UNIT-3 (1) (1) UNIT-3

WATER AND ITS TREATMENT · PART I & II

Water is natural wonderful and is the most common important and useful compound of hydrogen and oxygen for surviving of all living organisms.

Human body contains 70-75% of water which regulates life process such a digestion of food, transportation of nutrients, excreation of body wastes. It is important participant of photosynthesis.

Sources of Water

- Rain Water
- Surface Water
  - River Water
  - Lake Water
  - Sea Water
- Underground Water
  - Well Water
  - Spring Water etc.

Impurities of Water

There are the following impurities, which have been found as common present in water.

Dissolved Impurities - Water may contain soluble inorganic or organic salts, gases etc.

(i) Inorganic Salts These are usually bicarb[onates], chlorides, nitrates, Sulphates of Sodium, Mg, K, Ca, Al, Fe, Zn etc

(ii) Organic Salts - These are generally soluble organic compounds obtained by the domes[tic] sewage, industrial waste or decay of dead material (animals or plants) etc.

(iii) Gases - From ~~industrial~~ industries several ga[ses] like O_2, CO_2, H_2S, ammonia, oxides of N_2, SO_2 etc evolve which are soluble in water and make it i[mpure]. These gases are responsible for corrosion.

Suspended Impurities. Sand, clay, lime etc present in water get suspended. The heavy particles settle down after standing ~~something~~ sometimes while smaller particles remains in the water as collo[idal] particles.

Harmful Micro-organism. Various pathogenic micro-orga-nisms like bacteria, viruses etc enter in water through waste and sewage. These are causes of various disease.

Temporary hardness: It is due to the presence of bicarbonate of calcium or magnesium. It can removed by boiling process.

Permanent hardness: It is due to the presence of Sulphate and chloride of calcium or magnesium. It can't be removed by boiling.

Now-a-days temporary and permanent hardness is replaced by alkaline and non-alkaline hardness. When hardness of water is due to the presence of bicarbonate, carbonates and hydroxide of Ca^{2+}/Mg^{2+} is alkaline hardness or carbonate hardness.

The non-alkaline hardness is determined by the subtracting of alkaline hardness from the total hardness. Such type of hardness is due to the presence of sulphate, chloride etc of Ca^{2+}/Mg^{2+}.

Hardness is Expressed in Terms of $CaCO_3$ -

For comparing the hardness of difference sample of water it would be easier, if the hardness caused by different salts may be expressed in terms of single salt like $CaCO_3$. There are following reasons for choosing $CaCO_3$ as a standard compound for expressing the hardness.

1. $CaCO_3$ is completely insoluble salt thus it ca[n be] easily ppted completely during water treatment.

2. Its molecular weight is exactly 100 so ~~tha~~ the mathematical calculation becomes easy. It is very old convention and fact is not so.

3. Equivalent of $CaCO_3$ for a hardness causing subst[ance] is given by

$$\text{Equivalent of } CaCO_3 = \frac{\left[\begin{matrix}\text{Amount of substance}\\ \text{causing hardness (mg/L)}\end{matrix}\right] \times [\text{Eq mass of } CaCO_3]}{\text{Equivalent mass of hardness producing substance}}$$

If W = mass of substance causing hardness

E = equivalent mass of hardness producing substance

Then equivalent of $CaCO_3 = \dfrac{W \times 50}{E}$

[$\because$ equivalent mass of $CaCO_3 = 50$]

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...ater which is safe to drink is known as potable water. Drinking water has following characteristics.

1. It should be colourless, odourless, testeless and ~~transpart~~ transparent.

2. It should be free from hardness, suspended particles and pathogenic bacterias (microorganisms)

3. It should neither be very hard nor be very soft.

4. The turbidity should ~~be~~ not exceed 10 ppm.

5. Its pH value should be about 7.0 - 7.5

6. It should be free from harmful dissolved solids like compounds of arsenic or lead, etc and harmful dissolved gases like H_2S, SO_2 etc.

7. The Total dissolved solids (T D S) should be less than 500 ppm.

* Drinking water possesses about 60-70 ppm hardness.

HARDNESS (6)

Hardness is the characteristics of water by which does not form lather with soap. Hard water is not for cooking, drinking, loundry purpose etc. it also does not suitable in industries.

Soap Soaps are the heigher fatty acids of Na or K salts. When soap comes in contact with hard water the Ca^{2+} and Mg^{2+} present in hard water combines with soap and forms insoluble sticky precipi. So that hard water does not produce lather with soap.

$$\underset{(\text{Metal in H.W})}{M^{2+}} + \underset{\text{Sod. stearate (Soap)}}{2\,C_{17}H_{35}COONa} \longrightarrow (C_{17}H_{35}COO)_2M\downarrow + 2Na^{+}$$

$M^{2+} = Ca^{2+}$ or Mg^{2+}

☆ **Hard Water** - Water which does not produce lather with soap solution readily is called hard water.

☆ **Soft Water** - Water which produce lather with soap soln readily is called soft water.

Rain water is an example of this type of water.

Causes of Hardness.

It is due to the presence of Sulphate, Chloride and bicarbonate of calcium or magnesium.

Types of Hardness - Hardness are of two types

(i) Temporary hardness (ii) Permanent hardness

...mporary hardness :- It is based on the following principle

Principle - Temporary hardness is removed by boiling of water because Ca^{2+}/ Mg^{2+} bicarbonates get ppted as $Ca(HCO_3)_2$ and ~~$MgCO_3$~~ $Mg(HCO_3)_2$.

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

$$Mg(HCO_3)_2 \xrightarrow{Boiling} Mg(OH)_2 \downarrow + 2CO_2$$

Permanent Hardness :- Permanent hardness is removed by boiling of water with a known excess amount of standard Na_2CO_3. The chloride and sulphates of Ca^{2+}/ Mg^{2+} gets ppted as their carbonates. The residual Na_2CO_3 is then determined by titrating it against a standard HCl acid.

Reactions -

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

$$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3 \downarrow + 2NaCl$$

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

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 \downarrow + Na_2SO_4$$

Soap Titration Method When soap is added to hard water, it does not give lather because hardness producing metal ions (Ca^{2+} and Mg^{2+}) get ppted. After complete precipitation of Ca^{2+} and Mg^{2+}, further addition of soap gives lather

$$2C_{17}H_{35}COONa + Ca(HCO_3)_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaHCO_3$$

Sodium stearate
(Soap)

$$2C_{17}H_{35}COONa + Mg(HCO_3)_2 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + 2NaHCO_3$$

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$$

$$2C_{17}H_{35}COONa + MgCl_2 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + 2NaCl$$

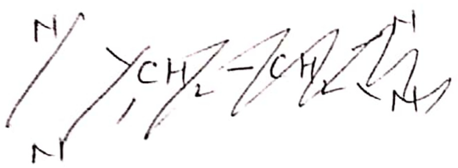
$$2C_{17}H_{35}COONa + CaSO_4 \longrightarrow (C_{17}H_{35}COO)_2Ca\downarrow + Na_2SO_4$$

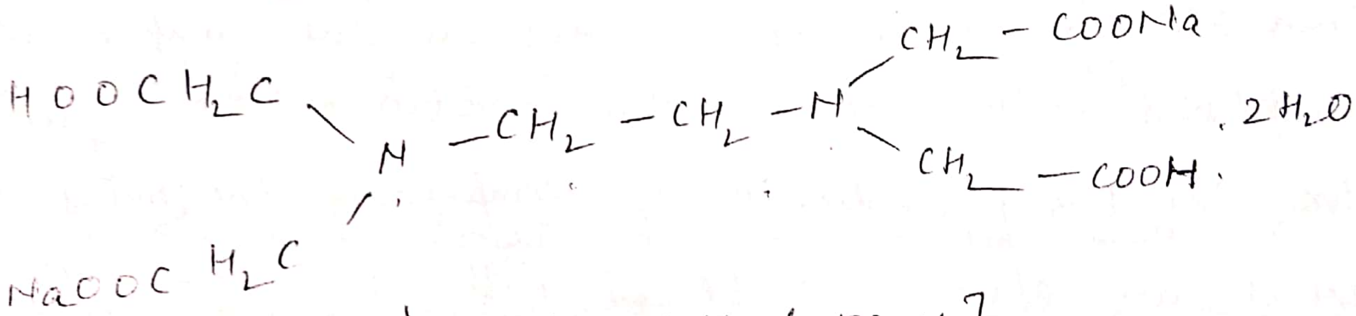
$$2C_{17}H_{35}COONa + MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$$

EDTA Method - It is the most important and more accurate method to determine the hardness of water.

Principle - The total hardness (permanent as well as tempora[ry]) in water is determined by titrating the water sample against standard EDTA solution in ammonia buffer soln having pH = 10 using EBT as an indicator. The calcium and Magnesium ion present in hard water forms stable compound with EDTA and less stable complex with EBT.

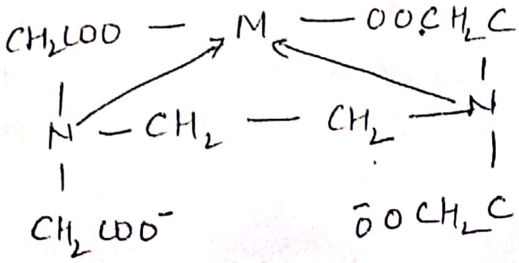
The structure of EDTA is as follow.





[Sodium Salt of EDTA]

It forms following type of stable complexes with bivalent metal ions (M^{2+})



N
(Ca)
Mg

The property of EDTA is used to estimate the of hardness causing ions in a water sample. For this purpose the water sample buffered at pH = 9 - 10 is against EDTA using EB-T.

Eriochrome black-T indicator is a blue colour dye. It forms unstable wine red coloured complexes with a free Ca^{2+} / Mg^{2+} ions at pH = 9 - 10.

$$M^{2+} + EB\text{-}T \xrightarrow{pH = 9-10} [M^{2+}\text{-}EB\text{-}T]$$

Less stable wine-red coloured complex

On addition of EDTA, the free uncomplexed Ca^{2+} and Mg^{2+} ions form metal ion EDTA complexes which are more stable than the metal ion - indicator complex.

$$M^{2+} + EDTA \xrightarrow{pH = 9-10} [M^{2+}\text{-}EDTA]$$

Stable metal ion - EDTA complex

When all the free metal ions present in the sample get complexed with EDTA, further addition of EDTA sets free the EB-T indicator by complexing the metal ions which are already complexed with EBT. This happens because metal ion - EDTA complexes are more stable than metal ion EB-T complexes

$$[M^{2+}\text{-}EBT] + EDTA \xrightarrow{pH = 9-10} [M^{2+}\text{-}EDTA] + EB\text{-}T$$

metal ion - indicator complex (wine red colour)

More stable metal ion - EDTA complex

Free indicator (blue colo

Americals sample of M

Numericals

1) A sample of water contains 16.8 mg/L of $Mg(HCO_3)_2$, 19.0 mg/L of $MgCl_2$, 24.0 mg/L of $MgSO_4$ and 22.2 mg/L of $CaCl_2$. Calculate the total hardness of water in terms of $CaCO_3$ equivalent.

Sln. Calculation of $CaCO_3$ equivalent of total hardness of water in terms of $CaCO_3$ equivalent.

Substance	Mass of the substance (W)	Equivalent mass of the substance (E)	$CaCO_3$ equivalent $\frac{W \times 50}{E}$
$Mg(HCO_3)_2$	16.8 mg/L	73	$\frac{16.8 \times 50}{73} = 11.51$ mg/L
$MgCl_2$	19.0 mg/L	47.5	$\frac{19.0 \times 50}{47.5} = 20.0$ mg/L
$MgSO_4$	24.0 mg/L	60	$\frac{24.0 \times 50}{60} = 20.0$ mg/L
$CaCl_2$	22.2 mg/L	55.5	$\frac{22.2 \times 50}{55.5} = 20.0$ mg/L

Hence total hardness of water in terms of $CaCO_3$ equivalent

$= 11.51 + 20.0 + 20.0 + 20.0 = 71.51$ mg/L

2. Calculate the carbonate and non carbonate hardness of a water sample containing following salts in mg/L.

$Ca(HCO_3)_2 = 26.8$, $Mg(HCO_3)_2 = 14.8$, $CaCl_2 = 11.0$, $MgSO_4 = 17.8$

Substance	Mass of the substance	Equivalent mass of substance	$CaCO_3$ eq. $\frac{W \times 50}{E}$
$Ca(HCO_3)_2$	26.8	81	$\frac{26.8 \times 50}{81} = 16.5$
$Mg(HCO_3)_2$	14.8	73	$\frac{14.8 \times 50}{73} = 10.1$
$CaCl_2$	11.0	55.5	$\frac{11.0 \times 50}{55.5} = 9.9$
$MgSO_4$	17.8	60	$\frac{17.8 \times 50}{60} = 14.8$

Carbonate hardness = $Ca(HCO_3)_2$ hardness + $Mg(HCO_3)_2$ hardness

16.5 + 10.1

∴ = 26.6 mg/L equivalents of $CaCO_3$

Total hardness of the sample = 16.5 + 10.1 + 9.9 + 14.8

= 51.3 mg/L equivalents of $CaCO_3$

Non carbonate hardness = 51.3 − 26.6

= 24.7 mg/L equivalents of $CaCO_3$.

A water sample contains 145 mg of $CaSO_4$ per litre. Calculate the hardness in ppm.

W = 145 mg and Equivalent mass of $CaSO_4$ = 68

Equivalent of $CaCO_3$ = $\frac{W \times 50}{E}$ = $\frac{145 \times 50}{68}$ = 106.6 mg/L

1 mg/L = 1 ppm

Therefore hardness of the given sample = 106.6 ppm equivalent of $CaCO_3$.

...ulation of Total Hardness (13)

(1)

~~Volume~~ for S.H.W = 20 ml (x)

Volume of EDTA used = V_1 ml

V_1 ml of EDTA = 20 ml of SHW

1 ml of EDTA = $\frac{20}{V_1}$ mg of $CaCO_3$

Total Hardness.

Let the volume of water sample = y (20 ml)

Volume of EDTA used = y ml (20 ml)

1 ml of EDTA = $\frac{20}{V_1}$ mg of $CaCO_3$

V_2 ml of EDTA = $\frac{20}{V_1} \times V_2$ mg of $CaCO_3$

So 20 ml (y) water sample contains $\frac{20}{V_1} \times V_2$ mg of $CaCO_3$

1000 ——— = $\frac{\cancel{20}^{(x)}}{V_1} \times \frac{V_2}{\cancel{20}(y)} \times 1000$ mg of $CaCO_3$

Total Hardness in terms of $CaCO_3$ equivalent =

$$\frac{\cancel{20} \times V_2 \times 1000}{V_1 \times \cancel{20}} \text{ ppm} = \frac{V_2}{V_1} \times 1000 \text{ ppm}$$

Units of Hardness.

1. Parts per million (ppm) - 1 part of $CaCO_3$ equivalent hardness per 10^6 part of water
2. Milligram per litre (mg/L) - 1 mg of $CaCO_3$ in 1 L water
3. 1 mg/L = 1 ppm
3. Clarke's (°Cl) - part of $CaCO_3$ eq. in 70,000 part of H_2O
4. Degree French (°F) - part of $CaCO_3$ eq = 10^5 part of H_2O

Relationship : 1 ppm = 1 mg/L = ·07°Cl = 0.1 °Fr

Equivalent of $CaCO_3$ = $\frac{W \times 50}{E}$

W = mass of substance causing hardness

E = equivalent mass of hardness producing substance.

Alkalinity of water – The alkalinity of water is due to the pnce of those type of substance which have tendency to increase the conc OH^- either by hydrolysis or dissoci-tion in water. Factors of alkalinity.

(i) The presence of salts of weak organic acids which undergo hydrolysis and consume H^+ of water.

(ii) The presence of HCO_3^-, ~~CO_3~~ SiO_3^{2-}, $HSiO_3^-$ etc in water which make the water alkaline.

Alkalinity of water is mainly classified as :-

(i) Hydroxide alkalinity. (ii) CO_3^{2-} alkalinity

(iii) HCO_3^- alkalinity.

Both alkalinity and hardness are expressed in terms of $CaCO_3$ equivalent. ppm or mg/L units

Water Softening.

Water plays very important role in industry and domestic purpose. The most common methods for softening of water are given below

1) Lime Soda process
2) Zeolite process (Base exchange process)
3) Demineralization (Ion exchange process)

LIME SODA PROCESS - It is very important and popular process for softening of water

Principle. Lime ($Ca(OH)_2$ and Soda [redacted] Na_2CO_3) are added to hard water. Soluble Ca^{2+}/Mg^{2+} salts that in hard water are converted into insoluble compounds like $CaCO_3$, $Mg(OH)_2$ etc. which are separated as ppted by filtration.

Functions of Lime $Ca(OH)_2$ -

1. Removal of temporary hardness

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

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

2. Removal of permanent Mg hardness.

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

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

3. Removal of dissolved Fe and Al salts.

$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2 + CaSO_4$

$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 \downarrow$

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

4. Removal of free mineral acids.

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

$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$

5. Removal of dissolved CO_2 and H_2S

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

$H_2S + Ca(OH)_2 \rightarrow CaS \downarrow + 2H_2O$

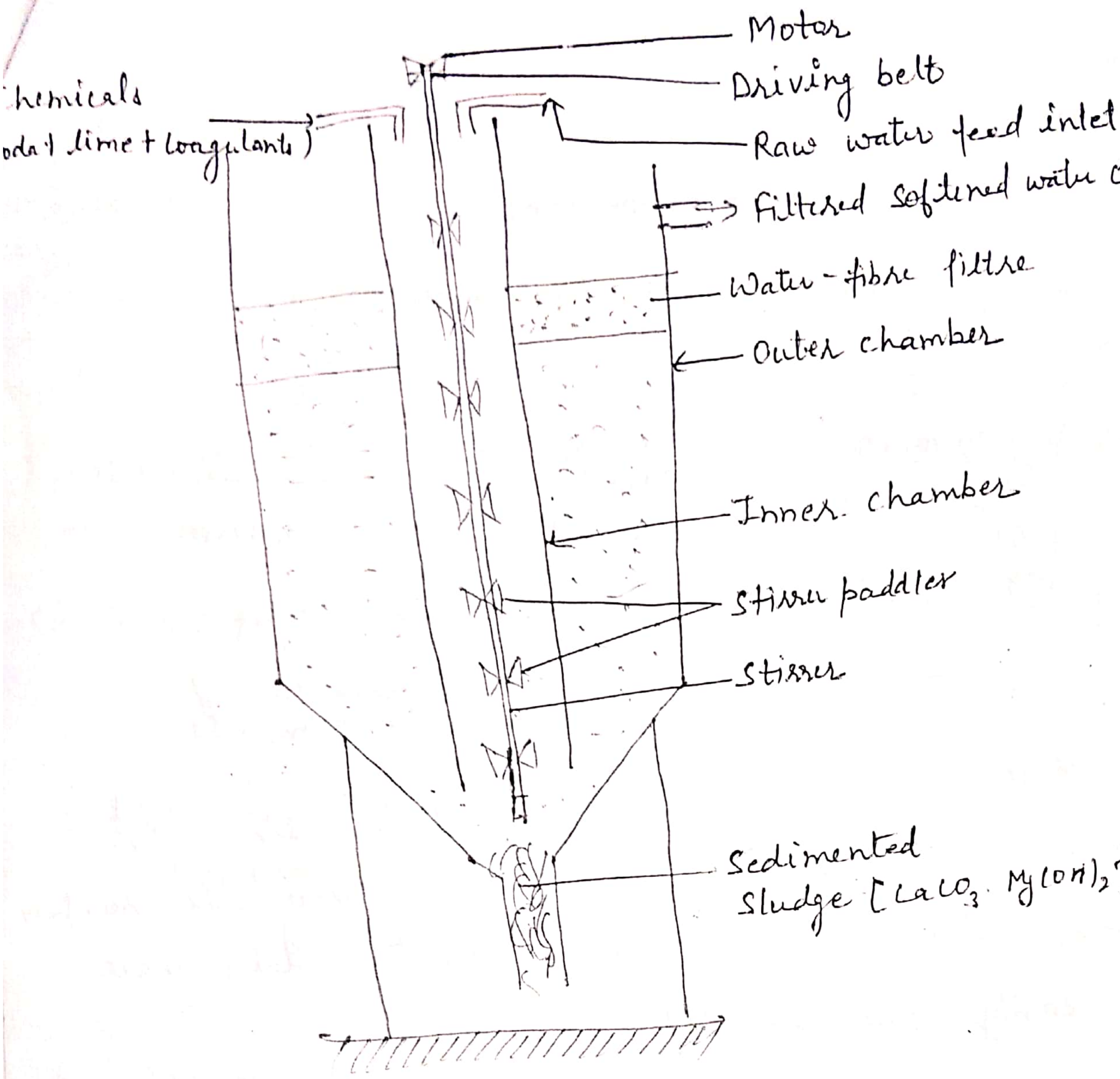
Function of Soda (Na_2CO_3) - When lime is used to remove the hardness producing substances like permanent Mg hardness or ions, Fe^{2+}, Al^{3+}, mineral acids etc

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

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

At room temp the ppts of $CaCO_3$ and $Mg(OH)_2$ are fine and do not settle down easily, so the filtration becomes difficult. So some chemicals like alum, sodium aluminate or ferrous sulphate etc are added to it.

d. lime-Soda process :-

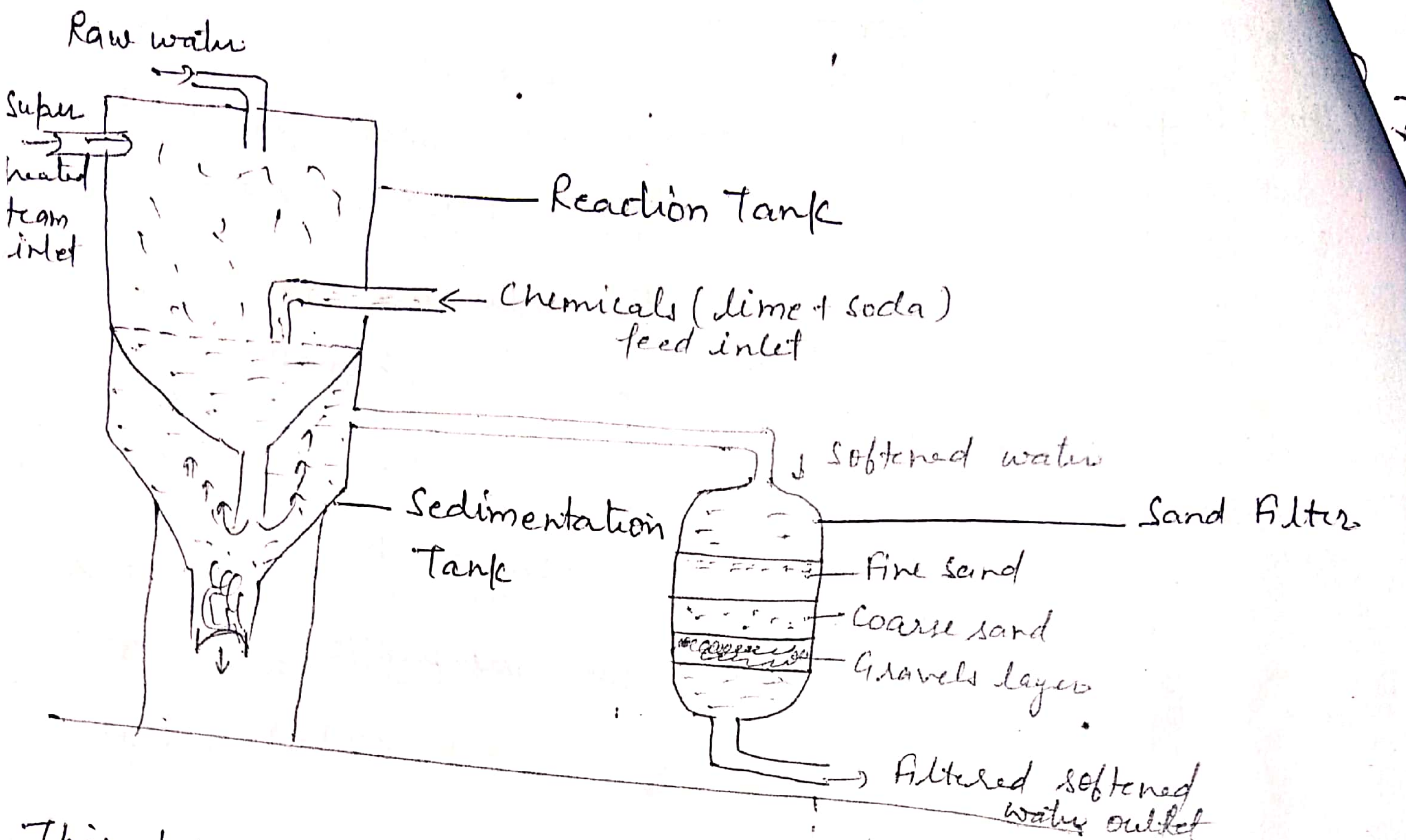


Lime Soda process is carried out at room temp as well as high temp (90° - 100°c)

Cold lime Soda process at Room temp.

Residual hardness - 50 - 60 ppm

Hot lime-soda method



This process is completed at 90–100°C. Since the temp is about the boiling of water hence the reaction becomes fast the pption and filtration takes place very easily and rapidly.

Hot lime soda apparatus consists of three parts.

1) A reaction tank

2) A conical sedimentation vessel

3) A sand filter.

It contains ~~too~~ residual hardness of about 15–30 ppm.

Advantages of Lime Soda Process-

a) It is economical

b) Hot soda lime process is much faster than the cold lime-soda process.

c) During this pH value of water is increased hence the corrosion of pipe is reduced.

d) Due to alkaline nature of water, amount of pathogenic bacterias in water get reduced.

e) It requires less amount of coagulants.

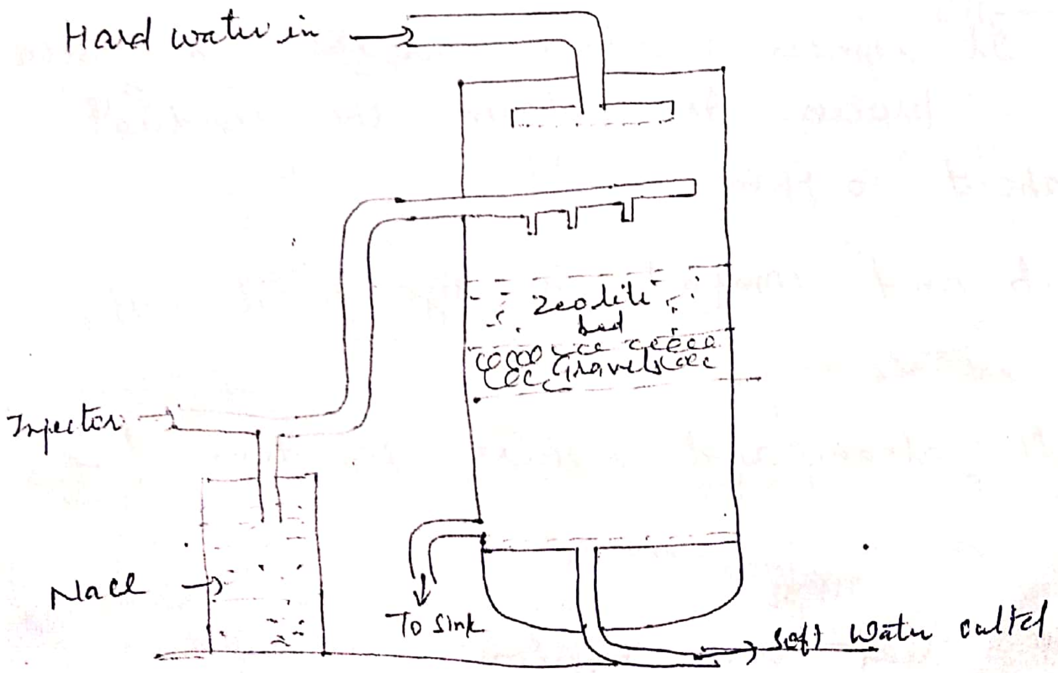
Zeolite Process (Permutit Process)-

Zeolite is also known as boiling stone.

formula of zeolite ($Na_2O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$)

where $x = 2-10$

$y = 2-6$



The hardness causing ions Ca^{2+}, Mg^{2+} etc present water are retained by the zeolite as calcium zeolite magnesium zeolite while the outgoing water contains sodium

$$Ca(HCO_3)_2 + Na_2Z \longrightarrow CaZ + 2NaHCO_3$$
(Sod. zeolite) (Cal. zeolite)

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

$Na_2O + Al_2O_3\ x\,SiO_2\ y\,H_2O$

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

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

$$CaSO_4 + Na_2Z \rightarrow CaZ + Na_2SO_4$$

$$MgSO_4 + Na_2Z \rightarrow MgZ + Na_2SO_4$$

dissolved Sod. salt does not cause any hardness.

Regeneration - $CaZ + 2NaCl \rightarrow Na_2Z + CaCl_2$

$MgZ + 2NaCl \rightarrow Na_2Z + MgCl_2$

Advantages - It remove hardness more than lime soda process. It contains the residual hardness about 10 ppm.

It is cheap and compact in size so it occupying a small space

It is quite clean and require less time for softening.

It does not creat any pollution.

Demineralization or Ion exchange or Deionisation Process.

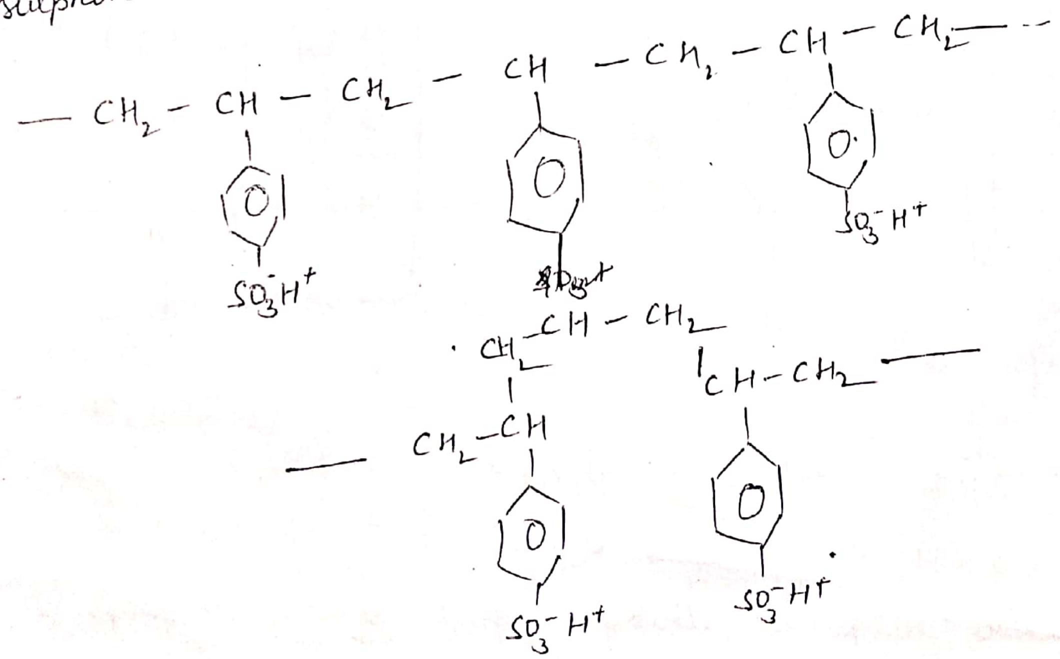
It is also known as ion exchange process. It is the process of complete removal of all ions (cations and anions) present in water by using ion-exchange resins.

Ion exchange resins consist of cross linked long chain organic polymer. Functional groups of resin may be acidic or basic. On the basic of functional group ion exchange resins are of two types.

a) Cation exchange resins

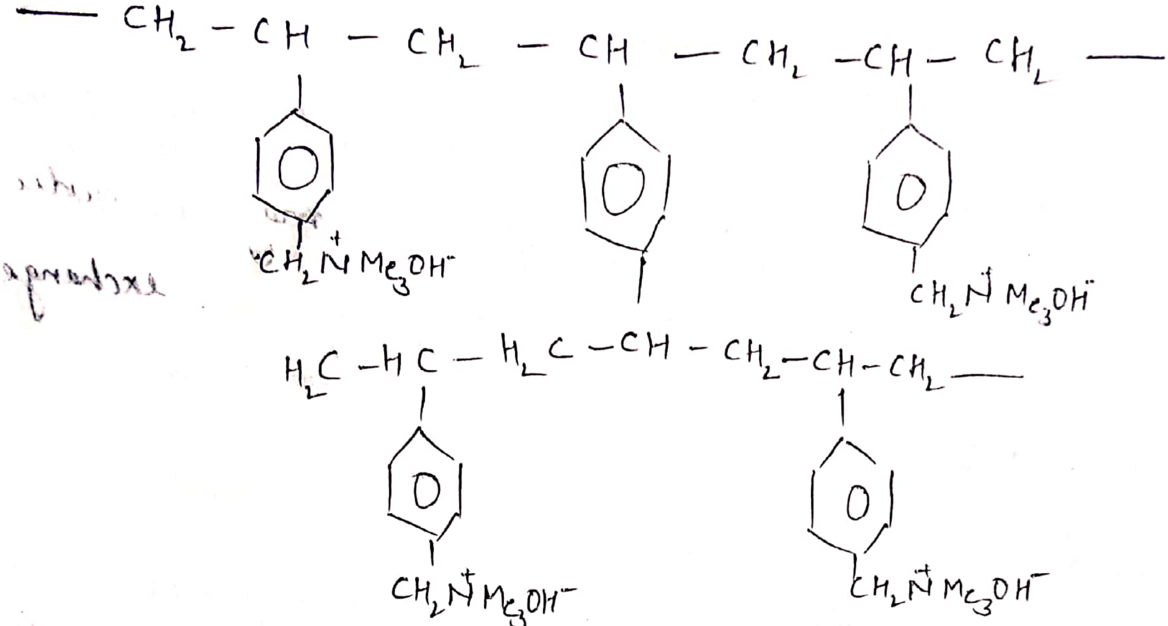
b) Anion exchange resins.

Cation exchange resins - They contain acidic groups like $-COOH$, $-SO_3H$. These are usually copolymer of styrene and ~~divi~~ divinylbenzene which on carboxylation or sulphonation become cation exchanger.



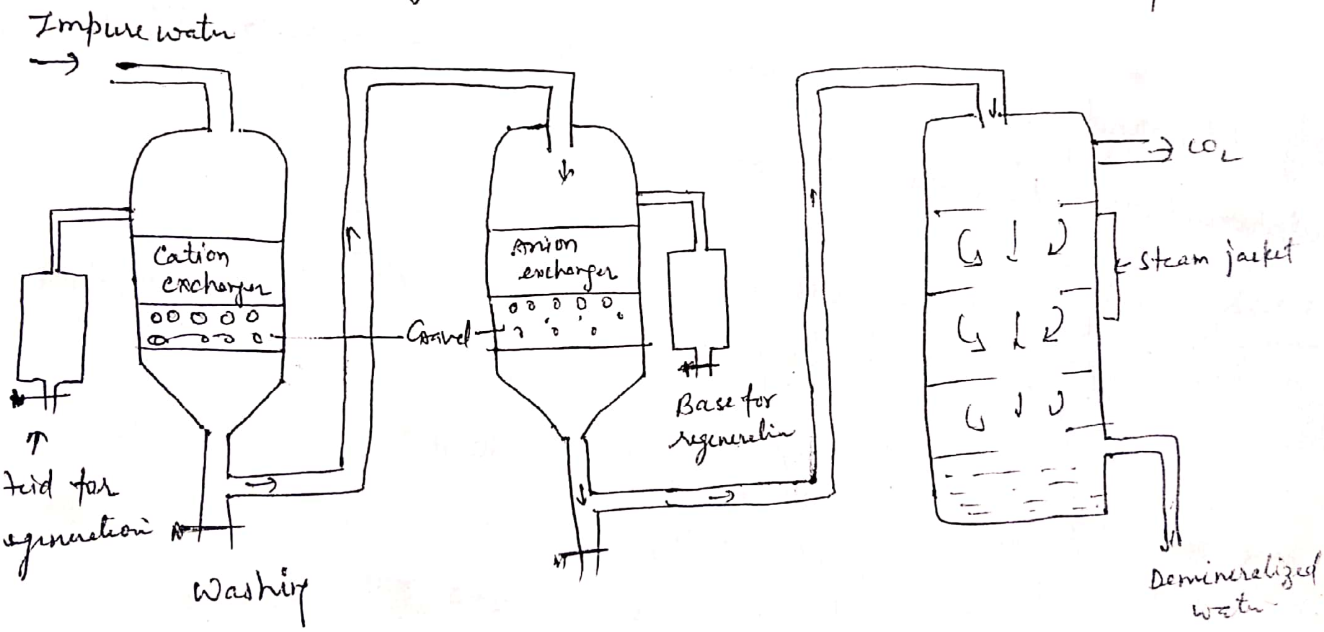
In general it is represented by RH where R represents the resin network for simplicity.

Anion exchanger resins. It contain basic functional groups. These are usually copolymer of styrene divinylbenzene containing amine or substituted amine.



(Where Me = $-CH_3$ - Methyl group)

It is generally represented as R'OH for simplicity.



Working.

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

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

The hard water is passed through first cation exchange resin. The Ca^{2+} & Mg^{2+} in water get exchange by H^+ from cation exchanger as of above rx.

(ii) the treated hard water is passed through anion exchanger resin columns where anions like SO_4^{2-}, Cl^- etc present in water are replaced by OH^- ions from resins as follows.

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

$$2R'OH + SO_4^{2-} \longrightarrow R'_2SO_4 + 2OH^-$$

The released H^+ from cation exchanger treatment and OH^- from anion exchanger treatment get combined to produced water.

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

It is called deionized water because it is free from cations and anions.

Regeneration of Resins. When these exchanger get exhausted and it is necessary to regenerate.
The cation exchanger is regenerated by passing suitable acids (2% HCl or H_2SO_4) and anion exchanger is regenerated by passing an alkali (dil NaOH)

For cation exchanger-

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

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

For Anion exchanger-

$$R'_2SO_4 + 2OH^- \longrightarrow 2R'OH + SO_4^{2-}$$

$$R'Cl + 2OH^- \longrightarrow R'OH + Cl^-$$

CO_2 is removed by degasifier.

* By this process water of contain very hardness about (≈2 ppm)
* By this water no corrosion will take place.
* highly acidic or highly alkaline water can softened.

- The equipment is costly.
- Regeneration is also ~~cos~~ costly.
- Turbid water decreases the efficiency of resins.

Mixed bed deionizer - It consists of a single column containing a mixture of strongly cation exchanger and a strongly anion exchanger. The hard water comes in contact with ~~have~~ both exchanger several times, so it is very efficient process than separate column of ion exchange process. The purified water contains very less (about 1 ppm or less) hardness It is more convenient and widely used. After long time working the resins are exhausted. For regeneration the beds of resins are back washed. The anion exchanger is regenerated by dil NaOH solution and cation exchanger is regenerated by dil H_2SO_4.