NARSIMHA REDDY ENGINEERING COLLEGE
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# Engineering Chemistry

## UNIT I

## WATER & ITS TREATMENT

Hard Water : The water which does not produce lather with soap is called Hard Water

- It is due to the presence of Calcium $Ca^{+2}$ and Magnesium $Mg^{+2}$ salts present in the water

Soft Water : The water which produce lather with soap is called soft water

Types of Hardness:

Hardness is of 2 types
Temporary Hardness
Permanent Hardness

Temporary Hardness: The hardness due to the presence of bicarbonates of calcium and magnesium salts is called Temporary hardness
EX: $Ca(HCO_3)_2$
It can be removed by boiling method

- Permanant Hardness:The hardness due the presence of chlorides, $cl^-$ Sulphates $SO_4^{2-}$ and nitrates $NO_3^-$ of calcium and magnesium salts is called permanent hardness
- Ex:$CaSO_4$,$MgSO_4$ etc
- It cannot be removed by boiling method.

# Hardness of water

- Hardness is the soap consuming capacity of water
- Hardness of water is due to the presence of Ca and Mg salts in it. Other ions responsible for hardness are $Al^{3+}$, $Fe^{3+}$ and $Mn^{2+}$
- If Ca and Mg salts are present in water then they react with the soluble sodium soap to form insoluble salts calcium and magnesium.
- $2C_{17}H_{35}COONa + CaSO_4 \dashrightarrow (C_{17}H_{35}COO)_2Ca + Na_2SO_4$
  Sodium stearate Insoluble salt
- $2C_{17}H_{35}COONa + MgCl_2 \dashrightarrow (C_{17}H_{35}COO)_2Mg + 2NaCl$

# Temporary Hardness

- Caused by the presence of dissolved bicarbonates of Ca, Mg and. This hardness is also known as alkaline hardness.
- Easily removed by heating :
- $Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$
- $Mg(HCO_3)_2 \xrightarrow{\text{Heat}} Mg(OH)2 \downarrow + CO_2 \uparrow$

# Permanent Hardness

- Due to the presence of sulphates and chlorides of Ca & Mg
- Cannot be removed simply by boiling.
- Special methods like lime soda process, zeolite process, ion-exchange method are used for the removal of permanent hardness.

# How to calculate harness in terms of $CaCO_3$ equivalent

Hardness in terms of CaCO3 equivalents

$$= \text{wt. of hardness producing sub.} \times \frac{\text{mol. mass of CaCO3}}{\text{mol. mass of hardness producing sub.}}$$

# Units of Hardness

| | | | |
|---|---|---|---|
| a) | parts per million | ppm | parts of $CaCO_3$ equivalent hardness per $10^6$ parts of water. |
| | | | |
| b) | Milligrams per litre | Mg/l | no. of milligrams of $CaCO_3$ equivalent hardness per litre of water. |
| | | | |
| c) | Degree Clark | °Cl | parts of $CaCO_3$ equivalent hardness per 70,000 parts of water. |
| | | | |
| d) | Degree French | °Fr | parts of $CaCO_3$ equivalent hardness per $10^5$ parts of water. |

Relation between various units of hardness

$$1\text{ppm} = 1\text{mg/l} = 0.1\,°\text{Fr} = 0.07\,°\text{Cl}$$

# DETERMINATION OF HARDNESS BY COMPLEXOMETRIC METHOD / EDTA METHOD

Principle: The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) using Eriochrome Black-T as an indicator and keeping the pH of the water at 9.0 - 10.0.

- The end point is the change in colour from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.

- $(Ca^{2+} \text{ or } Mg^{2+}) + EBT \rightarrow [Ca-EBT] \text{ (or) } [Mg-EBT]$
  Hardness-salts indicator Unstable complex (wine red)

- $[Ca-EBT] \text{ (or) } [Mg-EBT] + EDTA \rightarrow [Ca-EDTA] \text{ (or) } [Mg-EDTA] + EBT$ Unstable complex (wine red) stable complex (colourless) blue

# Various steps involved in this method:

## Standardization of EDTA solution:

- Rinse and fill the burette with EDTA solution.
- Pipette out 20 ml of standard hard water (M1) in a conical flask.
- Add 4ml of buffer solution and 2 drops of EBTindicator.
- Titrate with EDTA solution till wine-red colour changes to clear blue.
- Let volume used by 'X' ml.

$$M_1 V_1 = M_2 V_2$$

Where, $M_1$ = Molarity of Standard Hard water (0.01M),
$V_1$ = Volume of Standard Hard water (20 ml),
$M_2$ = Molarity of EDTA,
$V_2$ = Volume of EDTA (Xml).

# 2.Determination of Total Hardness:

- Rinse and fill the burette with EDTA solution.
- Pipette out 20 ml of sample water (V3) in a conical flask.
- Add 4 ml of buffer solution and 2 drops indicator.

Titrate with EDTA solution till wine-red colour changes to clear blue.

Let volume used by ‘Y’ ml.

$$M2\ V2 = M3\ V3$$

Where, M2 = Molarity of EDTA,

V2 = Volume of EDTA (Yml).

M3 = Molarity of sample water,

V3 = Volume of Sample water (20 ml).

Total Hardness = M3 × Molecular weight of CaCO3 (100) × One Litre (1000ml)

= M3 × 105 ppm

# 3. Determination of Permanent Hardness:

- Take 100 ml of sample water in 250 ml beaker.
- Boil it to remove temporary hardness to about half of its volume and cool to room temperature, filter through filter paper to remove insoluble salts.
- Make up the volume to the original 100ml by adding distilled water.
- Now Pipette out 20 ml of this solution (V4) in a conical flask.
- Add 4 ml of buffer solution and 2 drops indicator.
- Titrate with EDTA solution till wine-red colour changes to clear blue.

Let volume used by ‘Z’ ml. M2 V2 = M4 V4

Where,
M2 = Molarity of EDTA,
V2= Volume of EDTA (Z ml).
M4 = Molarity of Permanent hard water,
V4 = Volume of Permanent hard water (20 ml)

Permanent Hardness = M4 × Molecular weight of CaCO3 (100) × One Litre (1000ml)
= M4 × 105 ppm

# 4. Determination of Temporary Hardness:

- Temporary Hardness = Total Hardness - Permanent Hardness

**Potable Water**: The Water used for drinking purpose is called potable water

# Specification for drinking water

- It should be bacteria free
- It should not contain any suspended impurities
- It should not have bad taste.
- It should not contain toxic materials such as lead, arsenic, chromium and copper.
- pH should be in the range 7 to 8.5
- It should be slightly alkaline
- It should be free from dissolved gases like $H_2S$, $CO_2$ etc.
- Its turbidity should be less than 10 ppm.
- It should be cool
- It should be reasonably soft.

# Steps involved in the treatment of Potable water

Treatment of water for drinking purposes mainly includes the removal of suspended impurities, colloidal impurities and harmful pathogenic bacteria. The following stages are involved in purification.

1. **Screening**: The water is passed through screens having larger number of holes; it retains floating impurities like wood pieces, leaves, heaver objectives etc.

2. **Coagulation**: Coagulants like alum, sodium aluminates and Aluminum sulphate are added which produce gelatinous precipitates called flock. Flock attracts and helps accumulation of the colloidal particles resulting in setting of the colloidal particles.

# Steps involved in the treatment of Potable water

**Sedimentation**: Water is allowed to stand for few hours so that the suspended particles will det settle at the bottom of the tank.

**Filtration:** Filtration helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. In this filtration fine sand layer on the top supported by coarse sand layer, which is supported by gravel.

**Disinfection of water by sterilization**: The process of destroying the harmful bacteria is known as sterilization or disinfection.

# Disinfection of Potable water

- **By Ozonization:** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and breaks down to give nascent oxygen.

$O_3 \rightarrow O_2 + [O]$ nascent oxygen

The nascent oxygen is a powerful oxidizing agent and kills the bacteria. **Disadvantages**: This process is costly and cannot be used in large scale, due to unstable of ozone cannot be stored for long time.

- **By Chlorination:** The process of adding chlorine to water is called chlorination. Chlorination can be done by the following methods.

# Disinfection of Potable water

**By adding Chlorine gas**: Chlorine gas is a very good disinfectant, which can be bubbled in the water. In this process calculated amount of chlorine gas is passed in order to destroy the pathogenic bacteria is called chlorination. Chlorine is also reacts with water and generates hypochlorous acid and nascent oxygen, which acts a powerful oxidizing agent and kills the bacteria.

$$Cl_2 + H_2O \rightarrow HOCl \text{ (Hypochlorous acid)} + HCl$$

$$HOCl \rightarrow HCl + [O] \text{ nascent oxygen}$$

**By adding Chloramine**: When chlorine and ammonia are mixed in the ratio 2:1 a compound chloramine is formed.

$$Cl_2 + NH_3 \rightarrow ClNH_2 + HCl \text{ Chloramine}$$

# Disinfection of Potable water

$ClNH_2 + H_2O \rightarrow NH_3 + HOCl$ (Hypochlorous acid)

$HOCl \rightarrow HCl + [O]$ nascent oxygen

Chloramine compounds decompose slowly to give nascent oxygen which will be act as good disinfectant than the Chlorine.

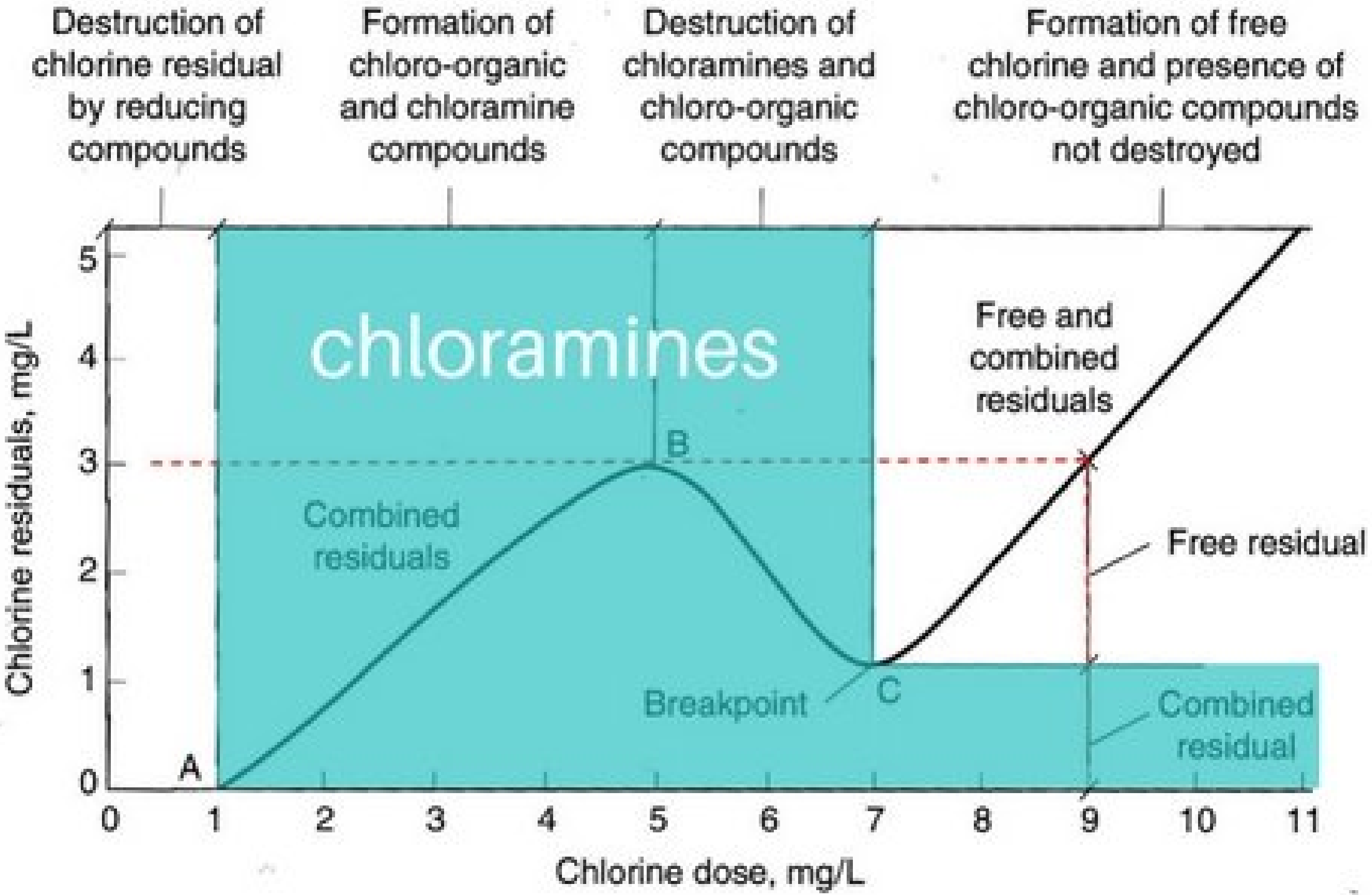
Chloramine gives good taste to the treated water.

# BREAK POINT CHLORINATION

**Break-point chlorination:** The amount of chlorine required to kill bacteria and to remove organic matter is called breakpoint chlorination.

The water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as shown below which gives the break-point chlorination.

From graph it is clear that: ‘a’ gms of chlorine added oxidizes reducing impurities of water.
‘b’ gms of chlorine added forms chloramines and other chloro compounds.
‘c’ gms of chlorine added causes destruction of bacteria.
‘d’ gms of chlorine is residual chlorine. ‘c’ gms is the break point for addition of chlorine to water. This is called break- point chlorination.

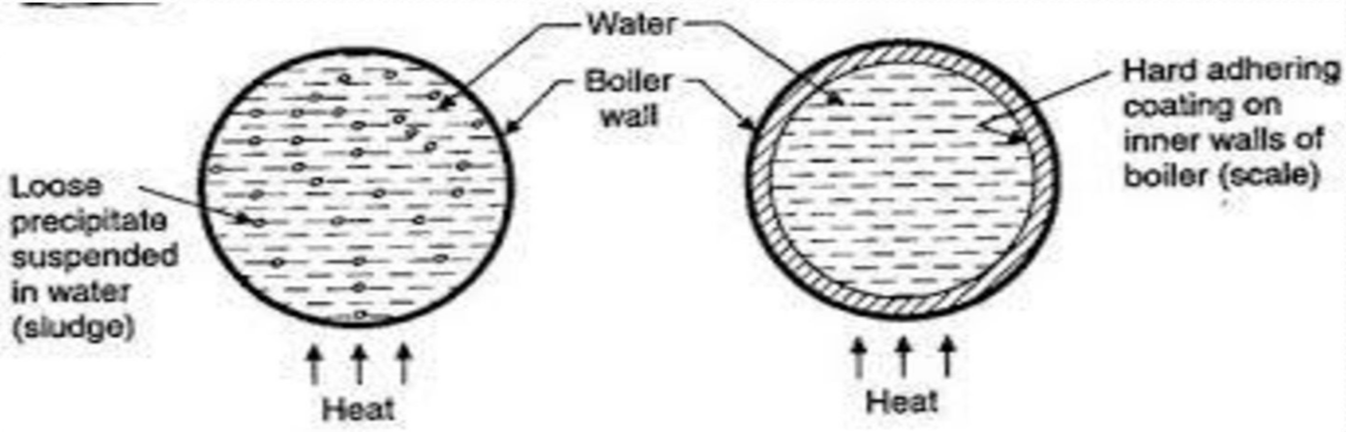


Destruction of chlorine residual by reducing compounds
Formation of chloro-organic and chloramine compounds
Destruction of chloramines and chloro-organic compounds
Formation of free chlorine and presence of chloro-organic compounds not destroyed
chloramines
Free and combined residuals
B
Combined residuals
Free residual
Breakpoint
C
Combined residual
A
Chlorine residuals, mg/L
0
1
2
3
4
5
Chlorine dose, mg/L
0
1
2
3
4
5
6
7
8
9
10
11

Boiler troubles

# Sludge & Scale

- Continous evaporation of water takes place & conc. of dissolved salts gets increased & at saturation point forms ppts. on the inner walls of the boiler.
- Sludges : If loose & slimy ppts formed.
- Scales : If sticky, hard & adhernt coat formed.
-
- Sludge Scale



# Sludge

## ❖ FORMATION:

- Where flow of water is slow
- At colder region
- By substances which have greater solubility in the hot water.
- $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

## ❖ DISADVANTAGES:

- Poor conductor of heat hence more consumption of time and fuel.
- Disturbs functioning of boiler & settles in the regions of poor water circulation.

## ❖ PREVENTION :

- By using soft water
- By using blow down pipe operation .

# Scale

## ❖ FORMATION :

➢ Decomposition of $Ca(HCO_3)_2$ :

- $Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$

  Soft Scale

- $CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$

➢ Deposition of $CaSO_4$ :

- Soluble in cold water
- As temp. ↑ solubility of $CaSO_4$ ↓

  hard scale

➢ Hydrolysis of Mg salts

- $MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$

➢ Presence of $(SiO_2)$

# Scale

## DISADVANTAGES

- Fuel Wastage
- Lowering of boiler safety
- Decreased efficiency
- Danger of explosion

## Removal

- Using wire brush
- By using chemicals :
- $CaCO_3$ scales by 5-10% HCl
- $CaSO_4$ scales by EDTA
- Blow down pipe operation
- By giving thermal shocks

# Caustic Embrittlement

- formation of brittle and incrystalline cracks in the boiler shell due to the accumulation of caustic substances

- Cause

- Presence of alkali-metal carbonates and bicarbonates in feed water
- presence of sodium sulphate.
- Sodium carbonate is used in softening of water by lime soda process, due to this some sodium carbonate may be left behind in the water.

## Process

- $Na_2CO_3$ used for softening of water & some of which remain unreacted

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

- As Conc. of NaOH increases, water flows into minute hair cracks by capillary action.
- As water evaporates, conc. of NaOH increases further and react with iron of boiler, (thereby dissolving Iron of boiler as Sodium ferroate), hence cause Embrittlement.
- This causes embrittlement of boiler parts such as bends, joints, reverts etc, due to which the boiler gets fail.etc.

## prevention :

- Use of $Na_3PO_4$ instead of $Na_2CO_3$
- By adding tanin & lignin that blocks the hair cracks
- By adding $NaSO_4$ that also blocks the cracks

# Internal Treatment of Water

Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into compounds is called internal treatment of the boiler feed water. Internal treatment can be done following types.

**Colloidal conditioning**:

The addition of organic substances such as Kerosene, tannin, Gel. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

# Internal Treatment of Water

**Phosphate conditioning:** The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation.

$$3CaCl2 + 2Na3PO4 \rightarrow Ca3(PO4)2 + 6NaCl$$

$$3MgSO4 + 2Na3PO4 \rightarrow Mg3(PO4)2 + 3Na2SO4$$

Generally three types of Phosphates are employed.

i. Trisodium Phosphate (Na3PO4): is too alkaline used for treat to too acidic water.

ii. Disodium Phosphate (Na2HPO4): is weakly alkaline used for treat to weakly acidic water.

iii.Sodium dihydrogen Phosphate (Na H2PO4): is too acidic used for treat to too alkaline water.

# Internal Treatment of Water

**Calgon conditioning**: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$. Calgon = Sodium hexametaphosphate = $Na_2 [Na_4 (PO_3)_6]$

$$Na_2 [Na_4 (PO_3)_6] \rightarrow 2Na^+ + [Na_4P_6O_{18}]^{-2}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{-2} \rightarrow [Ca_2 P_6O_{18}]^{-2} + 2Na_2SO_4$$

# Ion Exchange or De-ionization or De-mineralisation process

- Hard water is allowed to pass through ion exchangers when soft water, free from all the minerals and hardness causing as well as the other ions is obtained.

- Types
  - Cation Exchange Column represented with its $H^+$ ions
  - Anion Exchange Column represented with its $OH^-$ ions

# Ion exchange process

Ion exchange process is also known as demineralization process. Ion- Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the “functional Groups” attached to the chains are responsible for the ion-exchanging properties.

- Resins with acidic functional group are capable of exchanging H+ ions with other cations.
- Resins with basic functional groups are capable of exchanging OH− ions with other anions.

Resins are classified as:

- Cation Exchange Resins
- Anion Exchange Resins.

# Ion exchange process

- **Cation Exchange Resins:**

Cation exchange resins are styrene divinylbenzene co-polymers, which on sulphonation (or) carboxylation, which contains –COOH, –SO3H functional groups which responsible for exchanging their hydrogen ions with cations in water.

- **Anion Exchange Resins:**

Anion exchange resins are Phenol formaldehyde (or) amine formaldehyde copolymers, which contains amino or basic functional groups which responsible for exchanging their OH− ions with anions in water.

# Ion exchange process

**Process:**

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove $Ca+2$ and $Mg+2$ ions and exchange equivalent amount of $H+$ ions.

Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of $OH-$ ions.

Thus by passing hard water through cation hardness is observed by the following reactions. $H +$ and $OH-$ ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

$$H + + OH- \rightarrow H2O$$

The water coming out from the exchanger is ion free from anions and cations. Thus water of zero hardness is obtained.

## Process

### Cation Exchange column :

$$\underset{\text{Cation exchange resin}}{2RH^{+}} + \underset{\text{H. W.}}{Ca^{+2}} \longrightarrow \underset{\text{Cation exchange resin}}{R2Ca^{+2}} + \underset{\text{S. W.}}{2H^{+}}$$

### Anion Exchange column :

$$\underset{\text{Anion exchange resin}}{R'OH^{-}} + \underset{\text{H. W.}}{Cl^{-}} \longrightarrow \underset{\text{Anion exchange resin}}{R'Cl^{-}} + \underset{\text{S. W.}}{OH^{-}}$$

$$\underset{\text{Anion exchange resin}}{2R'OH^{-}} + \underset{\text{H. W.}}{SO4^{-2}} \longrightarrow \underset{\text{Anion exchange resin}}{R_2'SO4^{-2}} + \underset{\text{S. W.}}{2OH^{-}}$$

## Regneration:

### CationExchange column :

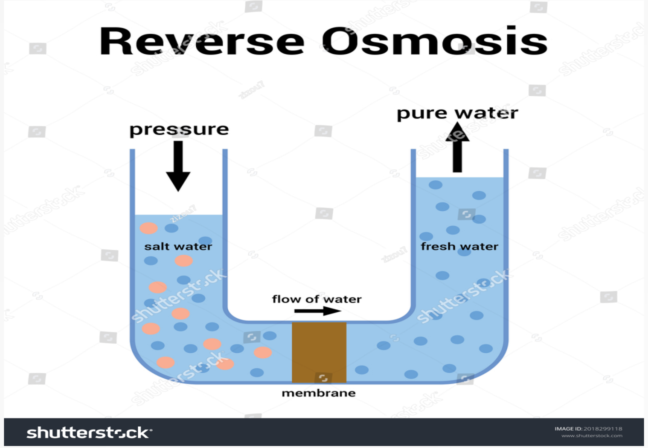
$$\underset{\text{Saturated Cation exchange resin}}{R_2Ca^{+2}} + \underset{\text{dil. acidic sol.}}{2H^{+}} \longrightarrow \underset{\text{Regenerated Cation exchange resin}}{2RH^{+}} + \underset{\text{washings}}{Ca^{+2}}$$

### Anion Exchange column :

$$\underset{\text{Saturated anion exchange resin}}{R_2'SO4^{-2}} + \underset{\text{dil. Basic sol.}}{2OH^{-}} \longrightarrow \underset{\text{Regenerated Cation exchange resin}}{2R'OH^{-}} + \underset{\text{washings}}{SO4^{-2}}$$

# Reverse osmosis:

- Reverse Osmosis is a process in which pressure greater than the osmotic pressure is applied on the high concentration side of the membrane, the flow of solvent move from concentrated side to dilute side across the membrane.



# Method:

- In this process pure water is separated from salt water. 15-40 kg/cm2 pressure is applied for separating the water from its contaminants.
- The membranes used are cellulose acetate, polymethyl acrylate and polyamide polymers.
- The process is also known as super or hyper filtration.

# Deflouridation

Fluorine is most active element found in naturally occurring rocks.

Defluoridation is the removal of excess fluoride from water

Fluoride is precipitated using 500mg/l of alum,30mg/l of lime with small amount of bleaching powder 3 mg/l for disinfection

# Steps involved in the Nalgonda technique:

Raw water → mixer → flocculation →
sedimentation → filtration → disinfection