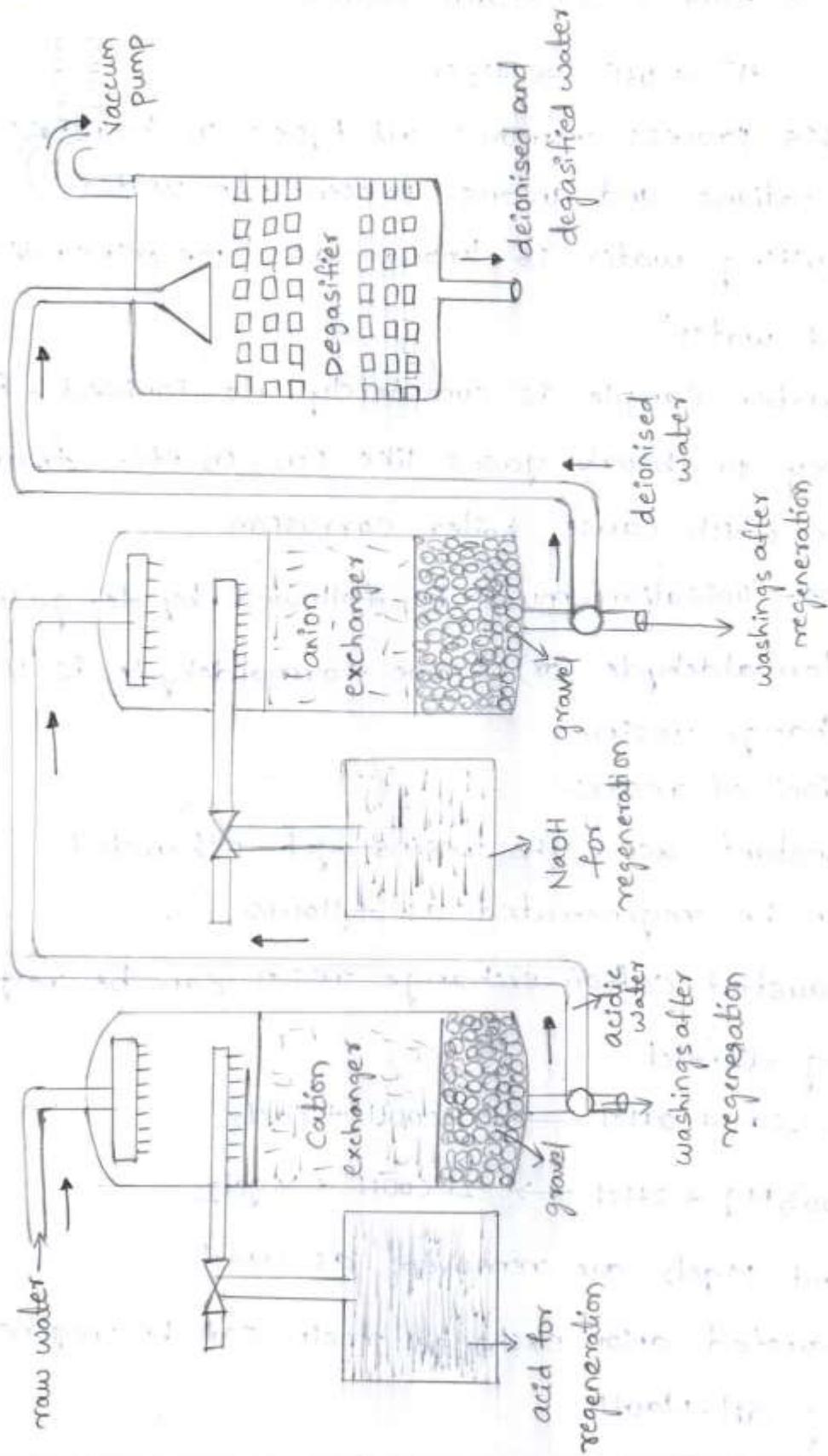


→  $CaCl_2$  and  $MgCl_2$  are removed as wash.

2. The exhausted anion exchange resin can be regenerated by passing dil. NaOH.



→  $NaCl$ ,  $Na_2SO_4$  and  $NaHCO_3$  are removed as wash.



### Advantages:-

- Highly acidic or Alkaline water samples can be purified by this process.
- The hardness possessed by de-ionized water is 2 ppm.
- The de-ionised water is most suitable for high pressure boilers.

### Disadvantages:-

- The ion exchanging resins are expensive, hence the cost of purification is high.
- Raw water should contain turbidity below 10 ppm otherwise pores in the resin will be blocked and output of the process is reduced.

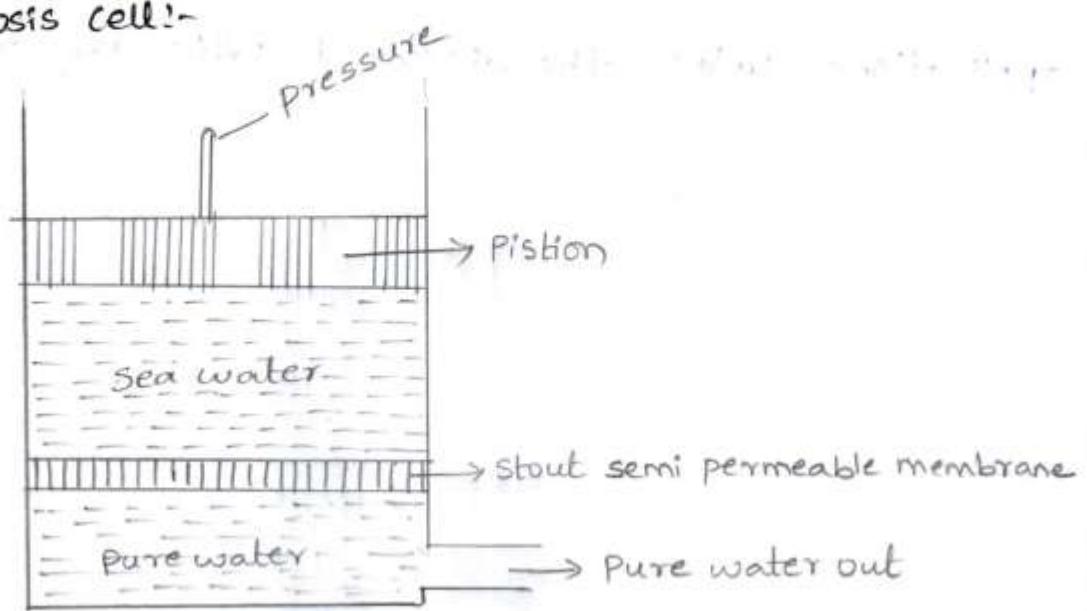
## DESALINATION OF WATER

- Water containing high concentrations of dissolved solids with a brackish taste is called brackish water.
- Sea water is an example of brackish water containing about 3.5 % dissolved salts.
- This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by

## REVERSE OSMOSIS

- When 2 solutions of unequal concentration are separated by semi permeable membrane.
- Which doesn't permit the passage of dissolved solid particles (molecules and ions)
- Flow of solvent takes place from the dilute solution to concentrated solution this is called osmosis.
- If a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side of the solvent, the solvent is forced to move from higher concentration to lower concentrated side across.
- Thus, the solvent flow is reversed hence this method is called reverse osmosis.
- Thus, reverse osmosis pure water is separated from the contaminated water
- This membrane filtration is called super filtration (OR) hyper filtration.

Reverse Osmosis cell:-



### Advantages:-

- cost of purification of water is less and maintenance cost is less.
- This water can be used for high pressure boilers.
- Both ionic and non-ionic, colloidal, high molecule weight, organic matter is removed from the water sample.