15.6 Types of Hardness

Types of hardness

1. Temporary or carbonate or alkaline hardness.
2. Permanent or non-carbonate or non-alkaline hardness.

There are two types of hardness, as :

1. Temporary or carbonate or alkaline hardness.
2. Permanent or non-carbonate or non-alkaline hardness.

15.6.1 Temporary or Carbonate or Alkaline Hardness

➤ [Second Sem. : 2002-2003]

- It is defined as the hardness due to carbonates and hydroxides of the bicarbonates of calcium, magnesium and other hardness-producing metals.
- Temporary hardness is mostly removed by mere boiling of water, where bicarbonates are decomposed producing insoluble carbonates or hydroxides.

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Calcium carbonate (Insoluble)}}{CaCO_3\downarrow} + H_2O + CO_2\uparrow$$

$$\underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{Heat}} \underset{\text{Magnesium hydroxide}}{Mg(OH)_2\downarrow} + 2CO_2\uparrow$$

$$\underset{\substack{\text{Bi-carbonates Calcium and} \\ \text{magnesium (Impurity)}}}{Ca(HCO_3)_2 / Mg(HCO_3)_2} + \underset{\substack{\text{Sodium salt of stearic acid} \\ \text{(Soluble soap)}}}{2C_{17}H_{35}COONa} \longrightarrow \underset{\substack{\text{Calcium / magnesium salt of stearic acid}}}{(C_{17}H_{35}COO)_2Ca \text{ or } (C_{17}H_{35}COO)_2Mg} + \underset{\text{Sodium Bicarbonate}}{2NaHCO_3}$$

$$\underset{\text{Or } CaSO_4 / MgSO_4}{CaCl_2 / MgCl_2} + 2C_{17}H_{35}COONa \longrightarrow (C_{17}H_{35}COO)_2Ca/Mg + 2NaCl / Na_2SO_4$$

- Soaps generally consist of sodium salts of long chain fatty acids such as oleic acid, palmitic acid and stearic acid.
- The soap consuming capacity of water is reduced due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in it.
- When the ions of these salts react with the sodium salts of long-chain fatty acids present in the soap, lather is not produced but it forms insoluble white scums or precipitates of calcium and magnesium soaps which do not possess any detergent value.

$$2\,C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2\,Ca\downarrow + 2\,NaCl$$

Sodium stearate (Sodium / Soluble soap)

Calcium stearate (Calcium / insoluble soap)

or

$$2\,C_{17}H_{35}COO^- + Ca^{2+} \longrightarrow (C_{17}H_{35}COO)_2\,Ca\downarrow$$

(ppt or curd)

$$2\,C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2\,Mg\downarrow + Na_2SO_4$$

Magnesium stearate (Magnesium / insoluble soap)

or

$$2\,C_{17}H_{35}COO^- + Mg^{2+} \longrightarrow (C_{17}H_{35}COO)_2\,Mg\downarrow$$

(ppt or curd)

- Other metal ions like Fe^{2+}, Mn^{2+} and Al^{3+} also react with soap in the same fashion, thus contributing to hardness.
- Further acids, such as carbonic acid can also cause free fatty acid to separate from soap solution and thus contribute to hardness.
- However, in practice, the hardness of a water sample is usually taken as a measure of its Ca^{2+} and Mg^{2+} content. Thus we can define hard and soft water as follows :

Hard water

Water which does not produce lather with soap solution readily but forms a white curd is called *hard water*.

Soft water

Water which lathers easily on mixing with soap solution is called *soft water*. Such type of water consequently does not contain dissolved calcium and magnesium salts in it.

Zeolite Process

$Na_2O\ Al_2O_3 . xSiO_2 . yH_2O$

$x = 2-10$, $y = 2-6$

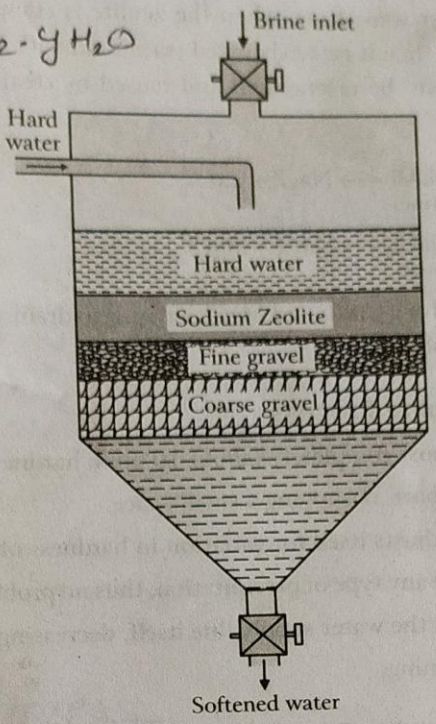


Fig. 8.6: Zeolite softener.

(ii) **Process :** In this process, hard water passes at a specified rate through a bed of active granular sodium zeolite, present in a zeolite softener, when, the Ca^{+2} and Mg^{2+} ions are taken up by the zeolite as CaZ and MgZ respectively, while the outgoing water contains equivalent amount of sodium salts.

The chemical reactions taking place in zeolite softener, are :

$$Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ + 2NaHCO_3$$

$$Mg(HCO_3)_2 + Na_2Z \longrightarrow MgZ + 2NaHCO_3$$

$$CaSO_4 + Na_2Z \longrightarrow CaZ + Na_2SO_4$$

$$CaCl_2 + Na_2Z \longrightarrow CaZ + 2NaCl$$

$$MgSO_4 + Na_2Z \longrightarrow MgZ + Na_2SO_4$$

$$MgCl_2 + Na_2Z \longrightarrow MgZ + 2NaCl$$

Small quantities of iron and manganese, present as the divalent bicarbonates, may also get removed simultaneously.

$$Fe(HCO_3)_2 + Na_2Z \longrightarrow FeZ + 2NaHCO_3$$

$$Mn(HCO_3)_2 + Na_2Z \longrightarrow MnZ + 2NaHCO_3$$

Zeolite process removes both temporary as well as permanent hardness of water.

(iii) **Regeneration** : After some time. when the zeolite is completely changed into calcium and magnesium zeolites, then it gets exhausted (saturated with Ca^{+2} and Mg^{2+} ions) and it ceases to soften water. It can be regenerated and reused by treating it with a 10% brine (sodium chloride) solution.

$$CaZ + 2NaCl \longrightarrow \underset{\text{(Brine)}}{} Na_2Z + CaCl_2$$

$$MgZ + 2NaCl \longrightarrow \underset{\text{(Brine)}}{} Na_2Z + MgCl_2$$

The washings (containing $CaCl_2$ and $MgCl_2$) are led to drain and the regenerated zeolite bed is again used for water softening.

8.13.1.1 Advantages of Zeolite Process

1. It removes the hardness almost completely (about 10 ppm. hardness only).
2. The equipment used is compact, occupying a small space.
3. The process automatically adjusts itself for variation in hardness of incoming water.
4. This process does not involve any type of precipitation, thus no problem of sludge formation occurs.
5. The plant can be installed in the water supply line itself, decreasing the cost of pumping.
6. It requires less time for softening.

8.13.1.2 Disadvantages of Zeolite Process

1. The outgoing water (treated water) contains more sodium salts.
2. This method only replaces Ca^{2+} and Mg^{2+} ions.
3. Zeolite process leaves all the acidic ions (like HCO_3^- and CO_3^{2}) as such in the softened water.
4. High turbidity water cannot be softened efficiently by zeolite process.
5. When softened water (from zeolite process) is used in boilers for steam generation, CO_2 liberated by the decomposition of $NaHCO_3$, causes corrosion.

8.13.1.3 Limitations of Zeolite Process

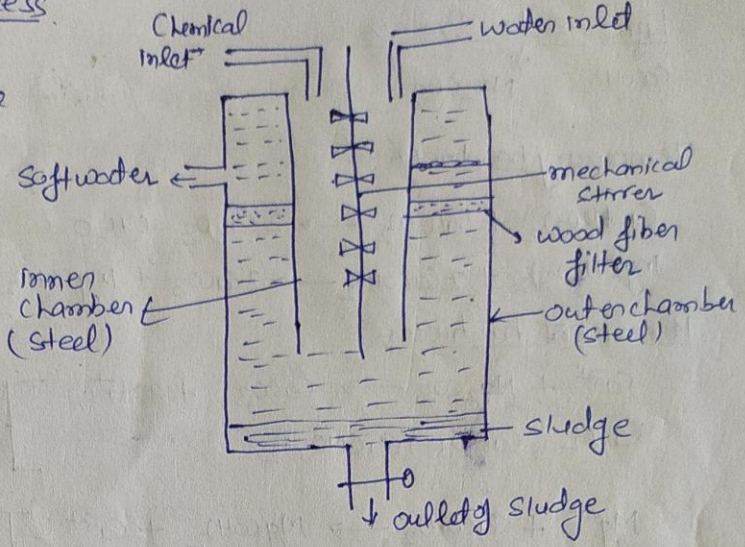
1. The water must be free from turbidity and suspended matter. Otherwise Zeolite bed (permutits) will be clogged and the rate of flow will be decreased.
2. Hot water should not be used as the zeolite tend to dissolve in it.
3. Coloured ions such as Mn^{2+} and Fe^{2+}, must be removed first, because these ions produce manganese and iron zeolites, which cannot be easily regenerated.
4. Water containing excess of acidity or alkalinity should not be used as mineral acids may destroy the zeolite bed.

8.13.2 Lime-Soda Process (L-S Process)

The principle involved in L-S process is to chemically convert all the soluble hardness-causing impurities into insoluble precipitates which may be removed by settling and filtration. In this process, a suspension of

Cold Lime- Soda Process

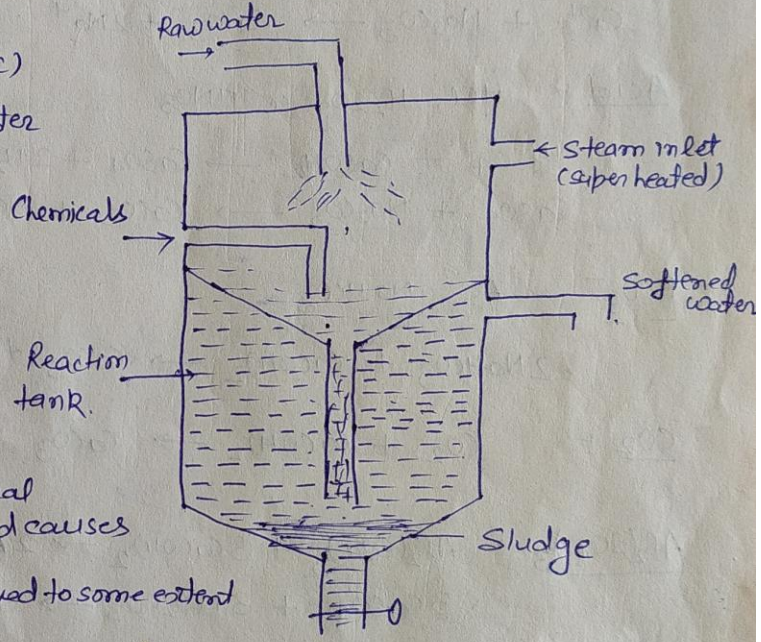
⇒ The $CaCO_3$ formed during the reaction does not ppt completely but formed supersaturated solution. Small amount of coagulants like, Alum or $Al_2(SO_4)_3$ are added for the formation of coarse precipitates.



Hot Lime- Soda Process

heated by steam (90–150°C)

Rate of reaction are much faster than cold process.



Advantages :-

① L-S process is economical
② Soft water is alkaline and causes less corrosion.
③ Fe and Mn is also removed to some extent

Dis Advantages :-

① Skilled supervision is required
② Sludge disposal is a problem
③ Can not be used for housed hold purpose as the requisite amount of chemicals is not known.
④ Softened water does not have zero hardness.

Lime-Soda Process :-

$Ca(OH)_2$ Na_2CO_3

Temporary hardness :-

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

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

Permanent hardness :-

$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$

$CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$] only 1-Soda.

$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$

$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$] 1L+1S.

Acid :- HCl, H_2SO_4 or HNO_3

$H_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O$

$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$] 1L+1S.

HCO_3^- → As $NaHCO_3$.

$2NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + Na_2CO_3$ [L-S]

CO_2 :- $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$ [1L]

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

$3CaSO_4 + 3Na_2CO_3 \longrightarrow 3CaCO_3 + 3Na_2SO_4$] 3[L+S].

$NaAlO_2$ →

Calgon Conditioning:- Calgon - Sodium hexa meta phosphate $Na_2[Na_4(PO_3)_6]$

Calgon is added to boiler water to prevent the scale and sludge formation. Calgon converts the scale forming impurity like $CaSO_4$ into soluble complex compound, which are harmless to boilers.

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

$$2CaSO_4 + [Na_4(PO_3)_6]^{2-} \longrightarrow [Ca_2(PO_3)_6]^{2-} + 2Na_2SO_4$$

(At low temperature & pressure) soluble complex

⇒ 0.5 to 5 ppm of calgon is required to prevent scale.

⇒ At high temperature & pressure →

$$2Na_2[Na_4(PO_3)_6] + 6H_2O \longrightarrow 6Na_2P_2O_7 + 6H_2$$

Sodium orthophosphate

$$CaSO_4 + Na_2P_2O_7 \longrightarrow CaP_2O_7 + Na_2SO_4$$

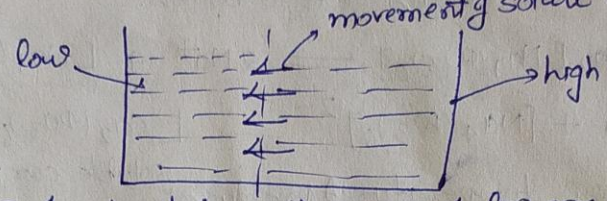
Calcium orthophosphate (loose sludge).

[Can be removed by blow down operation)

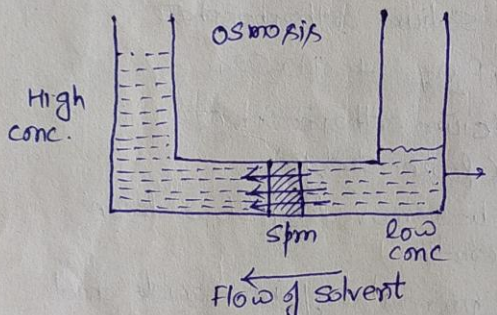
Limitation:- It is not applicable for the prevention of iron oxide and copper depositions.

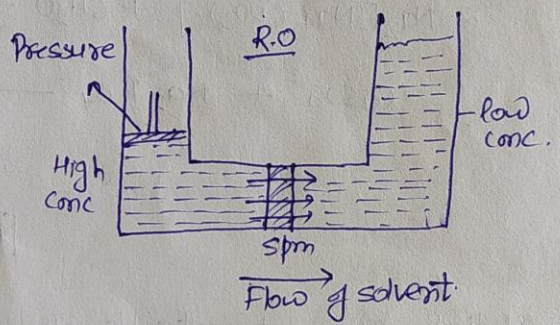
Reverse Osmosis :-

Diffusion — Movement of solute particles from region of higher concentration to region of lower concentration

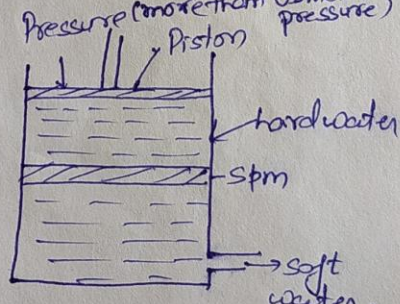


Osmosis :- The flow of solvent from the region of low conc. to high conc. through semi permeable membrane. The flow continues till the concentration is equal on both the side. The pressure developed on spm is called osmotic pressure.





R.O :- If a hydrostatic pressure more than osmotic pressure is applied on the concentrated side, the flow of solvent starts from high conc to low conc. side through spm.



Advantages :-

① Silica can be removed ② Maintenance cost is low
③ life time of membrane is high
④ low capital cost ⑤ operates at low temp.
(6) Water is free from micro organisms (bacteria)

Disadvantages :-

① Wastage of water.
② Water essential minerals are also removed
③ About 200psi more than the osmotic pressure is required.

Portable water :-

Boiler Feed water :- Used for generation of steam in industries.
conditions for boiler feed water.

(i) Hardness — below 0.2 ppm
(ii) Alkalinity — 0.15 - 0.45 ppm.
(Caustic)
(iii) Soda alkalinity → 0.45 - 1.00 ppm
(iv) Soda ash — 0.3 - 0.5 ppm.

Sludge & Scale formation :- In boiler, water is continously converted into steam, increasing the concentration of salt. A stage is reached when these changes into a loose and slimy ppt called sludge and if there are hard adhering coatings, these are called scales. Thus scales are hard deposits, which stick very firmly on the inner surface of boilers. Types of scales

(a) Alkaline earth metal scales — $CaCO_3$, $CaSO_4$, $Mg(OH)_2$, $Mg_3(PO_4)_2$,

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

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

(b) Iron oxide scale :- Iron oxide, silicates and phosphates
(c) Copper scales :- 20-30% of copper with iron oxide and salts of Ca & Mg.
(d) Silicates scales :- Calcium and aluminium silicates.

Effects of sludge or scale formation :-
(1) They are poor conductor of heat so they hinder the flow of heat to water
(2) Decreases the efficiency of boiler by blocking the boiler tubes
(3) Scales of $MgCl_2$ corrode the plates
(4) ~~Eat~~ Caustic embrittlement →

Prevention of Sludge & Scale formation :-
(1) By adding kerosene, tannins, These colloids gets coated over the scale, forming ppt, and are suspended in water, These can be easily blown off.
(2) By Carbonate conditioning :- Scales react with Na_2CO_3 and form insoluble $CaCO_3$.

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

(3) Phosphate conditioning :- Soluble Sodium phosphate is added to boiler to ppt Ca ions in the form of non adherent ppt of Calcium phosphate and thus scale formation is prevented.

$$2Na_3PO_4 + 3CaCO_3 \longrightarrow Ca_3(PO_4)_2 + 3Na_2CO_3$$

(4) Calgon Conditioning :-

Boiler Corrosion :-

(i) Dissolved oxygen :- in water at very high temp, attacks boiler materials.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2 \downarrow$$

$$\downarrow O_2$$

$$Fe_2O_3 \cdot 2H_2O$$

Rust.

Removel :- By sodium sulphite, hydrazine or sodium sulphide

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$

(ii) Dissolved CO_2 :-

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad \text{(slow corrosion)}$$

Removel by NH_4OH →

$$NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

(iii) Acids from dissolved salts :-

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

$$Fe + HCl \longrightarrow FeCl_2$$

$$\downarrow H_2O$$

$$Fe(OH)_2$$

Lignin → complex organic polymer – formation of cell walls of wood & bark

tanin → polyphenols – " " " "

Priming and Foaming :-

When a boiler is producing steam very rapidly, some water particles are carried along with the steam. The process of wet steam formation is called priming. It is due to:

(1) The presence of large quantities of alkali sulphate and chloride in water.
(2) Sudden boiling
(3) Sudden increase in steam production rate
(4) Improper boiler design.

Foaming is persistent formation of foam or bubbles in the boiler, which do not break easily. It is due to the presence of oil (reduces the surface tension of water).

Priming and foaming can be prevented by

(1) Addition of antifoaming agent like castor oil. (Arandi)
(2) " " sodium aluminate
3. Avoiding rapid change in steaming rate.

Caustic Embrittlement :- During L-S process some Na_2CO_3 is left with soft water which decomposes to NaOH & CO_2

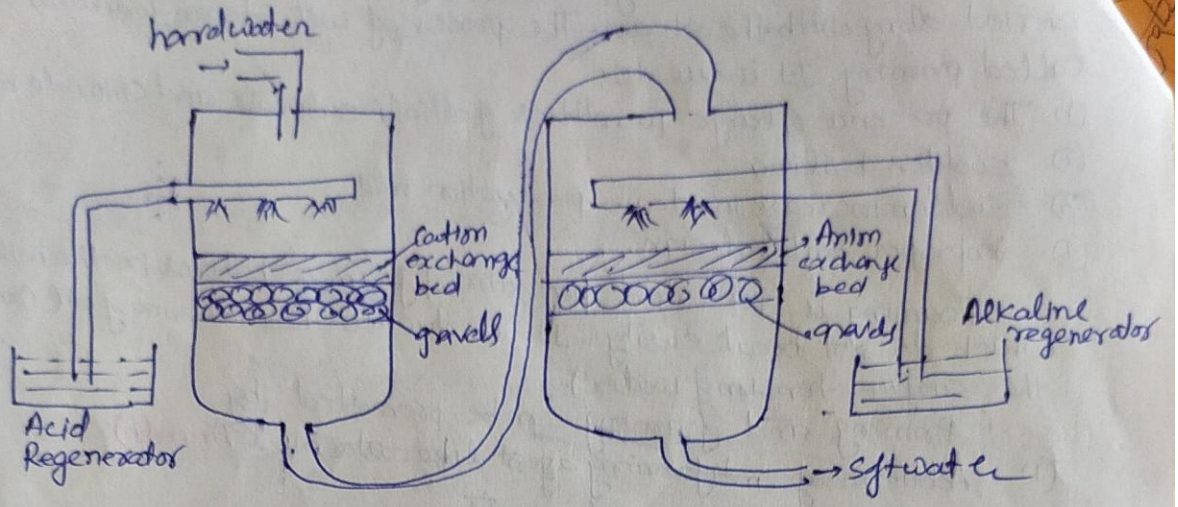
$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The NaOH containing water flows into the small cracks of boiler by capillary action, dissolving the iron of surrounding area inside the boiler. At these areas corrosion takes place in such a manner that intergranular cracks occur in an irregular fashion, this is called caustic embrittlement.

Prevention

1. By addition of tannin & or lignin.
2. Na_2CO_3 can be replaced by ~~$Na_2(PO_3)$~~ sodium phosphate
3. Sodium phosphate blocks hair cracks in the boiler.

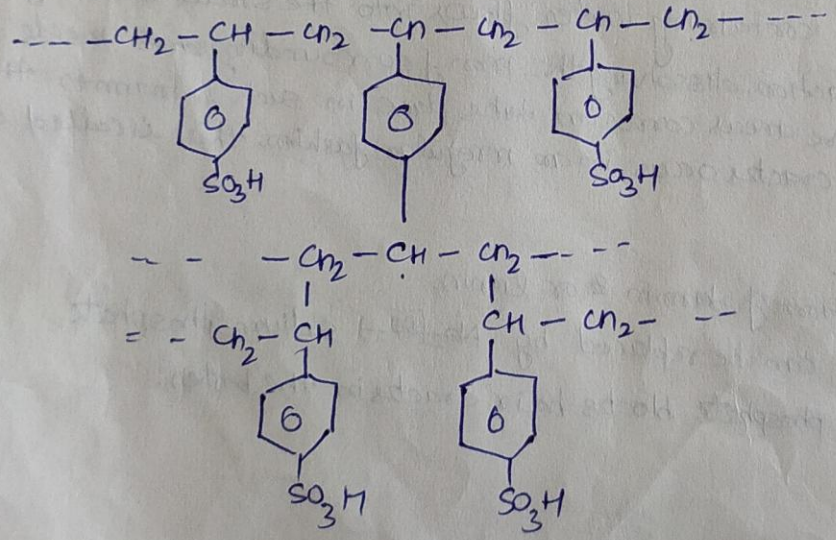
Ion exchange process :-



Cation ion exchanger have functional group → SO_3H, $COOH$, OH etc

Anion " " " " → $NMe_3^{\oplus}OH^{\ominus}$, NH_2, etc

Cation or anion exchange Resins → are mainly styrene – divinyl benzene copolymer



$SO_3H \longrightarrow CH_2\,NMe_2^{+}OH^{-}$

eactions cation exchanger -

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

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

Anion exchanger

$$R'OH^- + Cl^- \longrightarrow R'Cl^- + OH^-$$

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

$$2R'OH^- + CO_3^{2-} \longrightarrow R_2'CO_3^{2-} + 2OH^-$$

H^+ & OH^- ions released from cation and anion exchange columns respectively get combined to produce H_2O molecule

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

Thus the water coming out from the exchanger is free from cations as well as anions. Ion-free water known as deionized or demineralized water.

Regeneration :-

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+} \quad (HCl \text{ or } H_2SO_4 \text{ dil.})$$

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2R_2OH^- + SO_4^{2-} \quad (\text{dil } NaOH)$$

Advantages :-

① The process can be used to soften highly acidic or alkaline water.
② Water of hardness 2 ppm can be produced. which is good for high pressure boilers.
③ Resin can be regenerated

Disadvantages :-

① Equipment is costly and more expensive chemicals are needed.
② Turbidity of more than 10 ppm reduceses the output of process.