

Date	Unit No.	Lecture No.	Faculty	Subject Name	Subject Code	Main Topics:-

\* Classification of Water Sources

Source of water

sea/salty water  
(97%)

Fresh/Surface water  
(3%)

Ground water

↳ well  
↳ tube well

Rain water

Surface water

Flow water

Still water  
↳ pond  
↳ lake

\* Common Impurity

① Dissolved

- (a) dissolved gases - such as  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{S}$  etc
- (b) dissolved inorganic salts
  - (i) cations -  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Fe}^{+2}$
  - (ii) Anions -  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$
- (c) dissolved organic compounds - domestic and sewage, industrial waste

## ② Suspended impurities

(a) inorganic - sand and clay

(b) organic - vegetables and animal matters

## ③ Colloidal impurity

:- finely divided silica & clay & oil and colouring matters.

## ④ Bacterial impurity :- bacteria, algae, fungi.

\* HARDNESS OF WATER :- Soap consuming capacity of water characteristics property of water which prevents lathering of soap due to insolubility of certain salts of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metals like  $\text{Al}^{+3}$ ,  $\text{Fe}^{+2}$ , dissolved in water.

### ON BASIS OF BEHAVIOUR OF $\text{H}_2\text{O}$ with soap:

1) Hard water:- water which does not produce lather with soap easily

Ex. Sea water.

2) Soft water:- Produce lather easily with soap & water

Ex. Rain water.

#### HARD WATER.

#### SOFT WATER.

1) do not produce lather easily with soap.

• Produce lather

2) contain dissolved salt of  $\text{Ca}$  &  $\text{Mg}$

• not contain

3) large amount of soap is waste

• soap is not waste

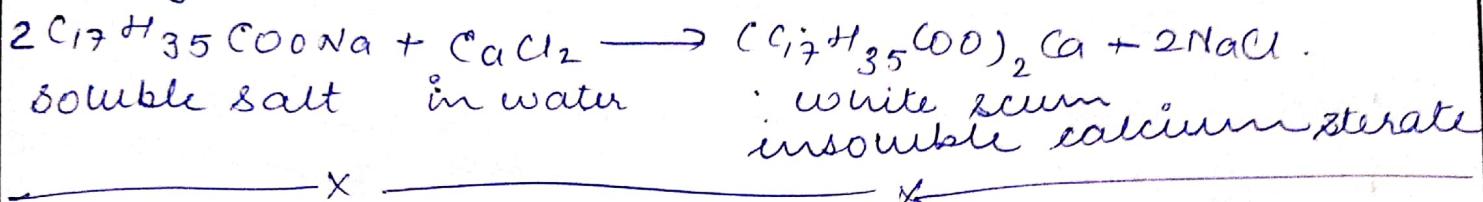
4) Ex. seawater

Ex. Rain water

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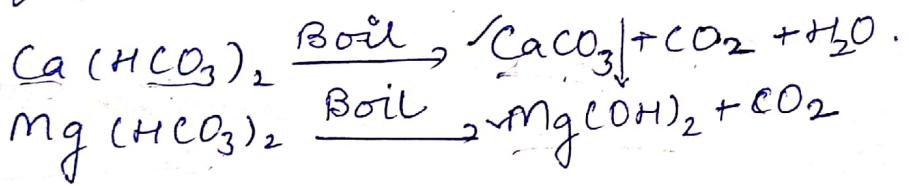
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→ When soap is treated with hard water it gives white ppt (scum) of insoluble  $\text{Ca/Mg}$  with resp. fatty acid.



## \* TYPES OF HARDNESS :-

① Temporary (carbonate) hardness :- due to the bicarbon ate ions ( $\text{HCO}_3^-$ ) of  $\text{Ca}$  &  $\text{Mg}$ . This hardness can be removed by boiling which converts  $\text{HCO}_3^-$  to insoluble hydroxide & carbonate ( $\text{CO}_3^{2-}$ ) which can be removed by filtration.



## ② Permanent Hardness (Non-Carbonate) :-

Permanent Hardness (Non-Carbonate)  
due to presence of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  of  $\text{Ca}^{2+}$  &  $\text{Mg}^{2+}$  &  
other heavy metal. Can't removed by boiling  
special method used to remove it such as  
lime water, zeolite, ion exchange method.

\* DEGREE OF HARDNESS. →  $\text{CaCO}_3$  equivalent.

Reason (i) Molar mass  $40 + 12 + 48 = 100$   
Equivalent wt = 50

(ii) most insoluble in water.

### **Main Ideas, Questions & Summary:**

→ one degree of hardness is hardness caused by one part of  $\text{CaCO}_3$  eq. in one million ( $10^6$ ) part of water.

→ degree of hardness of water is expressed in term of  $\text{CaCO}_3$  eq. because

- (i) It is most insoluble salt that can be ppt in water terminated.
- (ii) Molar mass = 100 & eq. wt. is 50 so its easy for calculation.

Hardness = multiplication factor of  $\text{CaCO}_3$  eq. producing substance (in term of  $\text{CaCO}_3$  eq.)

$$\text{M.F.} = \frac{\text{chemical eq of } \text{CaCO}_3 \times 2}{\text{chemical eq of hardness produced} \times 2}$$

#### \* UNITS OF HARDNESS.

(1) PPM (Parts per million)

1PPM =  $\frac{1 \text{ part of } \text{CaCO}_3 \text{ eq. hardness in } 10^6}{\text{parts of water}}$

(2) mg/L

1mg/L = 1mg of  $\text{CaCO}_3$  eq. to hardness in 1L of water.

(3)  ${}^{\circ}\text{Fr}$  = degree french.

$1{}^{\circ}\text{Fr} = 1 \text{ part of } \text{CaCO}_3 \text{ eq.}$

(4)  ${}^{\circ}\text{Cl}$  → degree clark.

$1{}^{\circ}\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ eq. Hardness in } 70000 \text{ part of water.}$

## # RELATIONSHIP

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

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

$$1^\circ \text{Fr} = 10 \text{ PPM} = 10 \text{ mg/L} = 0.7^\circ \text{Cl}$$

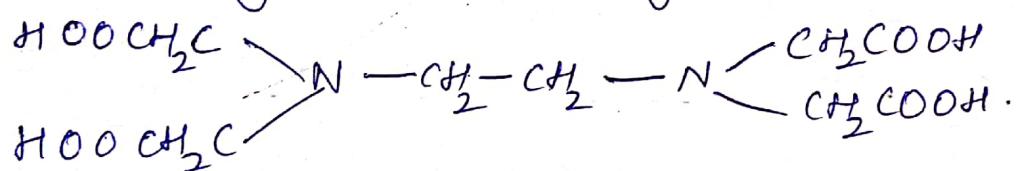
$$1^\circ \text{Cl} = 14.3 \text{ PPM} = 14.3 \text{ mg/L} = 1.43^\circ \text{Fr}$$

## # DETERMINATION OF HARDNESS BY EDTA METHOD

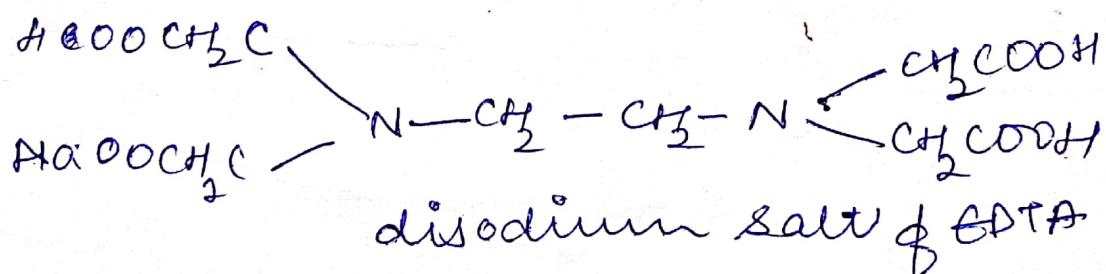
OR

### COMPLEXOMETRIC TITRATION

EDTA = Ethylene diamine tetra acidic acid is a strong complexing agent have structure



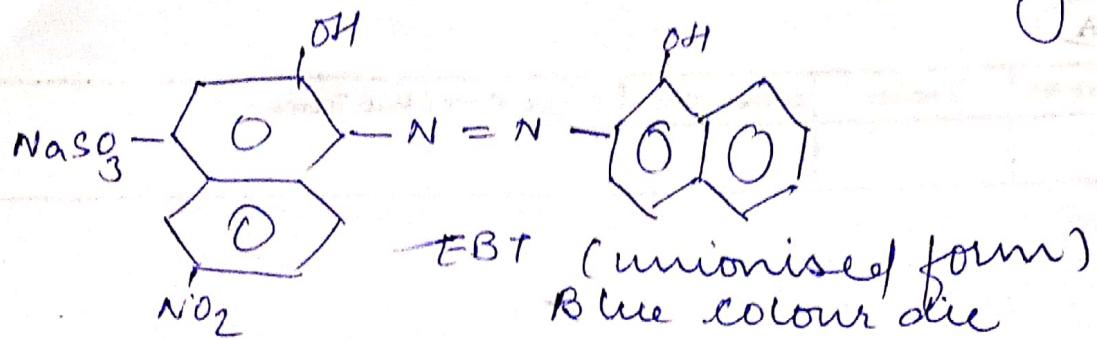
- Hexadentate ligand so has less solubility in  $\text{H}_2\text{O}$  the disodium salt of EDTA which is soluble in  $\text{H}_2\text{O}$  used in titration



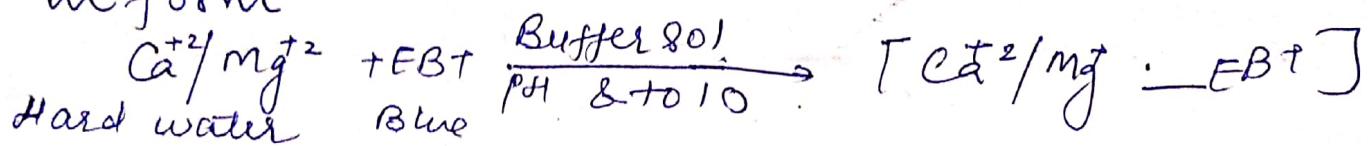
tetradentate in nature.

## Main Ideas, Questions & Summary:

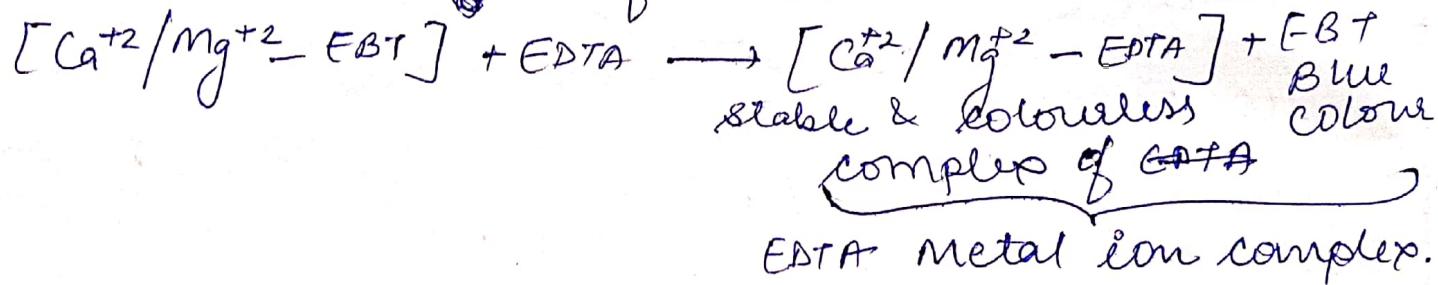
Eriochrome Black T (EBT) is used as indicator & having structure



when EBT which is blue colour mixed with water sample in presence of buffer soln at pH 8 to 10. The hardness producing  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$  salts reacts with indicator & forms red complex in form

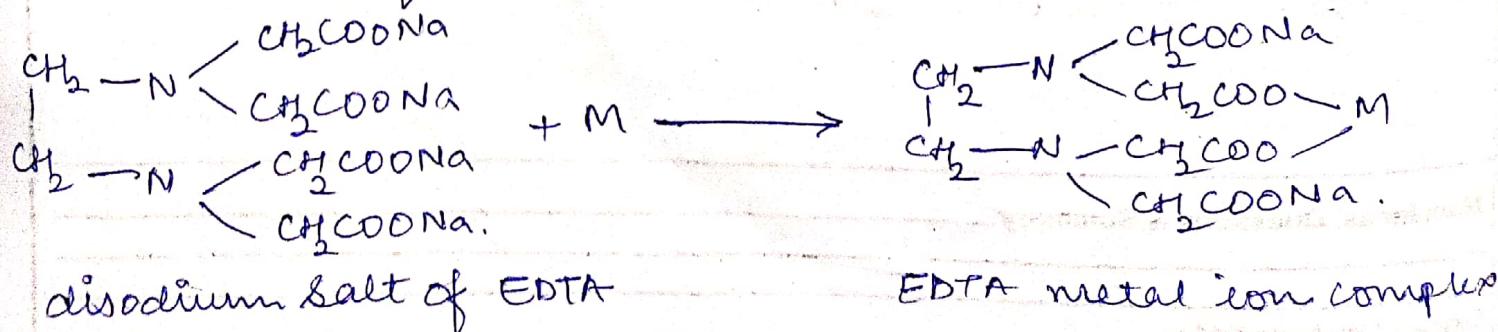


After titration with EDTA solution, this wine red complex is broken & colourless complex of EDTA metal is formed thus at end point soln becomes blue due to free EBT



All these reactions occur at pH 8-10 because indicator polymerise in acidic medium & metal EBT complex not form.

\* Structure of EDTA metal ion complex.



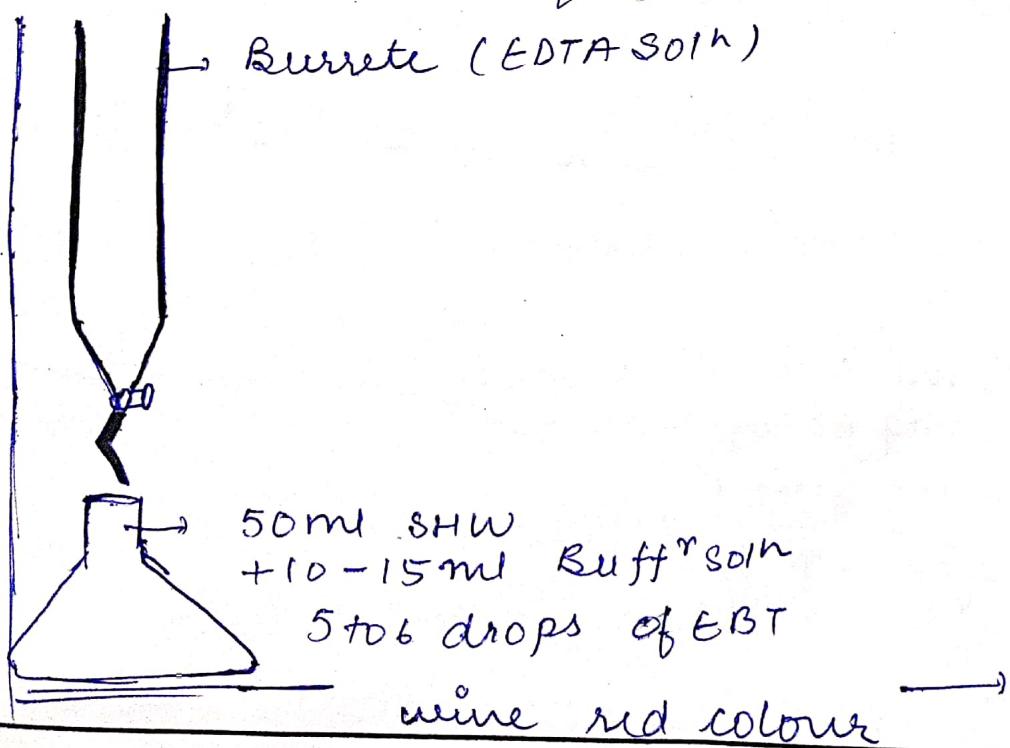
### \* PREPARATION OF SOLUTION

1gm pure dry  $\text{CaCO}_3$  diss. in min  
 amt of HCl → evaporate for  
STANDARD HARD WATER SOLUTION removal of excess  
 of  $\text{CO}_2$  ↓  
 dissolved in dis  $\text{H}_2\text{O}$   
 & make upto 1L soln.

- ② EBT - 0.5gm EBT dissolve. in 100ml alcohol
- ③ EDTA - 3.72gm or 4gm of EDTA dissolve in 1L distilled  $\text{H}_2\text{O}$
- ④ Buffer solution - 67.5 gm  $\text{Na}_2\text{HPO}_4$  mixed with 570 ml  $\text{NH}_4\text{OH}$  & make it 1L with distilled water.

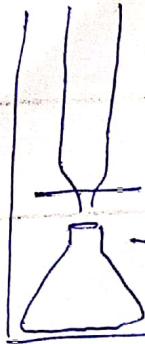
### # PROCEDURE:-

#### 1) Standardization of EDTA soln.



Till blue colour  
 disappears & vol  
 is noted as  $V_1$  ml

## 2) Determination of Total Hardness

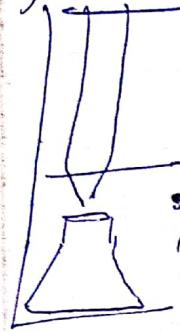


→ 50ml given HWS  
10-15 ml Buffer soln  
5-6 drop EBT

wine red colour →

Till blue colour appear  
→ vol. is noted as  
 $V_2$  ml.

## 3) Determine permanent Hardness



50ml Boiled water sample  
10-15 ml Buffer soln  
5-6 drop of EBT

wine red colour →

Till Blue colour appear  
volume noted as  
 $V_3$  ml.

## \* Preparing Boiled water sample

↓  
250 ml given HWS.  
↓  
till vol becomes 50 ml  
make it 250ml with distilled water

TRICK FOR ALL  
50ml. SHW / HWS / BWS → noted as  $V_1 / V_2 / V_3$ .

## \* CALCULATIONS

$$1). V_1 \text{ ml. EDTA} = 50 \text{ ml SHW}$$

$$1 \text{ ml SHW} = 1 \text{ mg } \text{CaCO}_3$$

$$V_1 \text{ ml EDTA} = 50 \text{ mg } \text{CaCO}_3$$

$$1 \text{ ml EDTA} = \frac{50}{V_1} \text{ mg } \text{CaCO}_3$$

## 2) Total Hardness

$$1 \text{ ml EDTA} = \frac{50}{V_1} \text{ mg } \text{CaCO}_3$$

$$V_2 \text{ EDTA} = \frac{50}{V_1} \times V_2 \text{ mg } \text{CaCO}_3$$

$$50 \text{ ml HWS} = \frac{50}{V_1} \times V_2 \text{ mg of } \text{CaCO}_3$$

$$1 \text{ ml given HWS} = \frac{50}{V_1} \times \frac{V_2}{50} \text{ mg CaCO}_3$$

$$1000 \text{ ml HWS} = \frac{50}{V_1} \times \frac{V_2}{50} \times 100 \text{ mg/l or ppm.}$$

### 3) PERMANENT HARDNESS

$$1 \text{ ml of EDTA} = \frac{50}{V_1} \text{ mg CaCO}_3$$

$$V_3 \text{ ml EDTA} = \frac{50}{V_1} \times V_3 \text{ mg CaCO}_3$$

$$50 \text{ ml BWS} = \frac{50}{V_1} \times V_3 \text{ mg CaCO}_3$$

$$1 \text{ ml BWS} = \frac{50}{V_1} \times \frac{V_3}{50} \text{ mg CaCO}_3$$

$$1000 \text{ ml BWS} = \frac{50}{V_1} \times \frac{V_3}{50} \times 100 \text{ mg/l CaCO}_3 \text{ or ppm.}$$

### \* ADVANTAGES

- 1) more rapid procedure
- 2) convenient method
- 3) greater accuracy.

SWC  
BWS.

## # Municipal Water / Drinking Water / Portable Water

Principle requirement for water to be supplied for drinking purpose that is municipal water must satisfy certain quality criteria wrt appearance, portability and health.

- The essential qualities for drinking water are as follows.

PTO

Main Ideas, Questions & Summary:

## ① Physical characteristics

- clear, colourless, odourless
- pleasant in taste
- perfectly cooled
- turbidity shouldn't exceed 10 ppm.

## ② chemical characteristics

- free from objectionable dissolved gases like  $H_2S$
- free from objectionable mineral such as lead; As, Cr, Mn, salts etc.
- pH should be 7-8.5
- chloride & sulphate should be less than 250 ppm
- Total hardness & total dissolved should be less than 500 ppm
- fluoride should be less than 1.5 ppm.

## ③. Biological characteristics

- free from disease producing bacteria
- E. coli should be under permissible limit.

## # Purification of Municipal water supply

Screening, sedimentation with coagulation, filtration and disinfection are usual artiases in raw water to make it drinkable/Portable.

- Actual treatment to be followed depend upon exact nature of impurity present in raw water.

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## IMPURITIES IN RAW WATER.

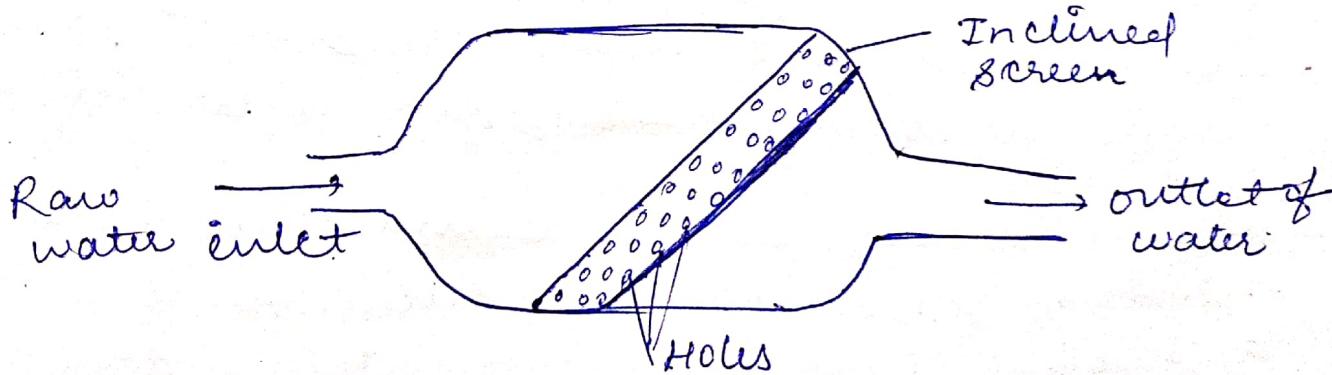
- 1) Floating impurities like leaves
- 2) Suspended impurities (sands & clay)
- 3) Fine suspended impurities (salts)
- 4) microorganisms and colloidal matters
5. Pathogenic bacteria

## PROCESS OF REMOVAL.

- Screening
- Sedimentation
- sedimentation with coagulation
- Filtration
- Disinfection and sterilization.

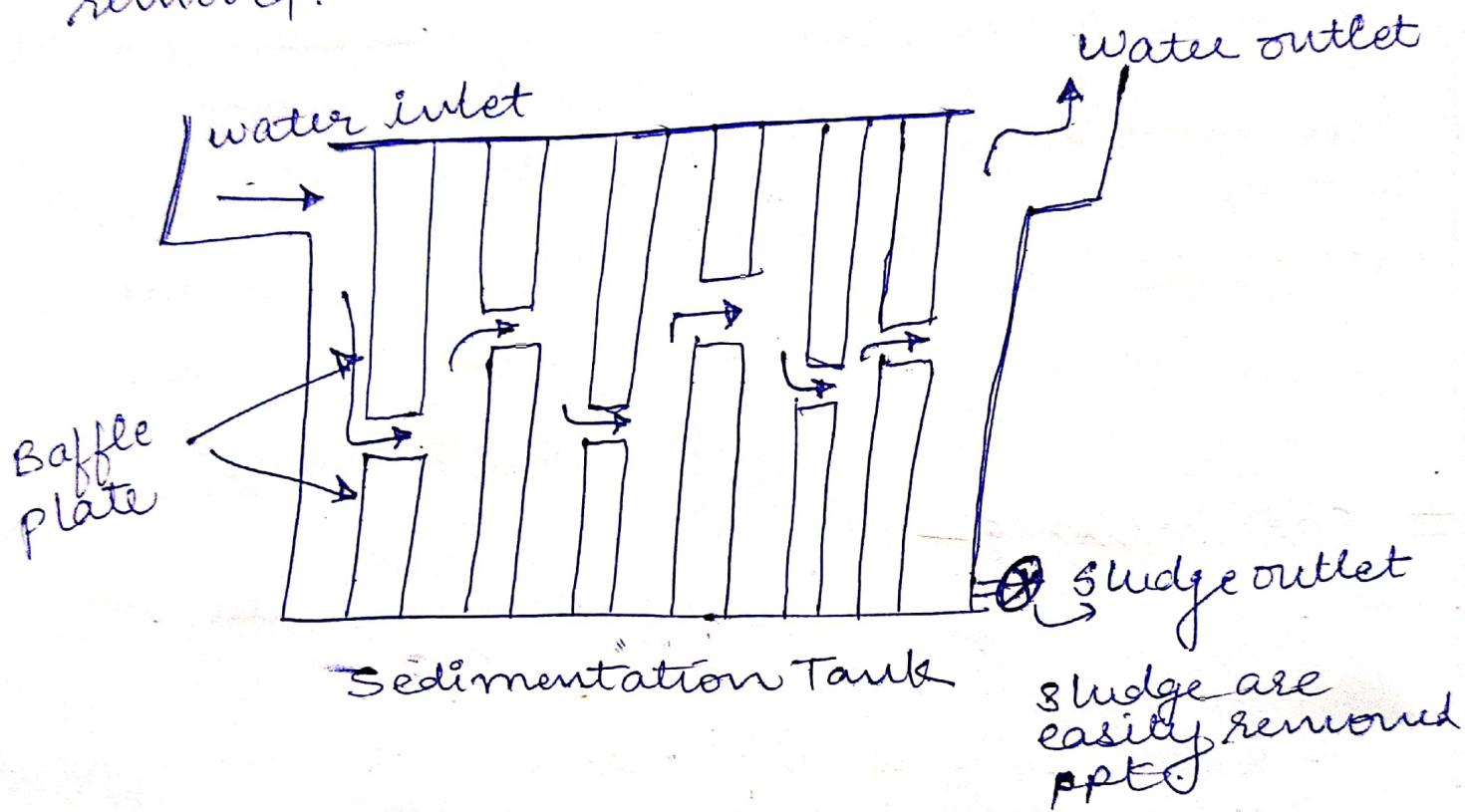
### # Screening :-

- process of removal floating impurities like leaves from raw water.
- water is pass through screens having holes wherein following floating matter retained by the that and water allowed to pass.



## # Sedimentation :-

- used to remove suspended impurities by allowing to stand undisturbed in big tank
- Most of suspended impurities are settle down at bottom by gravity.
- The settling time for sedimentation tank of 5 m depth is 2-8 hour. The clear water drawn out from tank.
- In process about 70-75% suspended impurities removed.



## # SEDIMENTATION with Coagulation :-

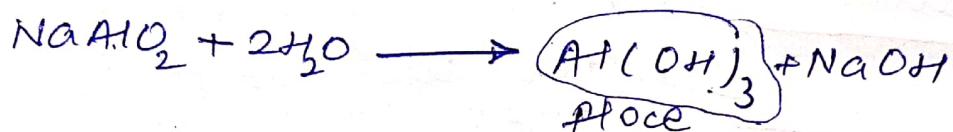
- when water contain fine clay particle it become necessary to apply sedimentation with coagulation.
- For the process certain chemical are added called coagulants which produce ions of appropriate charge that neutralise opposite charged colloidal particle & convert to dense particle which are settle down so this process called Sedimentation with Coagulation.

The most common coagulants used for this purpose are

① Alum  $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$

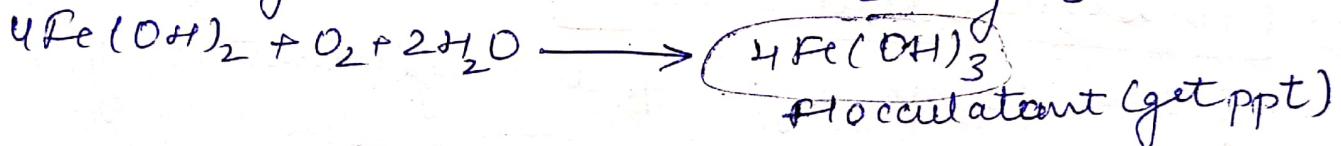


② Sodium Aluminate ( $NaAlO_2$ )



Degree of Hardness.

③ Ferrous Sulphate ( $FeSO_4 \cdot 7H_2O$ )



## # Filtration

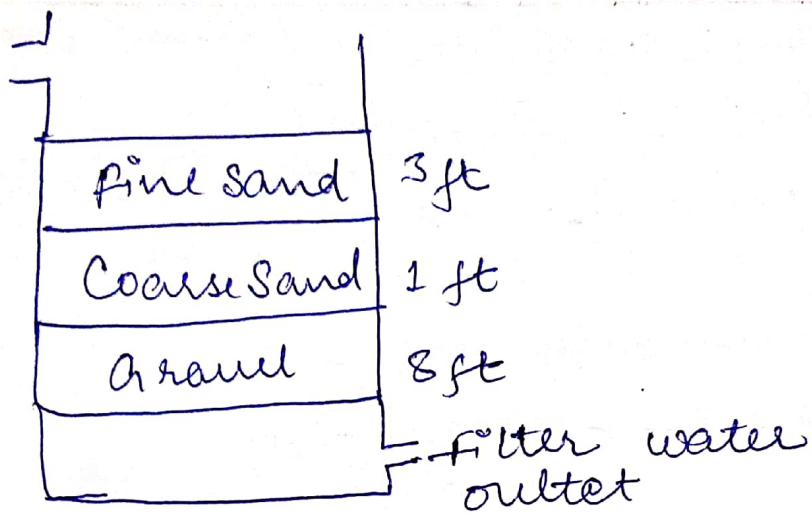
- It is used for removing microorganism, colour & unpleasant Odour.

- It is of two type 1) gravity sand filter 2) pressure sand filter

### 1) Gravity Sand filter

consist of large rect. tank consisting porous medium known as filter bed ; having fine sand at top then coarse sand below and gravel at bottom to depth of 1-2 meter

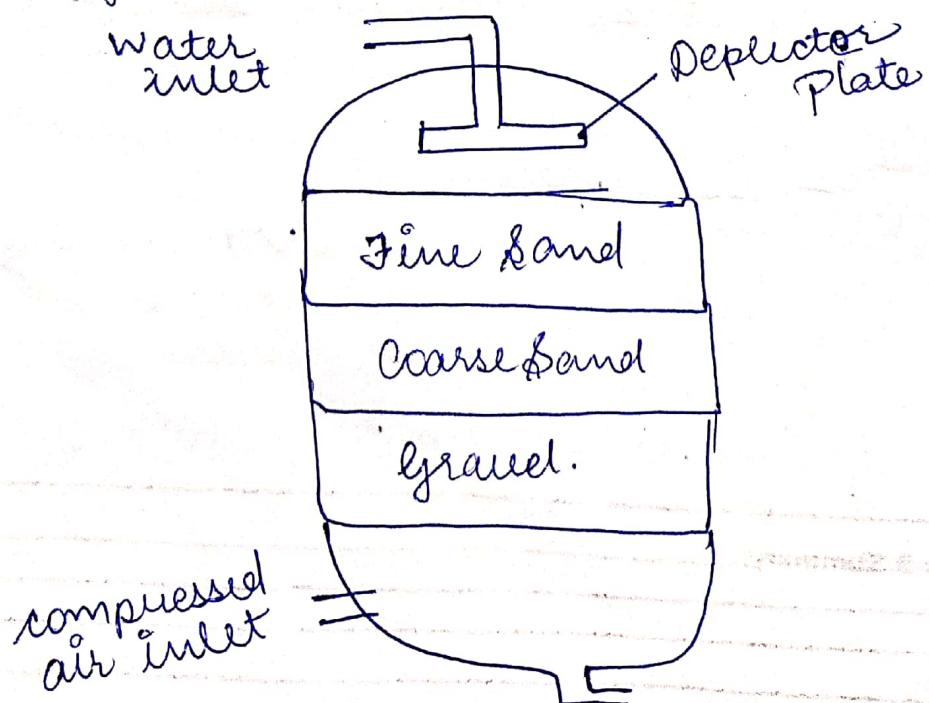
- also known as slow sand filter
- water enters in filter plants at the top and passes through the filter bag so the rest of suspended matter, colloidal matter and some bacteria are taken out from water



In this filter water passes through at atmospheric pressure due to gravity only

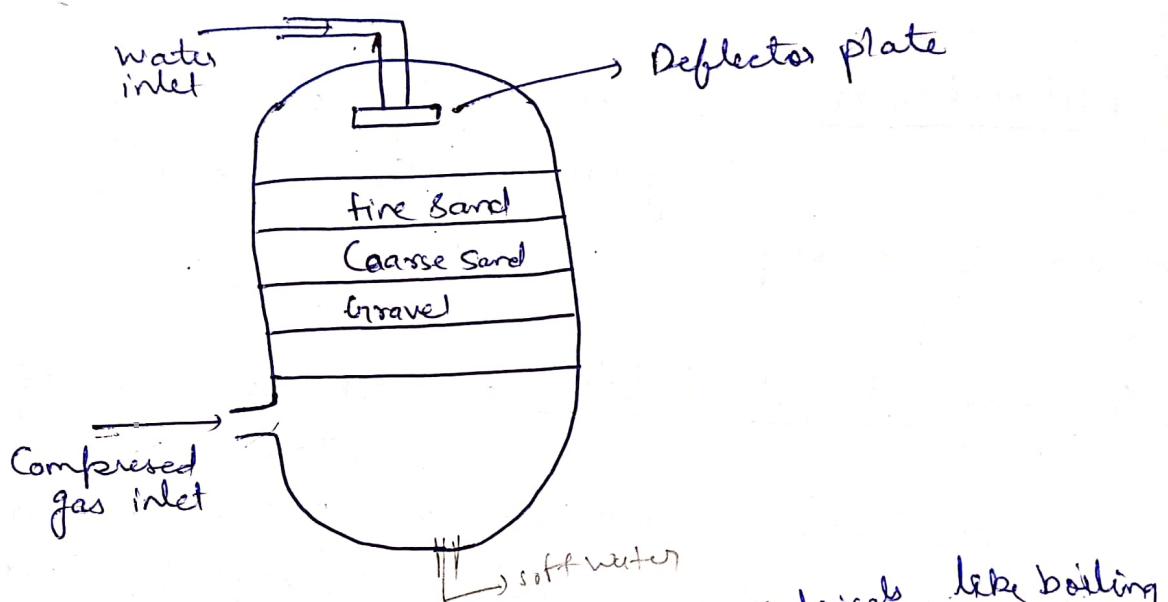
## 2) Pressure Sand Filter

- have same type of arrangement as gravity filter
- filter material kept in a closed cylinder and water is forced through filter bag by under pressure.



mauers colloidal matter & so bacteria are taken out from water. In this filter passes through atmospheric pressure due to gravity only.

(ii) Pressure Sand filter - This have the same type of arrangement as gravity filter. The filter material is kept in a closed cylinder and water is forced through filter bed under pressure.



\* Disinfection & sterilization -

Disinfection involve destruction of disease producing micro organism to make water save for use. It does not mean total destruction of all living organism while sterilization involves complete destruction and Ideal disinfectant or sterilizer should have following qualities:-

- (i) It should not have any toxic or harmful effect to human being.
- (ii) Should not produce ppt

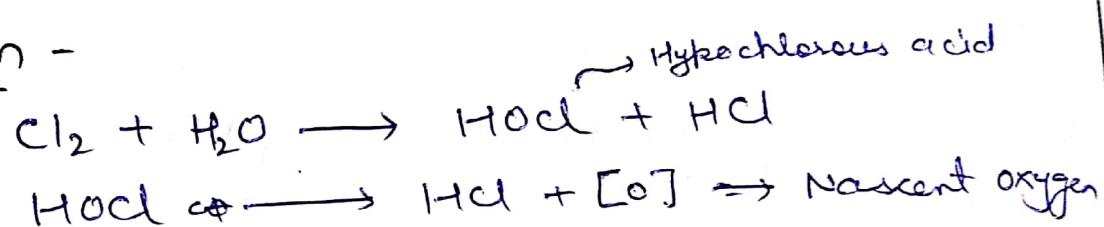
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(iii) Process should be simple & economical.

\* Method of disinfection & sterilization

- chlorination
- ozonolysis
- UV rays
- Bleaching powder method
- chloramine
- Boiling

→ chlorination -

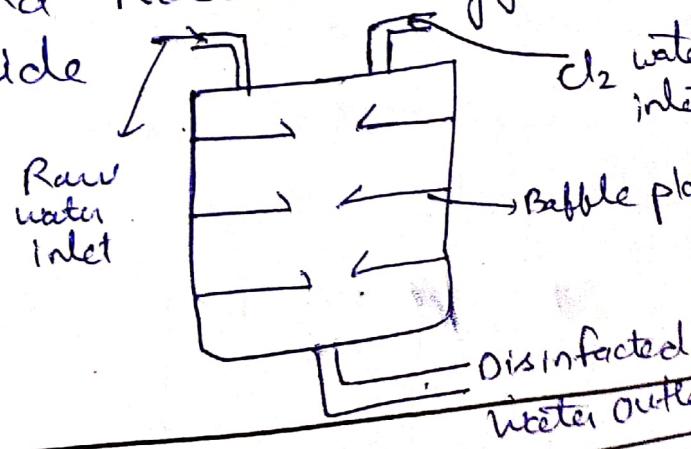


chlorine is most widely used germicide throughout the world. It may be added directly as gas or conc. sol<sup>n</sup> in water

$\text{HOCl} + \text{Bacteria} \rightarrow \text{Bacteria are killed}$

chlorine produces HOCl and Nascent oxygen which is very powerful germicide

chlorinator



## \* Advantages

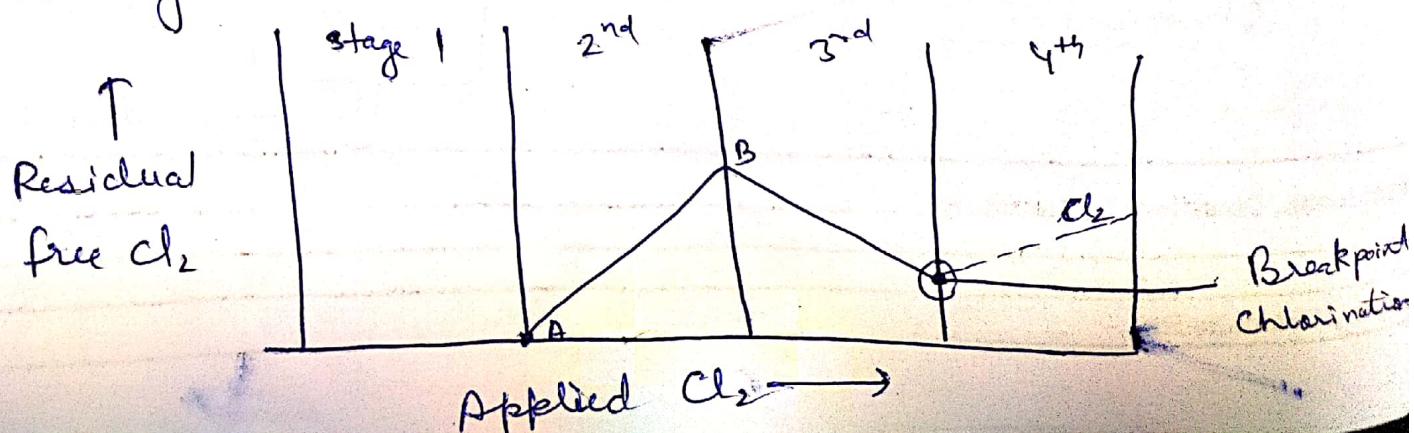
- It can be easily stored for a long time without any risk of deterioration.
- cheap & easily available
- Preventing re-growth of bacteria
- Does not produce salt impurities
- Used at high & low temp

## \* Disadvantage

- less effective at high pH & more effective at low pH
- excess of  $\text{Cl}_2$  produce unpleasant taste and odour
- free  $\text{Cl}_2$  in treated with water should not exceed than 0.1 to 0.2 ppm.

## \* Break point chlorination

It may be defined as the chlorination of water to such an extend that not only living organisms but also other organic impurities in water are destroyed.



stage 1 → Oxidation of reducing compounds

stage 2 → formation of chloroorganic & chloramine Compound

stage 3 → Destruction & chloro organic & chloramine Compound

stage 4 → free / residual  $\text{Cl}_2$

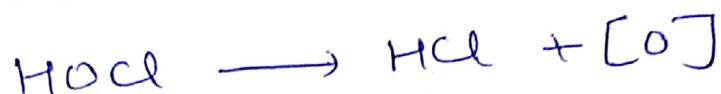
The addition of  $\text{Cl}_2$  at point 'c' is called break point at which free residual  $\text{Cl}_2$  begins to appear. Normally all taste odour disappear at break point

#### \* Advantages

- It completely oxidizes organic compound  $\text{NH}_3$  & other reducing compound.
- It removes colour, odours, unpleasant taste from water.
- It destroy disease producing bacteria completely
- It prevent further growth of any weed.

## \* Bleaching powder Method

Chlorine may be added in the form of bleaching powder.



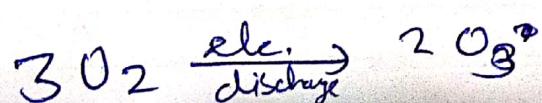
It produces powerful germicides HOCl & Nascent oxygen. which destroy the pathogens by oxidation

## \* Disadvantages

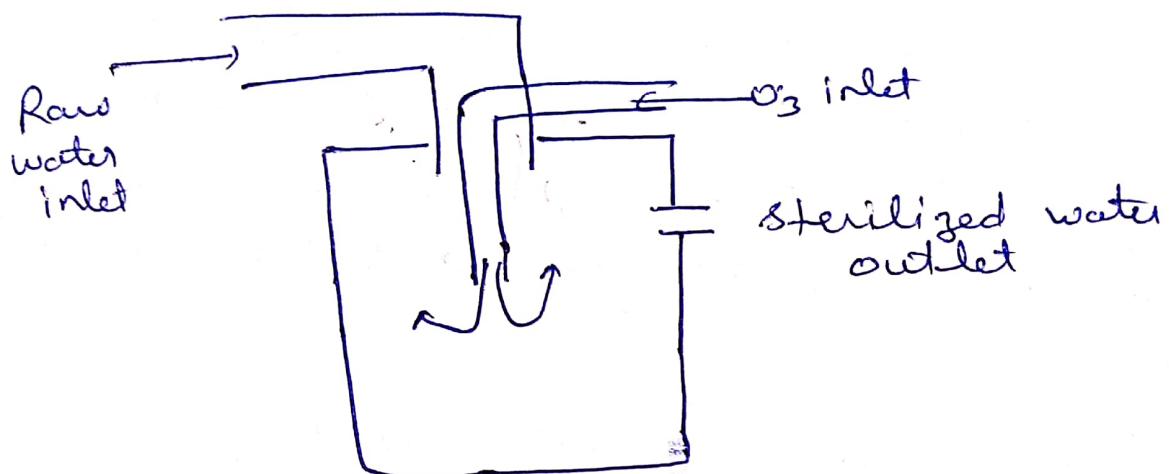
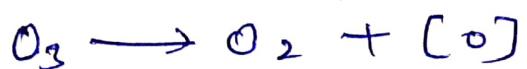
- Excess bleaching powder create bad taste and odour
- It deteriorates during storage not effective for long time period.
- It introduce calcium hardness  $[\text{Ca}(\text{OH})_2]$  in treated water.

## \* Ozonolysis Method

$\text{O}_3$  is very good disinfectant which is produced by passing electric discharge through dry & cold oxygen gas



$O_3$  is very unstable in nature and breakdown, liberating nascent oxygen. This nascent oxygen kill all the bacteria as well as oxidised organic matter present in water.



#### \* Advantages -

- Excess of ozone is not harmful because it releases  $O_2$  on decomposition.
- It removes colour, odour & improve the taste.

#### \* Disadvantage

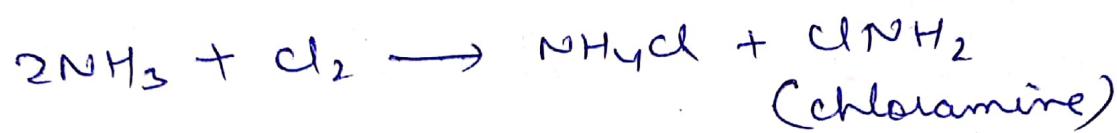
- It is an expensive method so cannot be used for multiple water supply.

→ It is complicated by the fact that  $O_3$  is a corrosive agent.

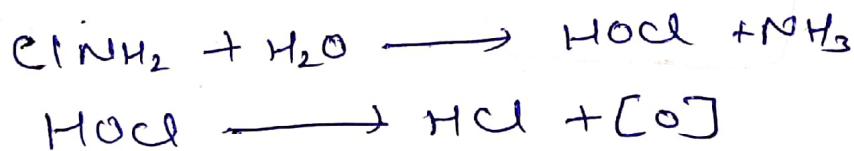
### \* Chloramine

It is obtained by mixing of chlorine and ammonia.

in 1:2



Now a days chloramine is used for disinfection of water because its excess does not produce any irritating odour and is more stable. More-over, it gives a better taste in treated water.



### \* U.V. rays

UV radiations emitted from electric mercury vapour are capable of disinfection of water. This process is particularly useful for disinfection of swimming pool water. This process is highly expensive.

### \* Boiling Method

Water becomes free from disease causing bacteria if water is boiled for 10-15 min.

## → Disadvantage

- i) It is costly method and can be useful for individual case it is impossible to empty it for municipal supply.
- ii) It kill the bacteria present in water at the time of boiling but do not provide any protection for future possible contamination.

## \* KMnO<sub>4</sub> method

In villages, the well water is sterilized by adding calculated amount of KMnO<sub>4</sub>. This method is very common and used by water works normally.

## \* Boiler troubles

Boilers are used for steam generation which is very important for industries and power houses. If hard water without softening treatment is directly fed into the boilers, the following problems will occur -

- Priming & foaming
- Caustic embrittlement
- Boiler corrosion
- Sludge & scale

## \* Priming & foaming (carry over)

Priming - when steam is produced rapidly in the boiler. Some very small droplets of water are carried along with steam and it contains dissolved salt in it.

### → Cause of priming

- i) Presence of dissolved and suspended matter
- ii) High level of boiler feed water
- iii) Improper design of boiler
- iv) High velocity of steam generation
- v) Sudden boiling of boiler feed water.

### → Minimization of Priming -

- i) By using soft water as boiler feed water
- ii) By boil feed water
- iii) By maintaining low level of water
- iv) By proper designing of boiler
- v) By controlling rapid change in steam velocity.

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- vii) By fitting mechanical steam purifiers
- viii) By blow-down operation.

Foaming — It is the formation of continuous foams or bubbles at the water surface in boiler with do not break easily.

→ Cause of foaming

- i) By presence of an oil, grease, alkali in water
- ii) Presence of finely divided sludge particle.

→ Prevention of foaming

- i) By adding coagulation  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Alum), Sodium aluminate. To remove oil, grease and finely sludge particle from boiled water.
- ii) Adding anti foaming agents like castor oil.

→ Carry over - This is mainly due to priming & foaming. In this priming and foaming usually occurs together for this priming. They are objectionable because -

- i) Dissolved salts or suspected solid in water carried by wet steam and they get deposited on heater and turbine blades of boiler.
- ii) Dissolved salt may enter into the parts of machinery and bring their life.

### \* Caustic Embrittlement

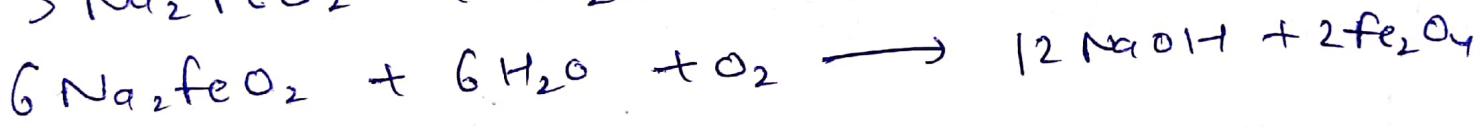


This is the phenomenon during which the boiler material become brittle due to the accumulation of casting substance. It is a type of corrosion by high concentration of NaOH in boiler feed water.

It is most likely to occur in boiler operating at high pressure where NaOH is produced by the hydrolysis of residual  $\text{Na}_2\text{CO}_3$  which is used for lime-soda water softening process.

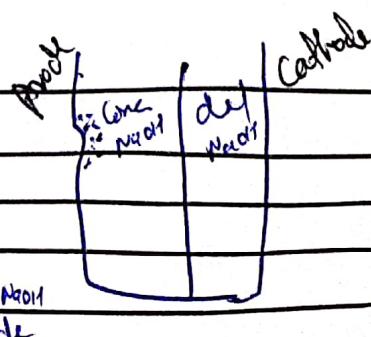
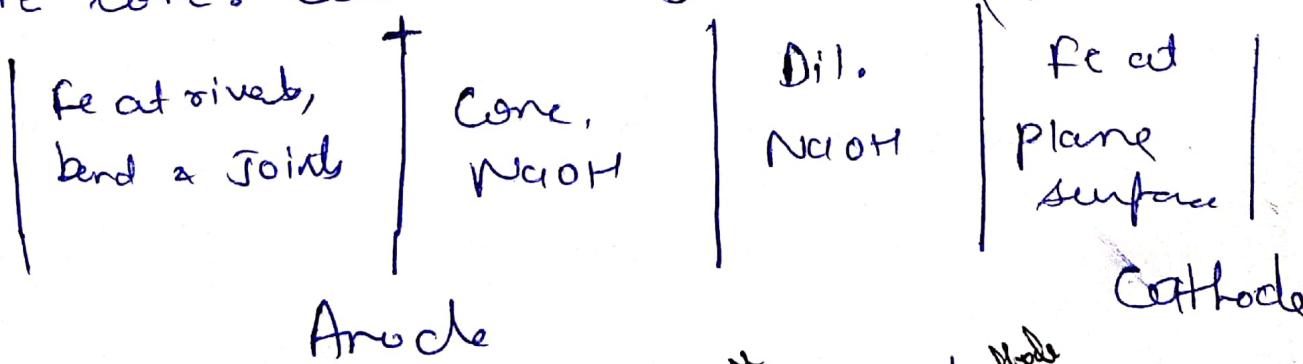


The formation of NaOH makes the boiler water caustic which penetrates into the minor cracks present in the inner side of boilers and when the water evaporate then the concentration of dissolved NaOH becomes possessively which attack the surrounding area and dissolved the iron of boiler as sodium ferrate.



Caustic embrittlement is a type of stress corrosion and it is localized electrochemical phenomenon.

The corr. cell during the -



main Ideas, Questions & Summary:-

Library / Website Ref.:-

Start of corrosion at conc. NaOH side

The iron surrounded by conc.  $\text{NaOH}$  acts as anode and gets dissolved or corroded.

### → Prevention of Caustic Embrittlement

- i) The water to be used in boiler should be soften by sodium phosphate instead of  $\text{Na}_2\text{CO}_3$ .
- ii) Tannin or lignins should be added to the boiler water which blocks the minute cracks.
- iii) Excess of alkali in boiler feed water should be neutralized.
- iv) Excess of  $\text{Na}_2\text{CO}_3$  in lime soda process should be avoided.
- v) The pH of boiler feed water should be adjusted to 8 to 9.

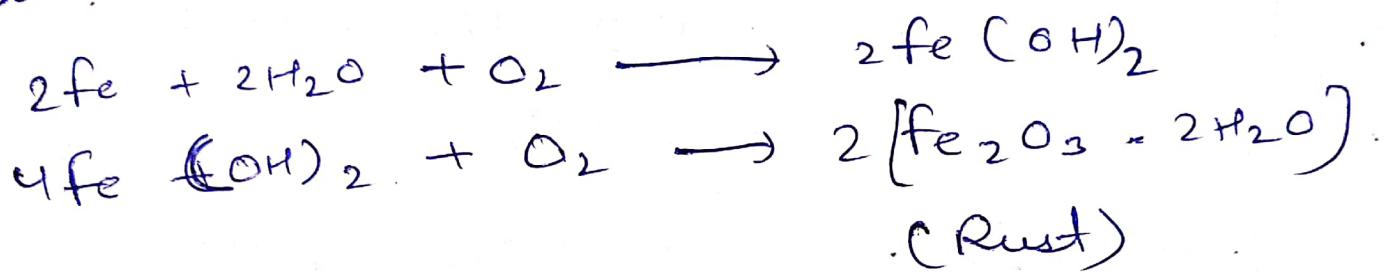
### \* Boiler Corrosion -

It is a disintegration or decay of boiler material due to chemical or electrochemical. Re. with its environment.

### → Cause of boiler corrosion

- i) Due to presence of dissolved gases such as  $\text{O}_2$ ,  $\text{CO}_2$ .
- ii) Due to dissolved acidic salts.
- iii) Due to formation of galvanic cell.

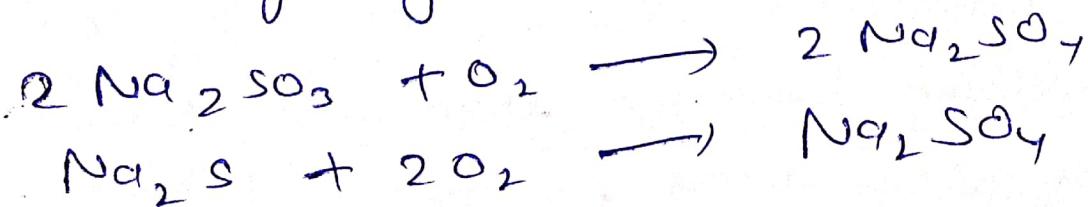
\* Due to presence of dissolved gases such as -  
(a) Dissolved Oxygen [DO] - In the presence of moisture and at high temp. dir. attack the boiler material

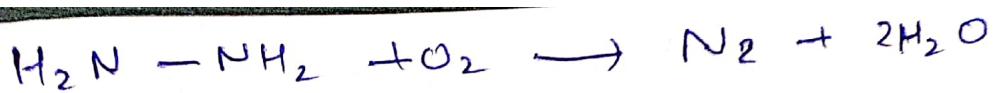


→ Removal of Oxygen

i) Pre heating - As solubility of gases decreases with  $\uparrow$  in temp. So at approx  $65^\circ\text{C}$  complete  $\text{O}_2$  segregate.

ii) chemical treatment - 'DO' is removed through addition of  $\text{Na}_2\text{SO}_3$  or  $\text{Na}_2\text{S}$  or hydrogen





(ii) Mechanical decration - Same as DD

\* Due to dissolved acidic salts -

The hydrolysis of  $\text{MgCl}_2$  and other acidic salt liberate  $\text{HCl}$  which react with boiler material in chain like Rx.



Consequently presence of small amount of  $\text{MgCl}_2$  will cause corrosion of Iron to a large extend.

→ Prevention

• By using soft water as a boiler feed water.

\* Due to formation of galvanic cell

Corrosion can also occur becz of galvanic cell formation between iron and other metals present in alloy used in boiler fittings. This may also lead to pitting corrosion.

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### \* Prevention

By using zinc plate which acts as sacrificial anode.

### \* Sludge & Scale -

Water evaporates continuously in boiler and conc. of dissolved salts increases gradually when their saturation point reached the salt are ppted on the inner valve of boiler.

→ Sludge - If the ppt formed is soft, slimy and loose it is called sludge

It is formed at comparatively colder portion of boiler & collect in the area where flow rate is comparatively slow.

It is formed by substances such as  $MgCO_3$ ,  $MgSO_4$  &  $CaCl_2$

### → Removal of Sludge

Remove by scrapping off with the brush.

## → Disadvantage of sludge formation

- i) fuel wastage
- ii) less working efficiency
- iii) Choking of pipes

## → Prevention of sludge formation

- i) By using soft water as boiler feed water.
- ii) By blow-down operation

\* Scale - If the ppt. formed is hard & adhering on the inner walls is called scale. which can be removed mechanically by abrasion or with the help of hammer & chisel.

## → Formation of Scale

- i) Decomposition of  $\text{Ca}(\text{HCO}_3)_2$

In low pressure boiler  $\text{Ca}(\text{HCO}_3)_2$  decomposes as -



[scale]

- ii) Yes in solubility of salt. few impurities deposited at high temp. becoz solubility decreases with Yes in temp. As solubility of  $\text{CaSO}_4$  decreases with Yes in temp & it gets ppt.
- iii) Hydrolysis of Magnesium salts. At high temp. brittle magnesium salt get hydrolysed and formed ppt of  $\text{Mg}(\text{OH})_2$
- $$\text{MgCl}_2 + 2\text{H}_2\text{O} \longrightarrow \text{Mg}(\text{OH})_2 + 2\text{HCl}$$
- iv) formation of  $\text{CaSiO}_3 \cdot 2\text{MgSiO}_3$ . If small quantity of  $\text{SiO}_2$  is present in water it forms hard deposits of  $\text{CaSiO}_3 \cdot 2\text{MgSiO}_3$

### → Removal of Scale

- (1) for soft scale - with the help of scrapper or wire brush.
- with the help of blow-down operation
- (2) for brittle scale - by giving them thermal shocks

e) for hard & adhering scale - by dissolving them in chemical like HCl

→ Disadvantage of Scale

- i) fuel wastage
- ii) ↓ in working efficiency
- iii) lowering of boiler safety
- iv) Danger of explosion.

→ Prevention of Scale

- (i) Internal treatment      (ii) External treatment

\* Internal treatment -

Treating the raw water inside the boiler is called internal or Internal conditioning or supersaturation.

In this treatment chemicals are added which ppt then & scale forming substance in loose sludge or convert into high soluble complexes which

present in dissolved form in boiler water without causing any scale formation and ~~deposition~~ <sup>decon.</sup> deposition.

→ Imp. Internal treatment methods are -

i) Colloidal Conditioning - Scale formation can be removed by adding organic substance like kerosene, tannin, agar-agar gel etc. They surrounds the minute particle of scale forming salts and formed non-sticky and loose deposits which can easily removed by blow-down operation.

ii) Carbonate Conditioning

When  $\text{Na}_2\text{CO}_3$  is added to boiler water it converts  $\text{CaSO}_4$  into  $\text{CaCO}_3$  which is loose sludge. This is used only for low pressure boilers.

In high. pr boiler the excess  $\text{Na}_2\text{CO}_3$  be converted into  $\text{NaOH}$  due to hydrolysis which cause caustic embrittlement.  $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4$   
(loose sludge)

Main Ideas, Questions & Summary:

Library / Website

iii) Phosphate Conditioning - When  $\text{Na}_3\text{PO}_4$  is added in boiler it forms soft sludge of Calcium & Magnesium phosphate.



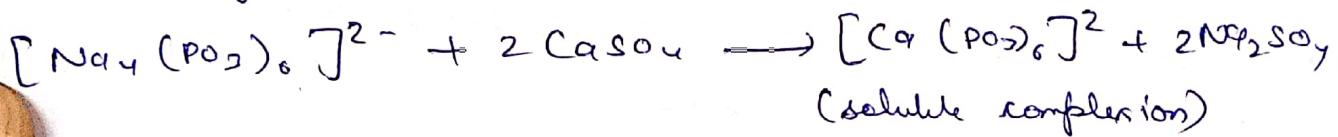
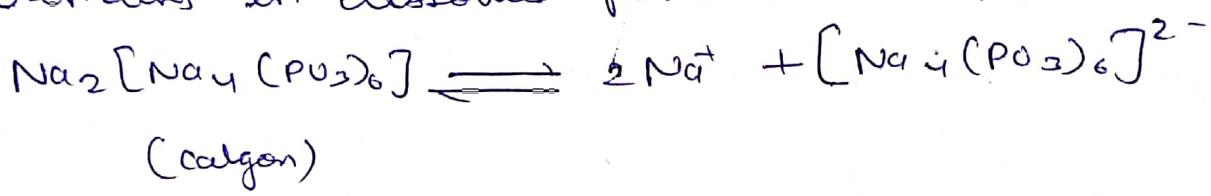
(a) In acidic medium  $\rightarrow \text{NaH}_2\text{PO}_4$

(b) In weak alkaline medium  $\rightarrow \text{Na}_2\text{HPO}_4$

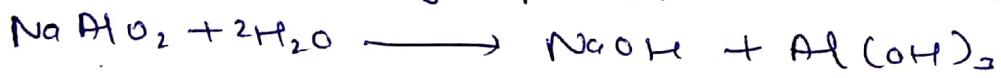
(c) In alkaline medium  $\rightarrow \text{Na}_3\text{PO}_4$

~~Any~~

iv) Calgon Conditioning - If calgon (sodium hexameta phosphate) is added to boiler feed water it forms soluble complex with  $\text{CaSO}_4$  which remains in dissolved form in water



v) Treatment with  $\text{NaAlO}_2$  -  $\text{NaAlO}_2$  get hydrolysed & form  $\text{NaOH}$  and gel ppt of  $\text{Al(OH)}_3$



This is loose slimy ppt which can easily remove by blowdown operation

vi) Complexometric Method - When EDTA added to water it converts the scale forming cations into stable & soluble complex which prevent the scale & sludge formation.

\* External Treatment - Treatment of water before feed into the boiler is called External treatment.

The process of removing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions from water is known as softening of water. Main process by which hard water is commonly softened are -

- (i) Lime- Soda method
- (ii) Zeolite method
- (iii) Ion- exchange method

① Lime- Soda Method - In this process, the soluble calcium & Mg and heavy metal salt present in hard water are chemically converted into insoluble compounds ( $\text{CaCO}_3$  &  $\text{Mg(OH)}_2$ ) by adding calculated amount Lime ( $\text{Ca(OH)}_2$ ) and Soda ( $\text{Na}_2\text{CO}_3$ ). Insoluble compound are then filtered off.

To accelerate the ppt of  $\text{CaCO}_3$  and  $\text{Mg(OH)}_2$  certain chemicals are added known as Coagulants or flocculants

→ Formula for lime- soda requirement

$$\text{Lime req.} = \frac{74}{100} \left[ \text{Temp. } \text{Ca}^{2+} + 2 \times \text{temp. } \text{Mg}^{2+} + \text{Perm. } \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+} + \text{H}^+ + \text{HCO}_3^- + \text{CO}_2^- - \text{Na}^+ \text{HO}_2^- \right] \times \text{Vol. of H}_2\text{O}$$

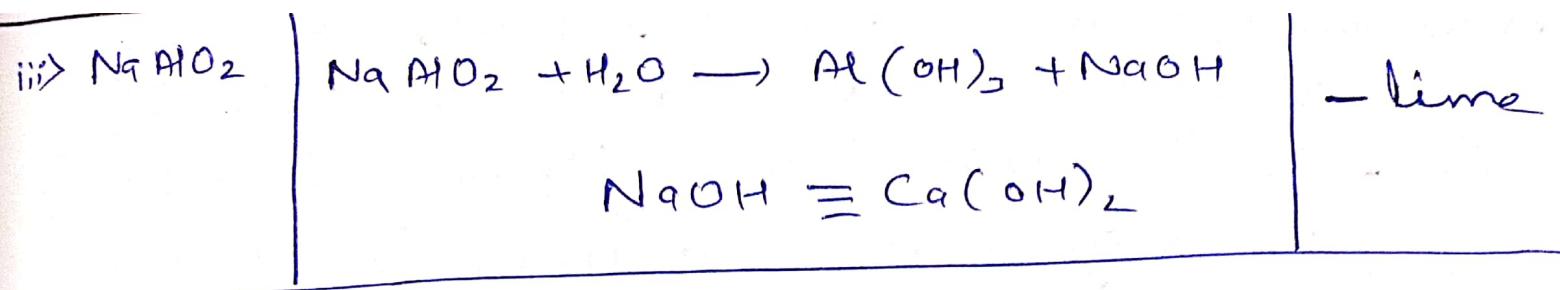
*\* All in terms of  $\text{CaCO}_3$  equivalent.*

Main Ideas, Questions & Summary:

$$\text{Soda req.} = \frac{106}{100} \left[ \text{Perm. } \text{Ca}^{2+} + \text{Perm. } \text{Mg}^{2+} + \text{Al}^{3+} + \text{Fe}^{2+} + \text{H}^+ - \text{HCO}_3^- \right] \text{ All in terms of } \frac{\text{CaCO}_3 \text{ equiv.}}{\text{Vol. of H}_2\text{O}}$$

### ~~Reactions involved in lime-soda method~~

constituent	chemical reaction	Requirement
1) Temp. $\text{Ca}^{2+}$ $\text{Ca}(\text{HCO}_3)_2$	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 \downarrow + 2\text{H}_2\text{O}$	Lime
2) Temp. $\text{Mg}^{2+}$ $\text{Mg}(\text{HCO}_3)_2$	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \rightarrow 2\text{CaCO}_3 + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2 lime
3) Perm. Hard. (i) $\text{Ca}^{2+}$	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	Soda
(ii) $\text{Mg}^{2+}$	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	Lime + Soda
4) $\text{H}^+$ ( $\text{HCl}/\text{H}_2\text{SO}_4$ )	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \rightarrow 2\text{H}_2\text{O} + \text{Ca}^{2+}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$	Lime + Soda
5) $\text{HCO}_3^-$ ( $\text{NaHCO}_3$ )	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} + \text{CO}_3^{2-}$	Lime - Soda
6) $\text{CO}_2$	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	Lime
7) Coagulants (i) $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{Fe}^{2+} + \text{Ca}(\text{OH})_2 \rightarrow \text{Fe}(\text{OH})_2 + \text{Ca}^{2+}$	Lime + Soda
(ii) $\text{Al}_2(\text{SO}_4)_3$ Alum	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{Na}^+$ $2\text{Al}^{3+} + 3\text{Ca}(\text{OH})_2 \rightarrow 2\text{Al}(\text{OH})_3 + 3\text{Ca}^{2+}$ $3\text{Ca}^{2+} + 3\text{Na}_2\text{CO}_3 \rightarrow 3\text{CaCO}_3 + 6\text{Na}^+$ $2\text{Al}^{3+} \equiv 3\text{Ca}^{2+}$	Lime + Soda



\* Lime Soda process - It is of two types

- (a) Cold L-S process
- (b) Hot L-S process

→ Cold L-S process

Calculated quantity of lime & soda are added to raw water at room temp. This process is called continuous lime - Soda process.

\* Construction

It consists of two concentric chamber

- (i) Inner chamber - small, open bottom, stirrer with peddles
- (ii) Outer chamber - big, having sludge valve and outlet for soft water

## A Process

Lime + Soda + Coagulants and raw water are fed from the top into the vertical inner chamber fitted with a motor control stirrer. Continuous mixing through the stirrer do the softening of water. As the softened water comes into outer chamber, it goes upward dir. The softened water passes through a wood-fibre filter to check complete removal of sludge.

Sludge settle down in the outer chamber and can be removed easily. The soft water obtain from these process has hardness of 50-60 ppm

At room temp' the ppt. form are finally divided and do not settle down easily so small amount of Coagulants are added which helps in setting down the ~~precipitate~~ precipitate

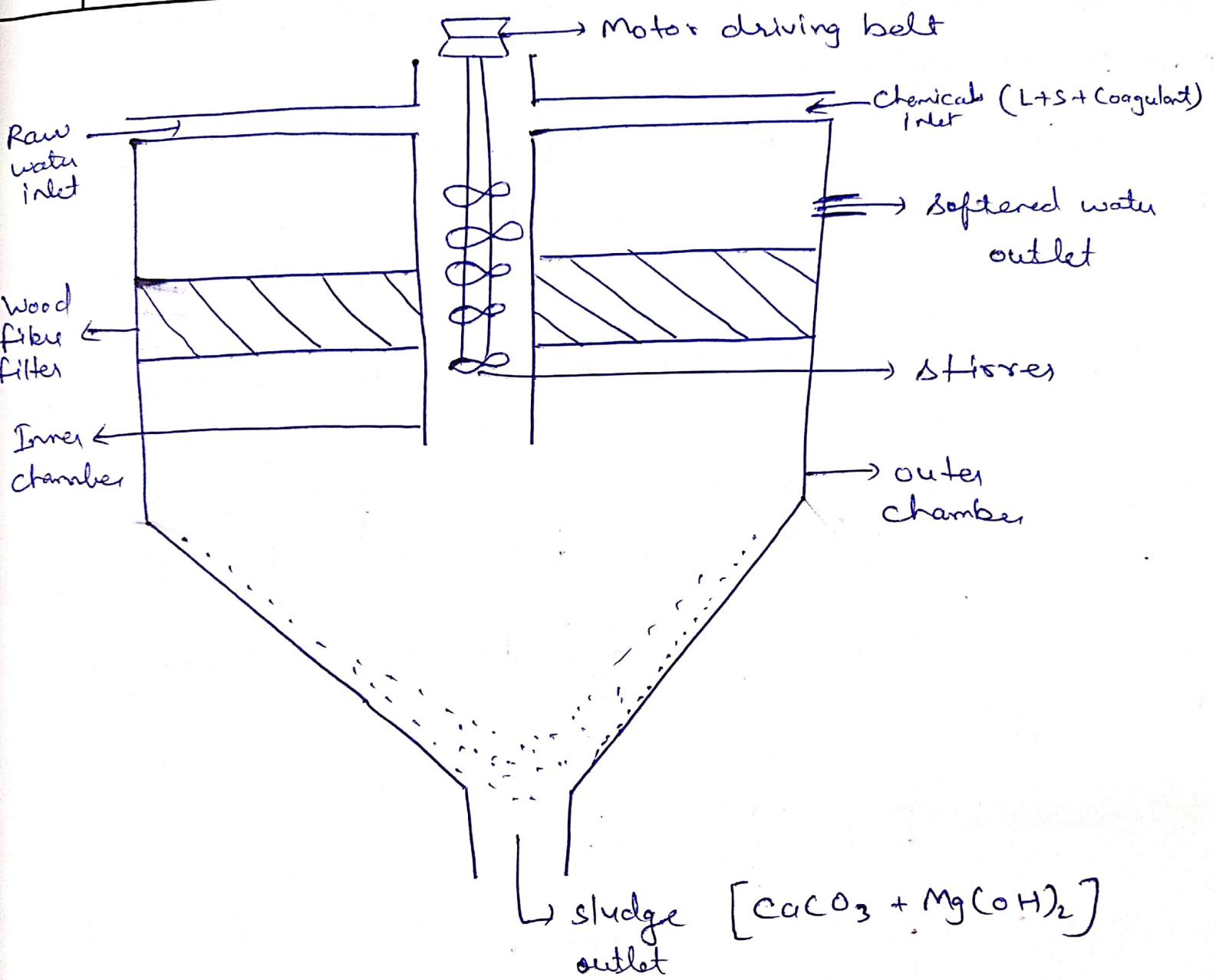
Hard feed water (contains  $\text{Ca}^{2+}, \text{Mg}^{2+}$ ) + lime + Soda

- ↓
  - (i) Addition of coagulants or flocculant
  - (ii) Proper setting lime

Ppt. of  $\text{CaCO}_3$  &  $\text{Mg}(\text{OH})_2$

→ Sodium Aluminate. ( $\text{NaAlO}_2$ )

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### → Hot L-S process

When L-S process is performed at temp  $80 - 150^\circ C$  it becomes hot L-S process. Since it is operated at high temp so the reaction proceed faster

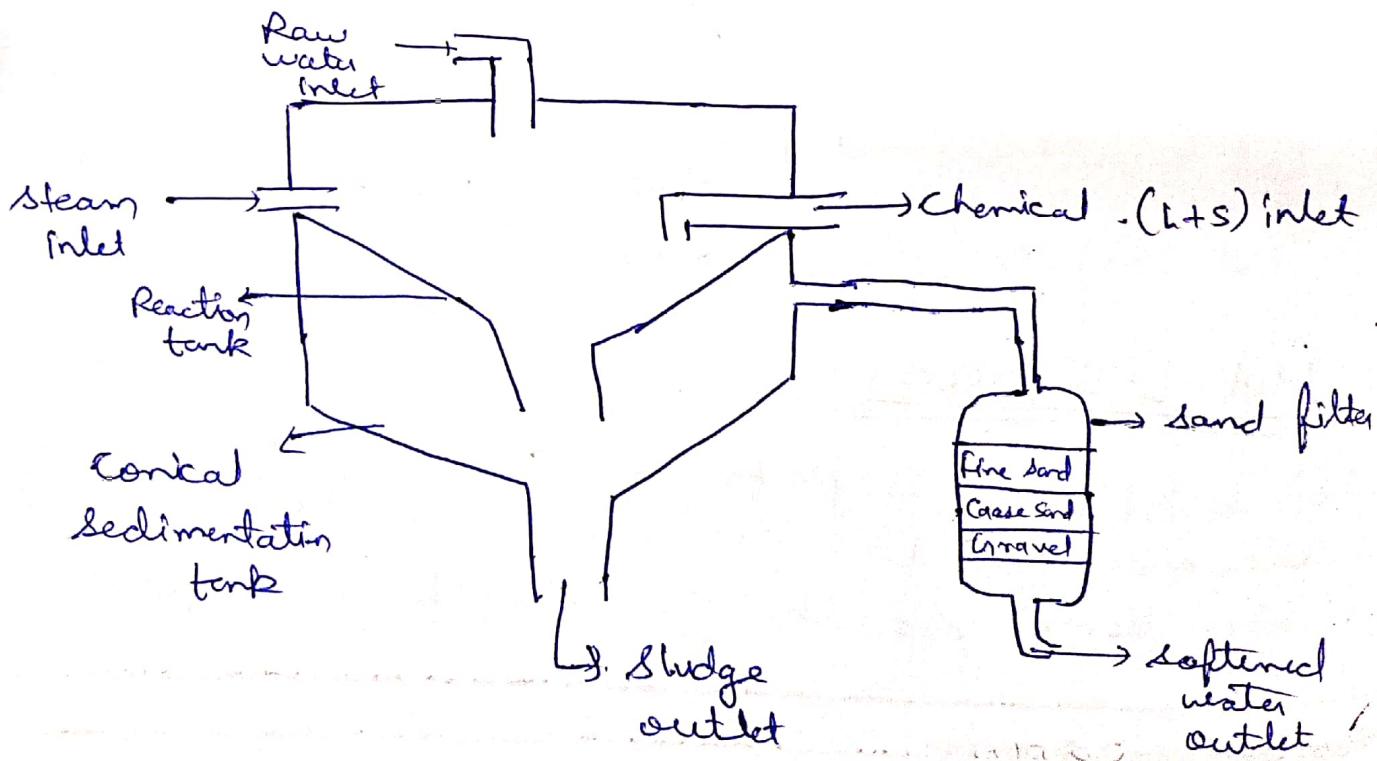
and it increases softening capacity of many ~~faults~~ faults

At high temp the sludge form settle down easily and hence no coagulants are needed. Better amount of dissolved gases such as  $\text{CO}_2$  &  $\text{O}_2$  are driven out of the water

The hot L-S plant consists of three parts

- i) Reaction tank - in which feed water, chemicals and steam are thoroughly mixed
- ii) Conical sedimentation tank - in which sludge are settle down
- iii) Sand filter - which ensure complete removal of sludge from the soft water.

The residual hardness after hot L-S process is 15-30 ppm



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## Advantages of L-S process

- ii) Economical process
- iii) This process not only remove the hardness in water but also reduces the quantity of minerals
- iv) This process increases the pH of water which helps in avoiding the corrosion possibility
- v) Alkaline nature of treated water control the amount of pathogenic bacteria in water
- v) This process also helps to remove the Fe (Iron) & Mn (Magnese) to some extent

## Disadvantages

- i) This process requires very skilled super-vision
- ii) During this process insoluble ppt (sludge) is form and disposal of it is a big problem
- iii) This process can remove hardness only upto 15 ppm which is not good for boilers

→ Diff. b/w Hot & Cold L-S process

### Cold L-S process

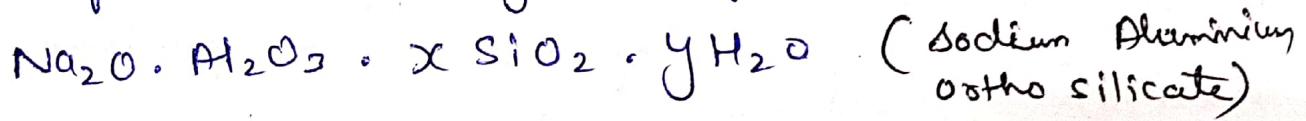
- less efficient
- Rx. are comparatively slow
- low softening capacity
- filtration is slow
- Coagulants are essential
- steam is not required
- Resultant hardness 50-60 ppm

### Hot L-S process

- Very efficient
- Rx. are complete and fast
- High softening capacity
- Filtration is high
- Coagulation are not required
- Steam is essentially used
- Resultant hardness 15-30 ppm

### ② Zeolite / Permulf Method

Zeolite is a greek word means boiling stone which means a certain group of naturally occurring minerals which released their water of hydration in the form of ~~steam~~. Its general formula is



$$x \rightarrow 2-10 \quad y \rightarrow 2-6$$

It is expressed as  $\text{Na}_2\text{Z}$  (sod. Zeolite)

It is a hydrated sodium Aluminosilicate which is capable of reversibly exchanging ~~to~~ its  $\text{Na}^+$  ions with the alkaline earth cations ( $\text{Ca}^{2+}, \text{Mg}^{2+}$ ) and other metal ions present in water.

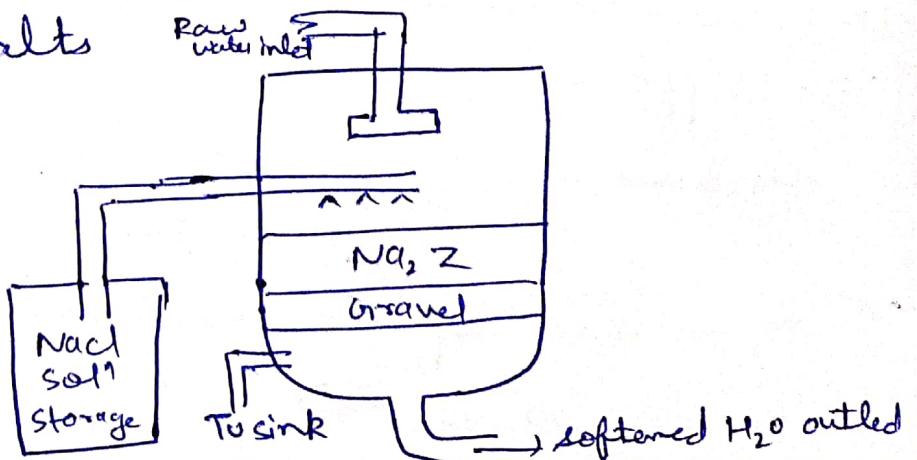
Zeolites are of two types -

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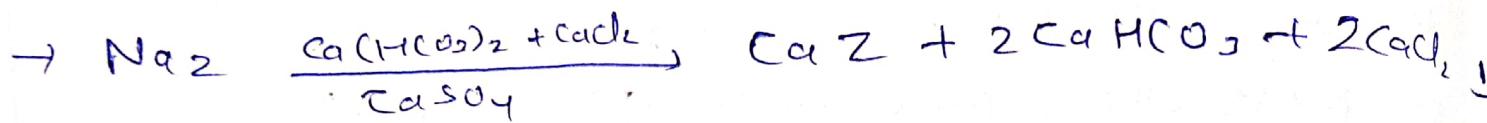
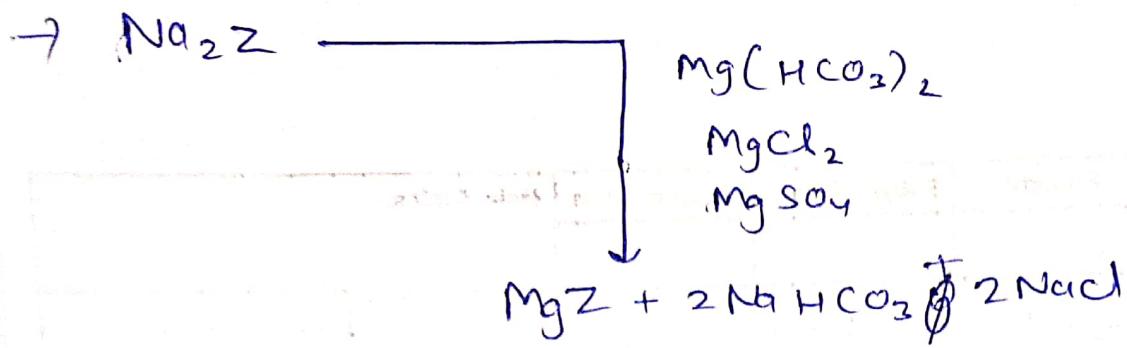
1) Natural Zeolite - It is non-porous and derived from green sand by washing, treating with  $\text{NaOH}$  & heating  
 eg Natrolite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ )

2) Synthetic Zeolite - gel structure and porous.  
 It can be prepared by heating together solution of Soda Silicates, Soda Aluminate and Aluminium Sulphate. They have comparatively higher exchange capacity than natural Zeolites  
 eg zeolite A ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 5\text{O} \div 6\text{H}_2\text{O}$ )

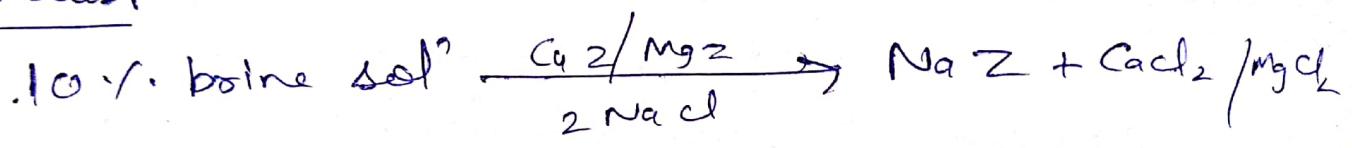
→ softening process - The zeolite or permuted <sup>bed</sup> is placed in a suitable column and it can be represented as  $\text{Na}_2\text{Z}$  and after cation exchange it is converted into  $\text{CaZ}$  and  $\text{MgZ}$  and equal amt. of sod. ions replaced and treated water contains sod. salts



Main Ideas, Questions & Summary:



Exhaust



Degeneration - When the zeolite bed is completely converted into CaZ & MgZ and it no further work as softener it gets exhausted, at this stage the supply of feed water is stopped and the exhausted zeolite degenerated by treating with conc. 10% brine (NaCl).



The regenerated zeolite bed is used again as softener. The hardness in treated water after zeolite process 0-15 ppm

$$\text{Hardness} = \frac{m \times V_2 \times 50 \times 1000}{V_1 \times 58.5}$$

†  $m \rightarrow$  mass of NaCl used for regeneration (gm)

$$V_2 = \text{Vol. of NaCl}$$

$$V_1 = \text{Vol. of water softened (lit.)}$$

## Limitation of Zeolite process

- 1) Hard water should be turbidity free otherwise it block the ports
- 2) Hard water should be acid free because it destroy the zeolite bed
- 3) If  $Mn^{2+}$  or  $Fe^{2+}$  present into feed water it must be remove. Otherwise they form  $Mn_2$  or  $Fe_2$  which cannot be remove easily during regeneration.

## Advantage of Zeolite process

- 1) Equipment req. less area
- 2) All most completely hardness is removed
- 3) There is no foam
- 4) Reg. less still for operation as well as maintenance

## Disadvantage

- 1) Turbid water cannot be treated.
- 2) Treated water contains more ~~of~~ sodium salt.

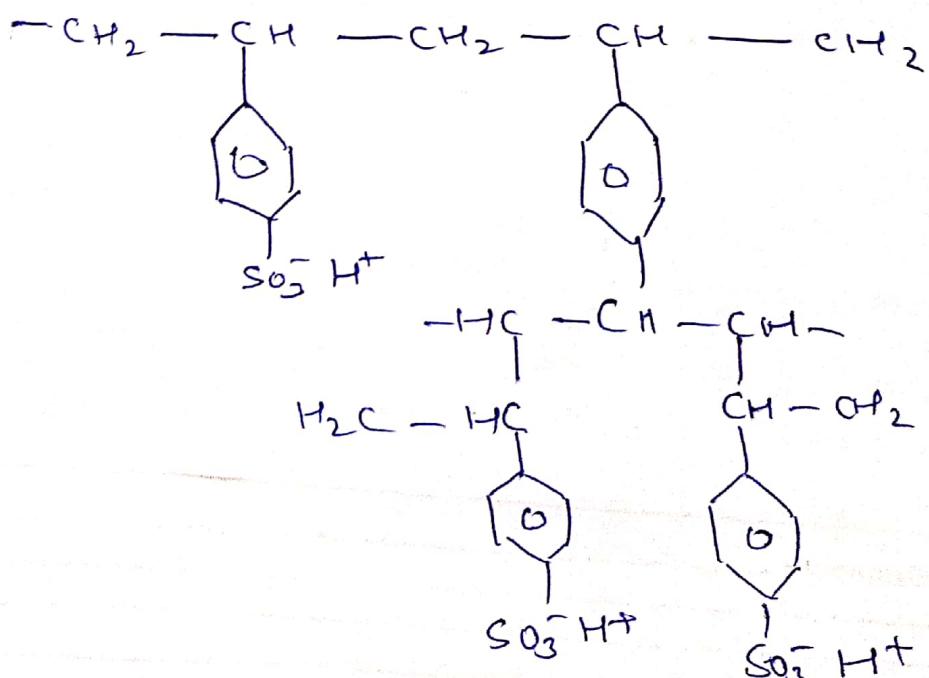
3) This process only remove  $\text{Ca}^{+2}$  &  $\text{Mg}^{+2}$  but all other ion remains as such in treated water which is harmful for boiler.

### ③ Ion Exchange / Deionization / Demineralization process

All the cation and anion are completely remove in this process so it is known as complete deionization. Ion exchange resins organic cross link insoluble polymers having functional group which are responsible for the ion exchanging property. ion exchange & resin can be classified as -

1) Cation Exchange resin - which have acidic functional group -  $\text{COOH}$ ,  $-\text{SO}_3\text{H}$  etc. are capable of changing their  $\text{H}^+$  ions with other cations which are present in feed water. They are present  $\text{R}-\text{H}^+$

are common

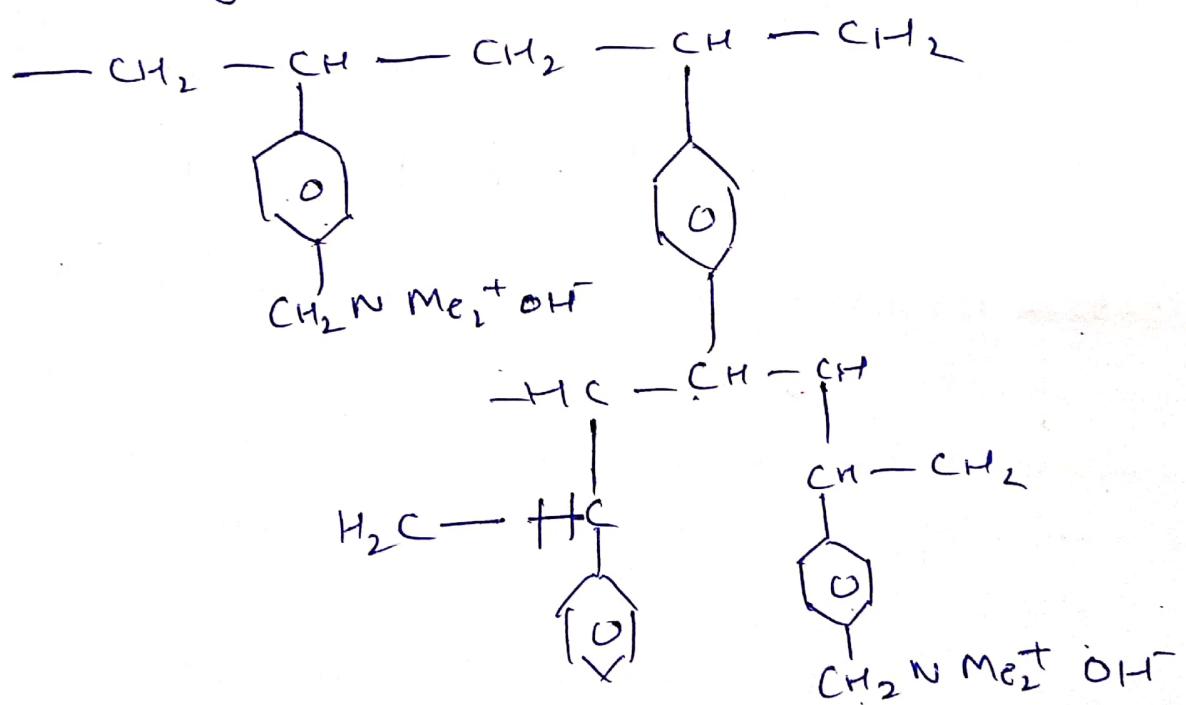


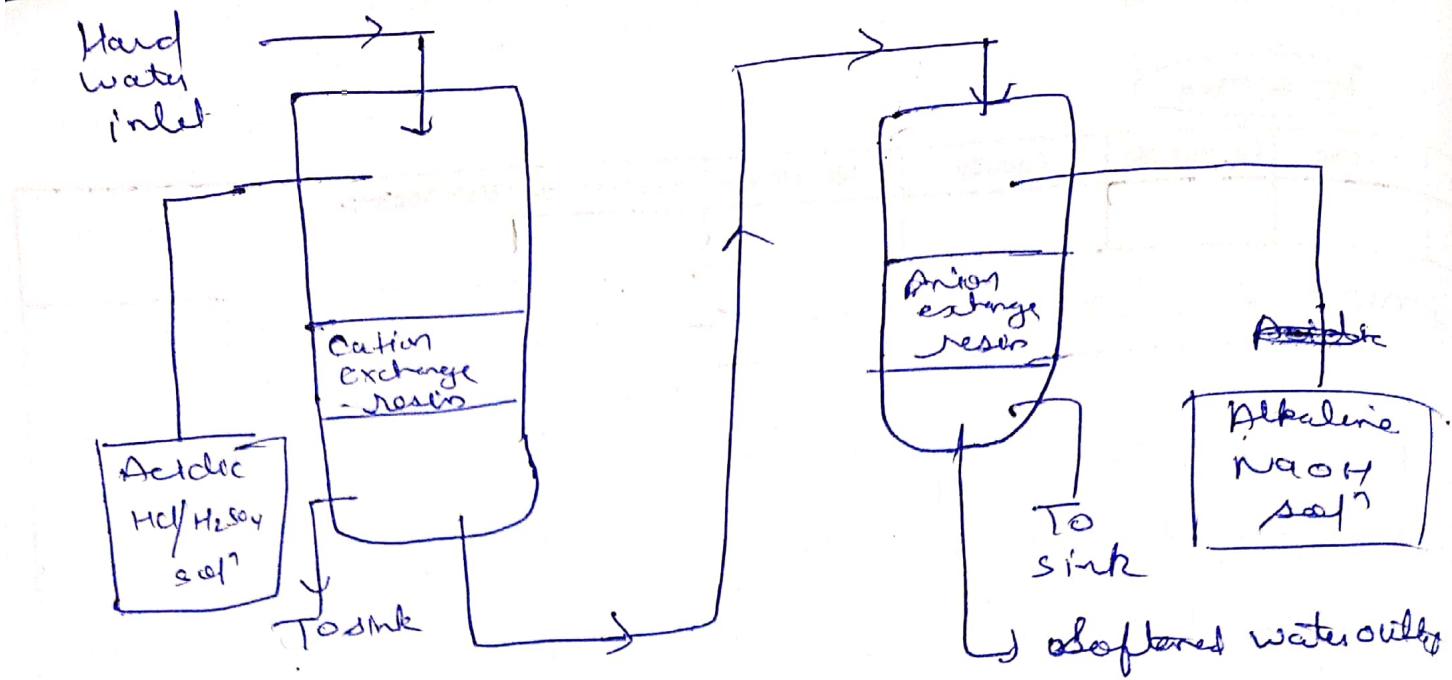
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2) Anion exchange resins - Having basic functional groups such as  $-NH_2$ ,  $=NH$  etc are capable of exchanging their  $OH^-$  ion with other ion present in feed water.

It is represented as  $R^+ OH^-$  where  $R^+$  is the insoluble polymeric heavy part.

e.g. Amberlite -400, Dowex -3 are commonly used in anion exchangers





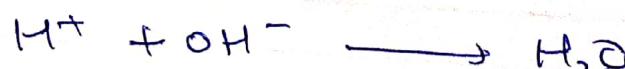
The hard water first pass through cation exchange resin column which remove all the cation like  $\text{Ca}^{2+}$  /  $\text{Mg}^{2+}$  etc. present in it and equal amt. of  $\text{H}^+$  ions are released from this column to water



After cation exchange column the hard water is passed in anion exchange resin column which remove all the anions like  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , etc. present in it and equal amt. of  $\text{OH}^-$  ions released from this column to water



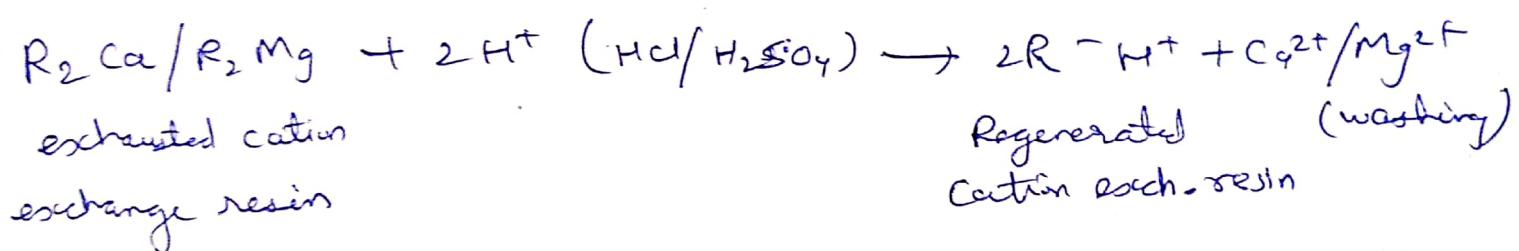
$\text{H}^+$  and  $\text{OH}^-$  ions released from reactions get combined to produce water volume



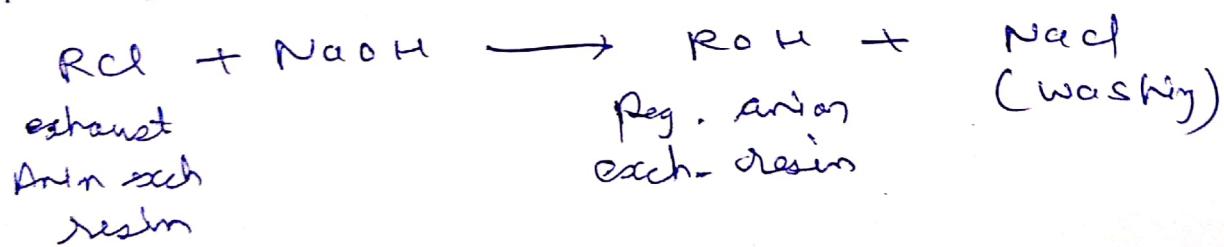
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Degeneration - When the cation exchangers and anion exchangers are fully saturated by the absorption of cation and anion resp. they lose their exchanging ability and become exhausted.

The exhausted cation exchange resin is regenerated by passing dilute HCl or  $H_2SO_4$



The exhausted anion exchange resin is regenerated by passing dil.  $\text{NaOH}$  soln.



The regenerated exchange can be used again the residual hardness of this method 0-2 ppm

## Advantage

ij It can be used to soften slightly acidic or alkaline water

iii) It produce water of very low hardness about 2 ppm

### Disadvantage

- ii) The process and equipment is very costly and more expensive chemicals are needed
- iii) If the process is turbid then the output of the process is reduced