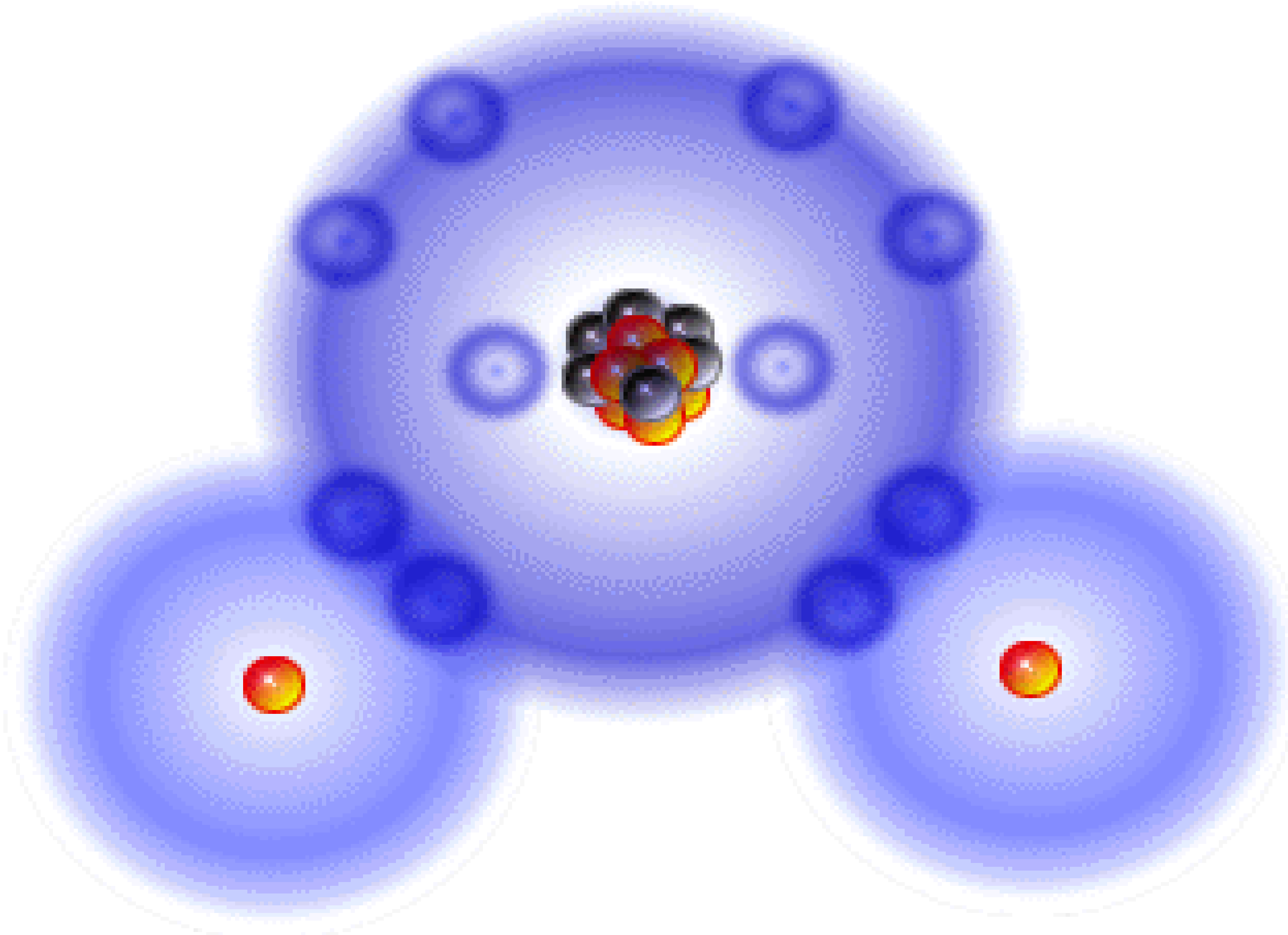
Water Chemistry



Contents

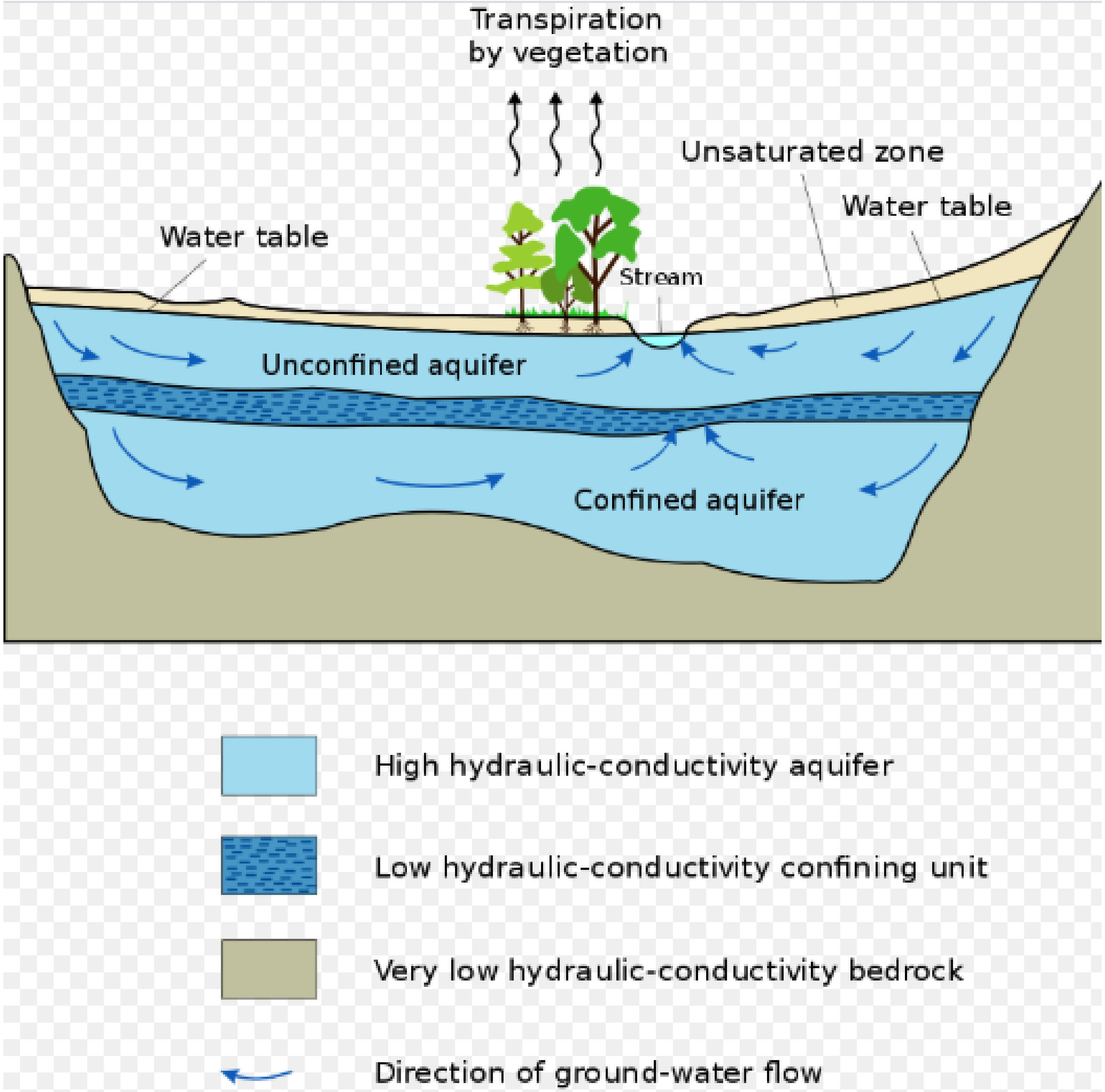
- Types of water
- Impurities
- Hardness
- Alkalinity
- Softening of water

Sources of water

Surface water:

- **Rain water:** Purest form of water.
- **River water:** Contains dissolved chlorides, sulfates & bicarbonates of Na, Mg, Ca & Fe.
- **Lake water:** Less minerals, high organic matter.
- **Sea water:** Most impure form, containing dissolved salts.

- Underground water
  - Spring water
  - Well water


Transpiration
by vegetation
Unsaturated zone
Water table
Water table
Stream
Unconfined aquifer
Confined aquifer
High hydraulic-conductivity aquifer
Low hydraulic-conductivity confining unit
Very low hydraulic-conductivity bedrock
Direction of ground-water flow

Impurities

1. Physical
2. Chemical
3. Biological

1. Physical Impurities

S.No.	Type	Example	Effect
1.	Metallic substances	Salts of Fe, Mn, etc.	Color
2.	Colloidal impurities	Clay, slit	Turbidity
		Unusual amounts of salts	Brackish taste
		Fe, Mn, Al, SO_4^{-2}, excess of lime	Bitter taste
		Large amount of Na_2CO_3	Soapy taste
		Dissolved CO_2 & nitrates	Palatable taste
3.	Organic & Inorganic substances	Sulfides, alcohols, aldehydes, phenols, etc.	Odour

2. Chemical Impurities

S.No.	Type	Example	Effect
1.	Inorganic & organic chemicals	Toxic substances released from dyeing, paints, insectides, pesticides industry, etc.	On human health
2.	Dissolved oxygen		Corrosion

3. Biological Impurities

- Microorganisms
- Bacteria
- Algae
- Fungi

Hardness

- Prevention of lathering of soap.

$$2C_{17}H_{35}COONa \; + \; Ca^{+2}/Mg^{+2} \rightarrow (Mg^{+2}/Ca^{+2})(C_{17}H_{35}COO)_2 + 2Na^{+}$$

sod stearate (soap) — Insoluble scum

Types of Hardness

- **Temporary:**
  - ➢Dissolved bicarbonates of Ca, Mg & other heavy metals.
  - ➢Carbonates of iron.
  - ➢Removed by boiling water.
  - ➢$Ca(HCO_3)_2 \xrightarrow{Boil} CaCO_3\downarrow + H_2O + CO_2\uparrow$
  - ➢$Mg(HCO_3)_2 \xrightarrow{Boil} Mg(OH)_2\downarrow + 2CO_2\uparrow$

- **Permanent:**
  - ➢Due to dissolved chlorides & sulfates of Ca, Mg, Fe & other heavy metals.
  - ➢Cannot be removed by boiling.

Advantages of Hardness

- Better taste
- Strength to teeth due to dissolved Ca^{+2} ions
- Prevention of poisonous lead in drinking water

Disadvantages of Hardness

- Production of scum with soap
- Washing and bathing
- Cooking and drinking
- Textile industry
- Sugar industry
- Dyeing industry
- Paper industry
- Laundry
- Concrete
- Pharmaceutical
- Steam generation

Scale formation inside the pipes/boilers

Hardness-scale

1. **ppm:** Parts of $CaCO_3$ per 10^6 parts of water.
2. **Clarke's degree (˚Cl):** Parts of $CaCO_3$ per 70,000 parts of water.
3. **Degree French (˚Fr):** Parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

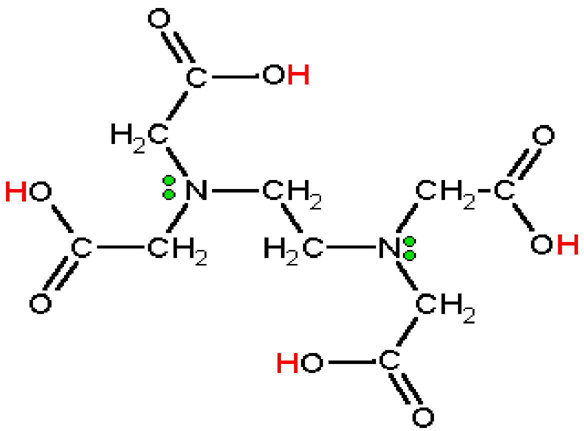
Relation between different units:

$$1ppm = 1mg/lt = 0.1^\circ Fr = 0.07^\circ Cl$$

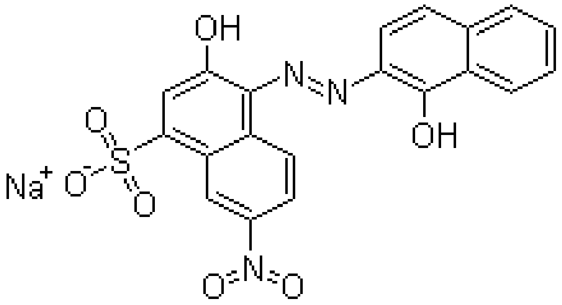
Determination of Hardness

1. EDTA Method
2. Soap Titration Method

1. EDTA Method



Ethylene diamine tetraacetic acid

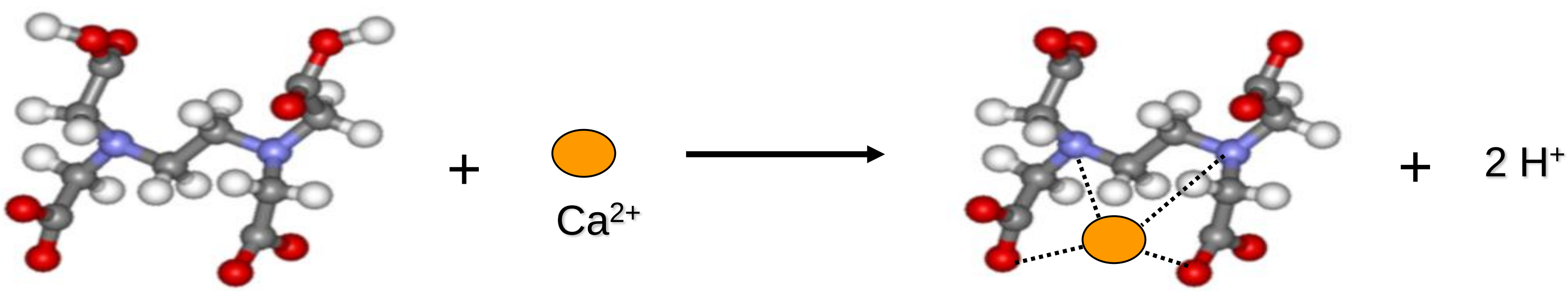


3-Hydroxy-4-(1-hydroxy-2-naphthylazo)-7-nitro-1-naphthalene sulfonic acid sodium salt

(Mordant Black 11)

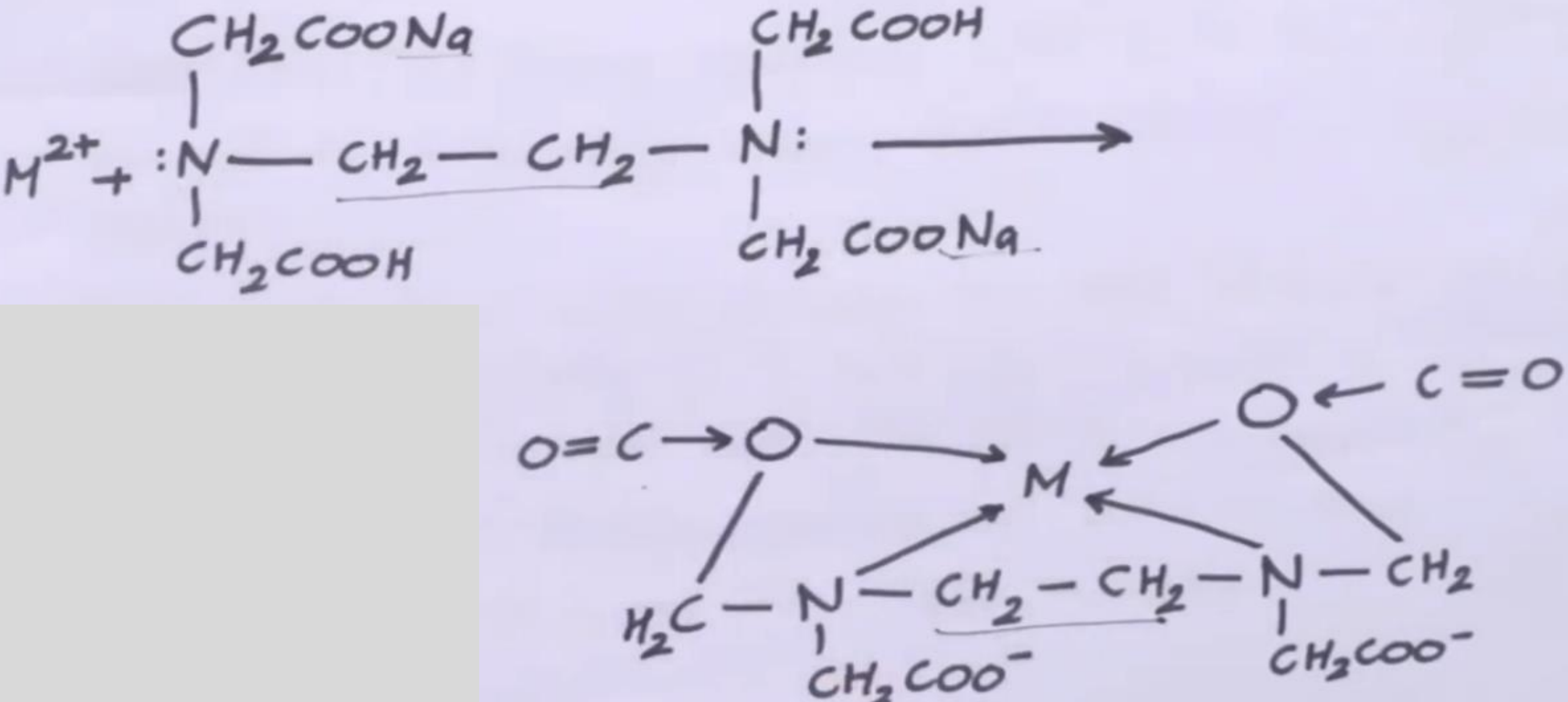
→ EDTA is a hexadentate ligand. It binds the metal ions in water i.e. Ca^{2+} or Mg^{2+} to give highly stable chelate complex. (These metal ions are bonded via oxygen or nitrogen from EDTA molecule).

→ Therefore, this method is called as complex metric titration



H_2EDTA^{2-}

Ca^{2+} ion chelated by EDTA

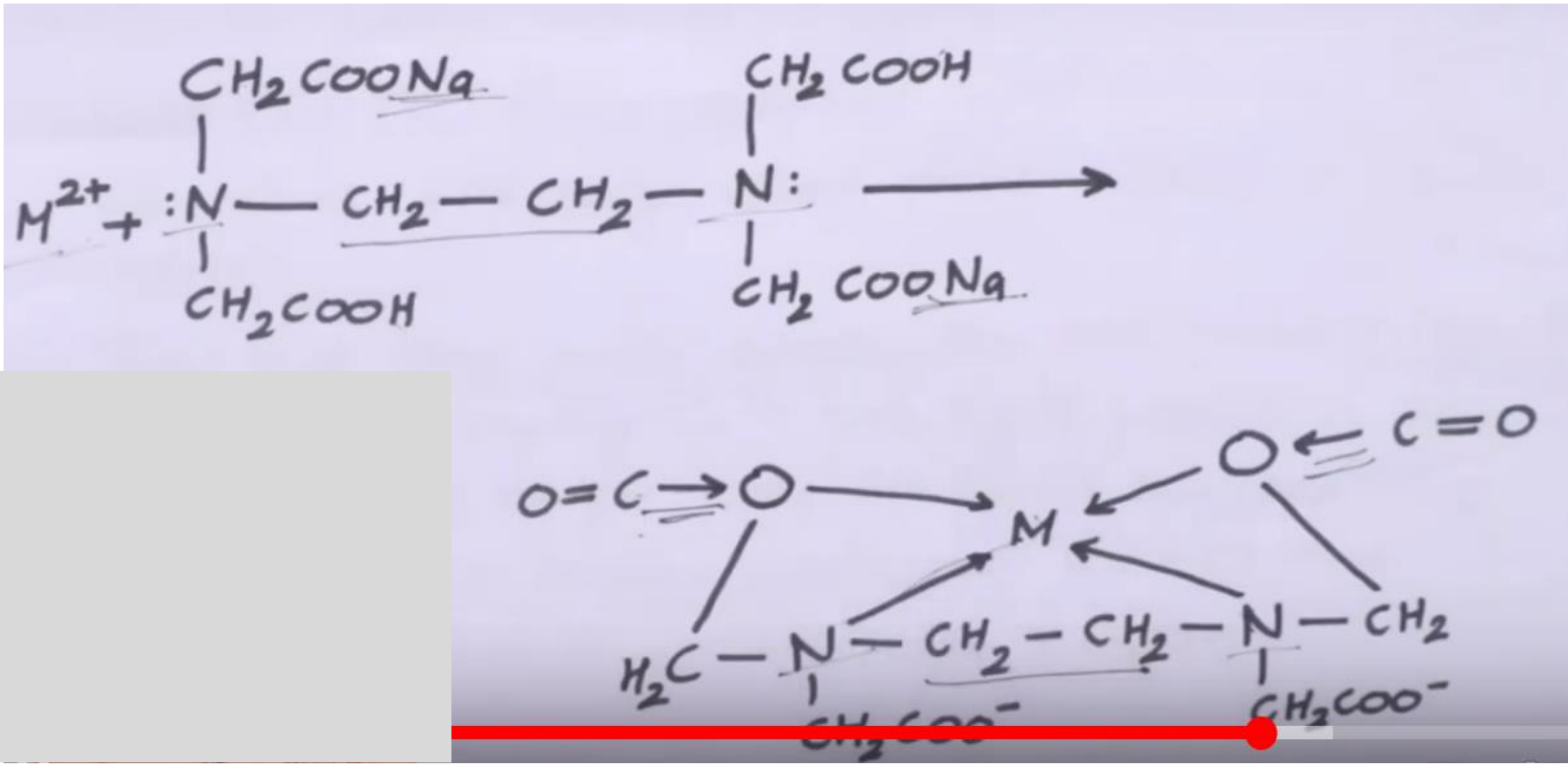


CH2COONa
M2+ + :N— CH2— CH2— N:
CH2COOH
CH2 COOH
CH2 COONa
O=C→O
M
O← C=O
H2C — N— CH2 – CH2 — N — CH2
CH2COO−
CH2COO−

Principle of EDTA Method

→ The di-sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) forms complexes with Ca^{2+} and Mg^{2+}, as well as with many other metal cations, in aqueous solution.

→ Thus, in a hard water sample, the total hardness can be determined by titrating Ca^{2+} and Mg^{2+} present in an aliquot of the sample with Na EDTA solution, using NH_4Cl. NH_4OH buffer solution of pH = 10 and Eriochrome Black T as the metal indicator.



→ At pH 10, EBT indicator form wine red coloured unstable complex with Ca^{+2}/Mg^{+2} ions in hard water.

→ This complex is broken by EDTA solution during titration, giving stable complex with ions; and releasing EBT indicator solution which is blue in colour. Hence the colour change is from wine red to blue.

Blue is EBT's own colour.

REACTION

$$Mg^{+2}/Ca^{+2} + EBT \xrightarrow[pH=10]{\text{Buffer} \; NH_4Cl-NH_4OH} \left[\begin{matrix}Mg^{+2}\\ Ca^{+2}\end{matrix} - EBT\right]$$

(Wine coloured unstable complex)

$$\Big\downarrow \text{Titration with EDTA solution}$$

$$EBT + \left[\begin{matrix}Mg^{+2}\\ Ca^{+2}\end{matrix} - EDTA\right]$$

(Blue coloured indicator released) (Colourless stable complex)

Advantages of EDTA Method

- Greater accuracy
- Easy to run
- Rapid

2. Soap Titration Method

- No indicator.
- Indicated by the formation of lather, persisting for at least 2 minutes.

Problems…….

1. A water sample contains 204mg of $CaSO_4$ per litre. Calculate the hardness in terms of $CaCO_3$.

   [150ppm]

2. How many grams of $FeSO_4$ dissolved per litre gives 210.5ppm of hardness?

   [319.96g]

3. Calculate the temporary and permanent hardness of a water sample containing: $Mg(HCO_3)_2$ = 7.3mg/lt; $Ca(HCO_3)_2$ = 16.2mg/lt; $MgCl_2$ = 9.5mg/lt; $CaSO_4$ = 13.6mg/lt.

   [15ppm, 20ppm]

Alkalinity

- **Responsible ions:** CO_3^{-2}, HCO_3^-, OH^-
- **Coexisting ions:** CO_3^{-2}-HCO_3^- & CO_3^{-2}-OH^-
- HCO_3^-—OH^-:

$$HCO_3^- + OH^- \rightarrow CO_3^{-2} + H_2O$$

- **Indicators:** Phenolphthalein

  Methyl orange

Calculation of Alkalinity of water

- $OH^- + H^+ \rightarrow H_2O$ [P]
- $CO_3^{-2} + H^+ \rightarrow HCO_3^-$ [M]
- $HCO_3^- + H^+ \rightarrow H_2O + CO_2$

Relation between P & M	OH^-	CO_3^{-2}	HCO_3^-
P = 0	0	0	M
P = 1/2M	0	2P	0
P < 1/2M	0	2P	(M – 2P)
P > 1/2M	(2P - M)	2(M - P)	0
P = M	M	0	0

SOFTENING OF HARD WATER

1. Lime-soda process
2. Zeolite or permutit process
3. Calgon process
4. Ion exchange or deionization or de-mineralization process

1. Lime-soda process

- Lime removes temporary & permanent hardness (mainly due to Mg; not useful for Ca).

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + Mg(OH)_2\downarrow + 2H_2O$$

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$$

$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2\downarrow + CaSO_4$$

$$2Fe(OH)_2 + H_2O + [O] \longrightarrow 2Fe(OH)_3\downarrow$$

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3\downarrow + 3CaSO_4$$

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

Contd.....

- Soda removes permanent hardness due to Ca.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

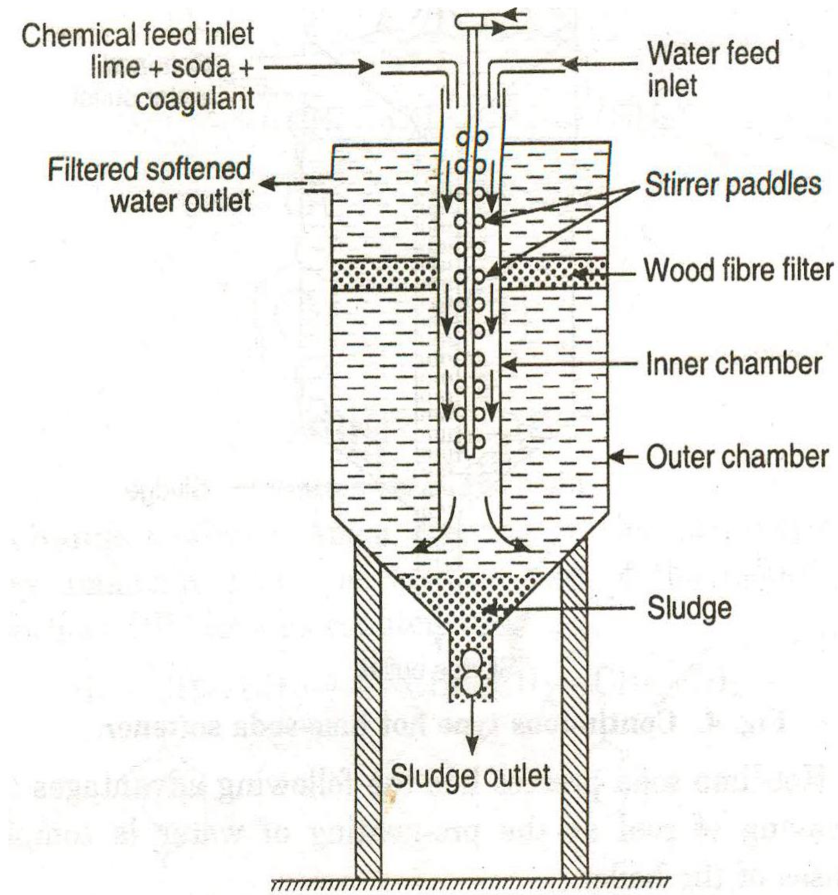
Types of Lime soda process

Two types:

1. Cold lime-soda process
2. Hot lime-soda process

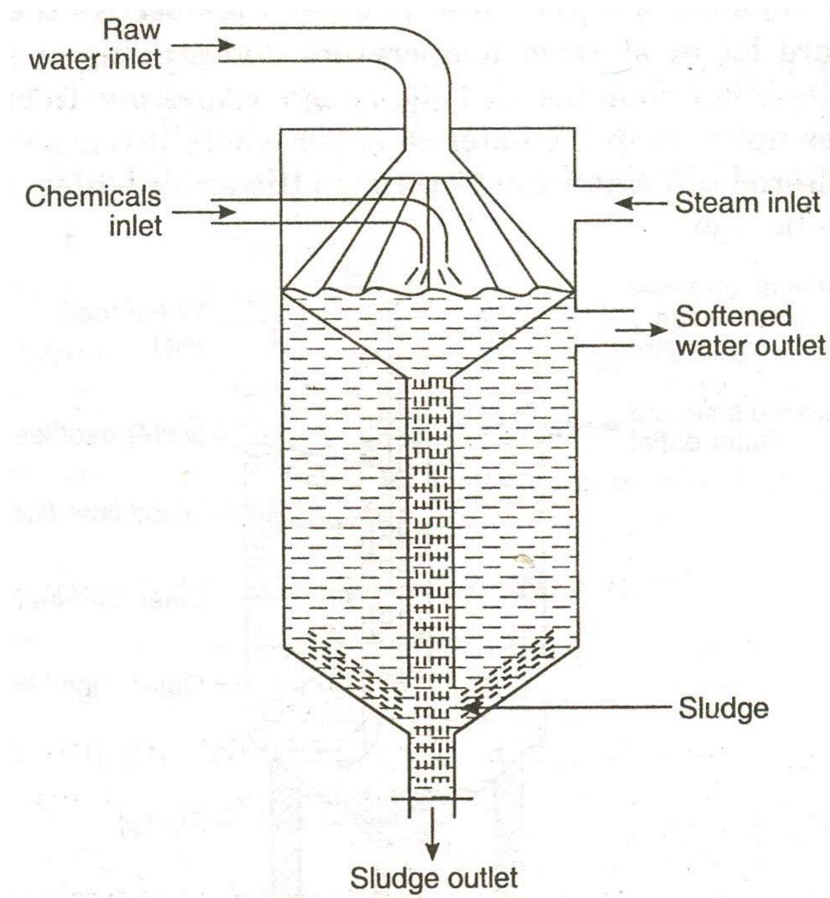
Cold Lime-soda process

- Calculated amount of lime/soda mixed with water at RT.
- Addition of coagulants to increase the size of precipitate.



Hot L-S Process

- Reaction at 80-150˚C.
- Saving of coal.
- Required time is reduced.
- Requirement of chemicals is reduced.
- No coagulant is required.



Impt……

- Lime requirement for temporary Mg hardness is double w.r.t. that for Ca hardness.
- Lime removes permanent Mg hardness, but introduces an equivalent amount of permanent Ca hardness.
- Soda is required for permanent Ca hardness. Generated Ca hardness also requires soda to be removed.

Calculations

$$Lime\ requirement = \frac{74}{100} x\ (Temporary\ Ca\ hardness + 2xTemporary\ Mg\ hardness + Permanent\ Mg\ hardness)$$

$$Soda\ requirement = \frac{106}{100} x\ (Permanent\ Ca\ hardness + Permanent\ Mg\ hardness)$$

Problem……

Calculate the amount of lime-soda needed for softening of water containing following per litre:

$Ca(HCO_3)_2$ = 162mg; $Mg(HCO_3)_2$ = 73mg; $MgCl_2$ = 95mg; $CaSO_4$ = 136mg; NaCl = 585mg.

Advantages of Lime-Soda Process

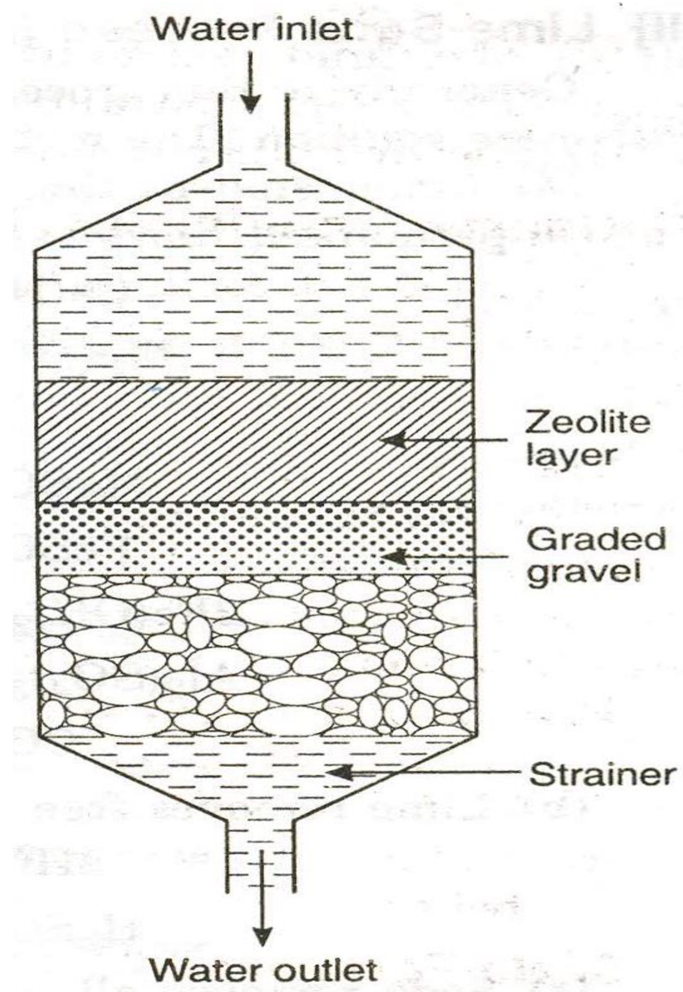
- Economical
- Removes minerals also
- Partial removal of iron & magnesium
- Produces alkaline water
  - corrosion decreases
  - Pathogenic bacteria are reduced

Disadvantages of Lime-Soda Process

- Careful operation
- Sludge disposal
- Leaves soluble salts (e.g. sodium sulfate)

2. Zeolite Process

- **Zeolite:** Sodium aluminium orthosilicate ($Na_2O.Al_2O_3.xSiO_2.yH_2O$) where, x = 2-10; y = 2-6.
- Natural or synthetic.
- Exchange their Na^+ ions by Ca^{+2} or Mg^{+2} ions in hard water.



Chemistry involved

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Ze \longrightarrow MgZe + 2NaHCO_3$$

$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$

$$CaSO_4 + Na_2Ze \longrightarrow CaZe + Na_2SO_4$$

$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

$$MgCl_2 + Na_2Ze \longrightarrow \underset{\text{(Exhausted zeolite)}}{MgZe} + 2NaCl$$

Reusage of exhausted zeolite:

$$CaZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \longrightarrow MgCl_2 + Na_2Ze$$

- **Limitations:**
  - ➢Water must be free from suspended matter & acids.
  - ➢Colored impurities should not be there.
  - ➢Lead can’t be removed.

- **Advantages:**
  - ➢Zero hardness.
  - ➢Small equipment, easy to operate.
  - ➢No sludge formation.
  - ➢Economic.

- **Disadvantages:**
  - ➢More sodium.
  - ➢HCO_3^- & CO_3^{-2} is not removed.
  - ➢No treatment to high turbidity.
  - ➢Liberation of free CO_2.

Problem…..

Hardness of 10,000lt of a water sample was completely removed by passing it through a zeolite softener. Zeolite softener required 200lt of NaCl solution containing 20,000mg/lt of NaCl for regeneration. Calculate the hardness of water sample.

[341.88ppm]

3. Calgon Process

- Calgon: Sodium hexametaphosfate $[Na_2P_6O_{18}]$

$$\underset{\text{Calgon}}{Na_2[Na_4(PO_3)_6]} \longrightarrow 2Na^+ + \underset{\text{Loose sludge}}{[Na_4P_6O_{18}]^{2-}}$$

$$[Na_4P_6O_{18}]^{2-} + 2CaCO_3 \longrightarrow \underset{\substack{\text{Soluble}\\\text{complex ion}}}{[Ca_2P_6O_{18}]^{2-}} + 2Na_2CO_3$$

4. Ion Exchange Process

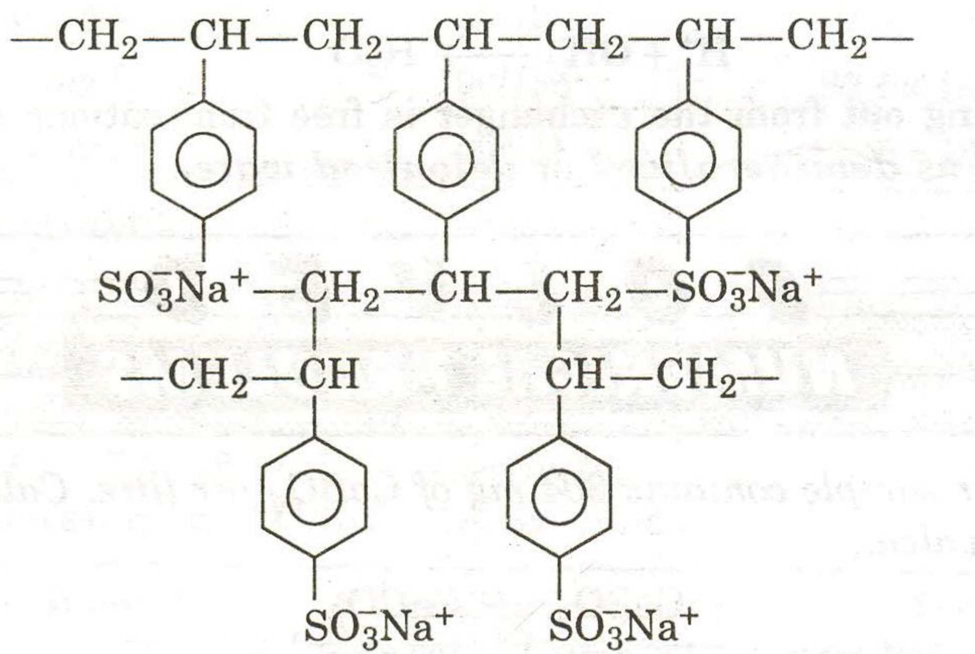
- Reversible process of ion exchange between stationary ion exchange phase & external liquid mobile phase.
- **Types of Ion Exchange Resins:**

  Cation exchange resin

  Anion exchange resin

Cation Exchange Resin

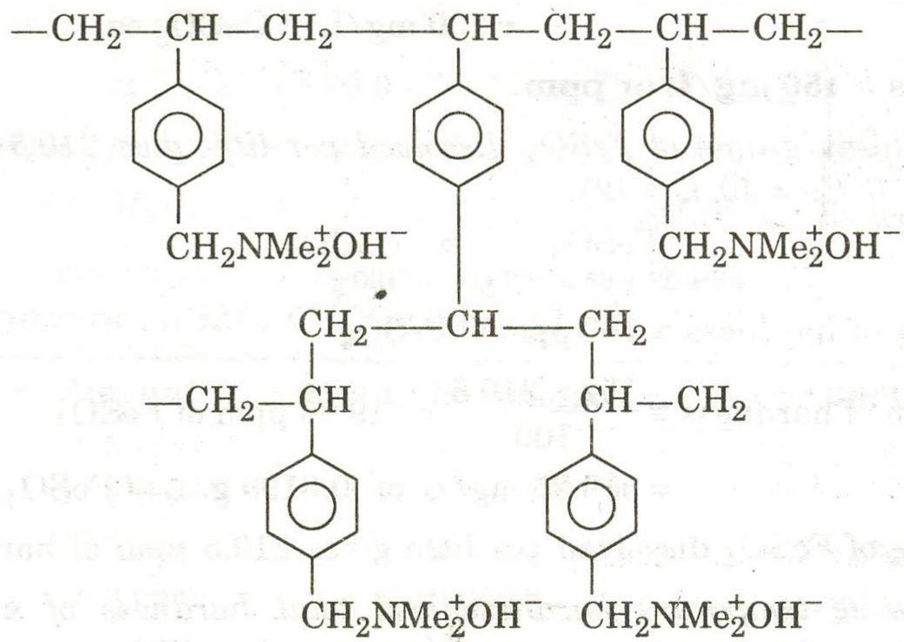
- Containing immovable sulfate ions & equal numbers of replaceable Na^+ ions.



Cation exchange resin

Anion Exchange Resin

- Containing amine or quaternary ammonia groups & equivalent amount of replaceable anions, e.g. OH^-.



Anion exchange resin

Reactions

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$

$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$

$$ROH^- + Cl^- \longrightarrow RCl^- + OH^-$$

$$2ROH^- + SO_4^{2-} \longrightarrow R_2SO_4^{2-} + 2OH^-$$

$$2ROH^- + CO_3^{2-} \longrightarrow R_2CO_3^{2-} + 2OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$

Regeneration of exchange resins:

$R_2Ca^{+2} + 2H^+ \rightarrow 2RH^+ + Ca^{+2}$ (washings)

$R'_2SO_4^{-2} + 2OH^- \rightarrow 2R'OH^- + SO_4^{-2}$ (washings)

Advantages:

- For the softening of acidic as well as alkaline water.
- Produces water of very low hardness.

Disadvantages:

- Costly.
- Expensive chemicals.