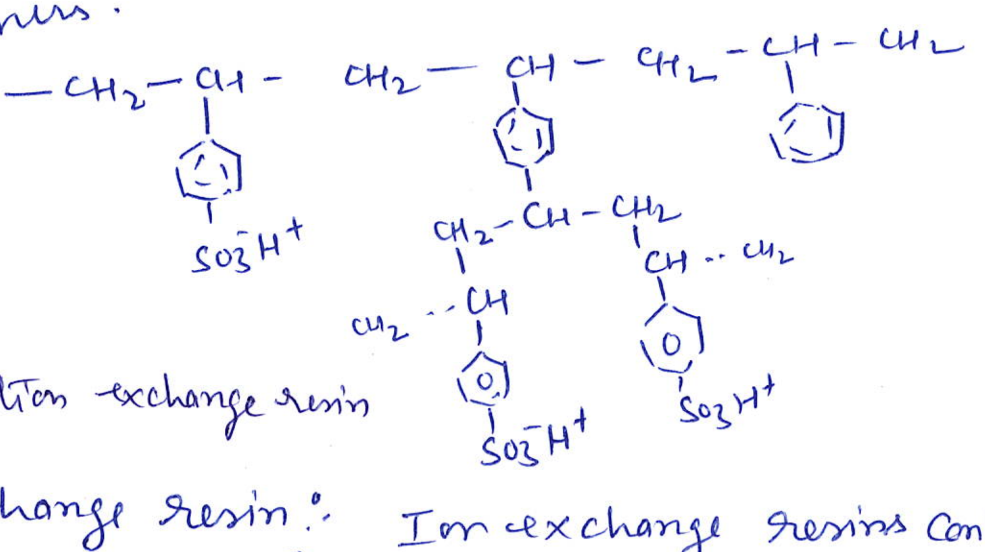
Ion-Exchange process :- Ion-exchange resins are high molecular weight, insoluble cross linked organic polymers containing functional groups which are responsible for the ion exchange properties.
Depending upon the functional groups ion exchange resin are of two types.

1) cation Exchange resin   2) Anion exchange resin

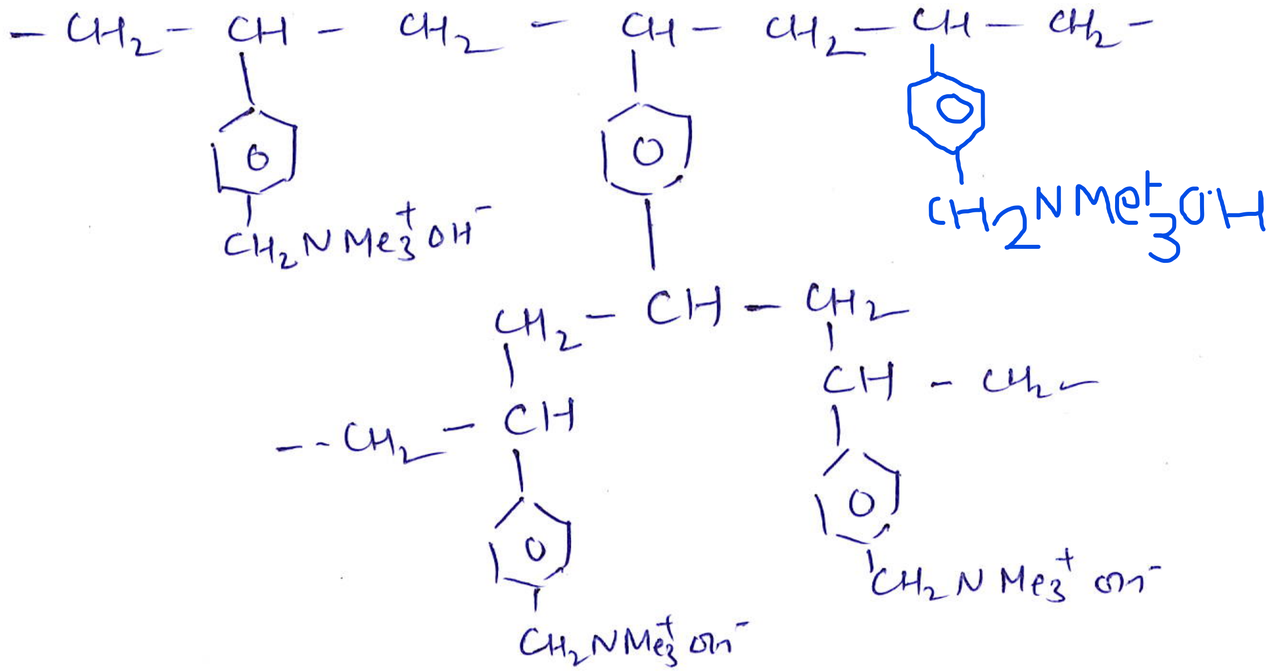
1) Cation Exchange resin :- Ion exchange resins containing acidic functional groups like $-COOH$, $-SO_3H$ etc. are capable of exchanging their H^+ ions with other cations and are known as cation exchange resin. They are generally denoted by RH^+. They are mainly sulphonated or carboxylated styrene and divinyl benzene copolymers.



Cation exchange resin

(2) Anion exchange resin :- Ion exchange resins containing basic functional groups like $-NH_2$, $=NH$ as hydroxide are capable of exchanging their anions with other anions are known as anion exchange resin. They are represented R^+OH^- where R^+ represent the insoluble organic matrix.

They are mainly styrene - divinyl benzene or Amine formaldehyde copolymers which contain amino or quaternary ammonium groups. These after treatment with dilute solution of NaOH soln. become capable of exchanging their OH^- Ion with the anion of hard water.



Anion Exchange resin

Principles: Theory:- when hard water is passed through cation exchange tank all the cations are taken up by the resin and an equivalent amount of H^+ is released from the resin to water

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

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

Therefore, all the cations are removed from water.
After cation exchange tank, this water is passed through anion exchange column when all the anion like Cl^-, SO_4^{--} etc. are taken up by the resin and equivalent amount of OH^- ion is released from this tank to water

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

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

Thus water becomes free from all anions.
The H^+ & OH^- ions released from cation and anion exchange tank respectively will combine to form water.

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

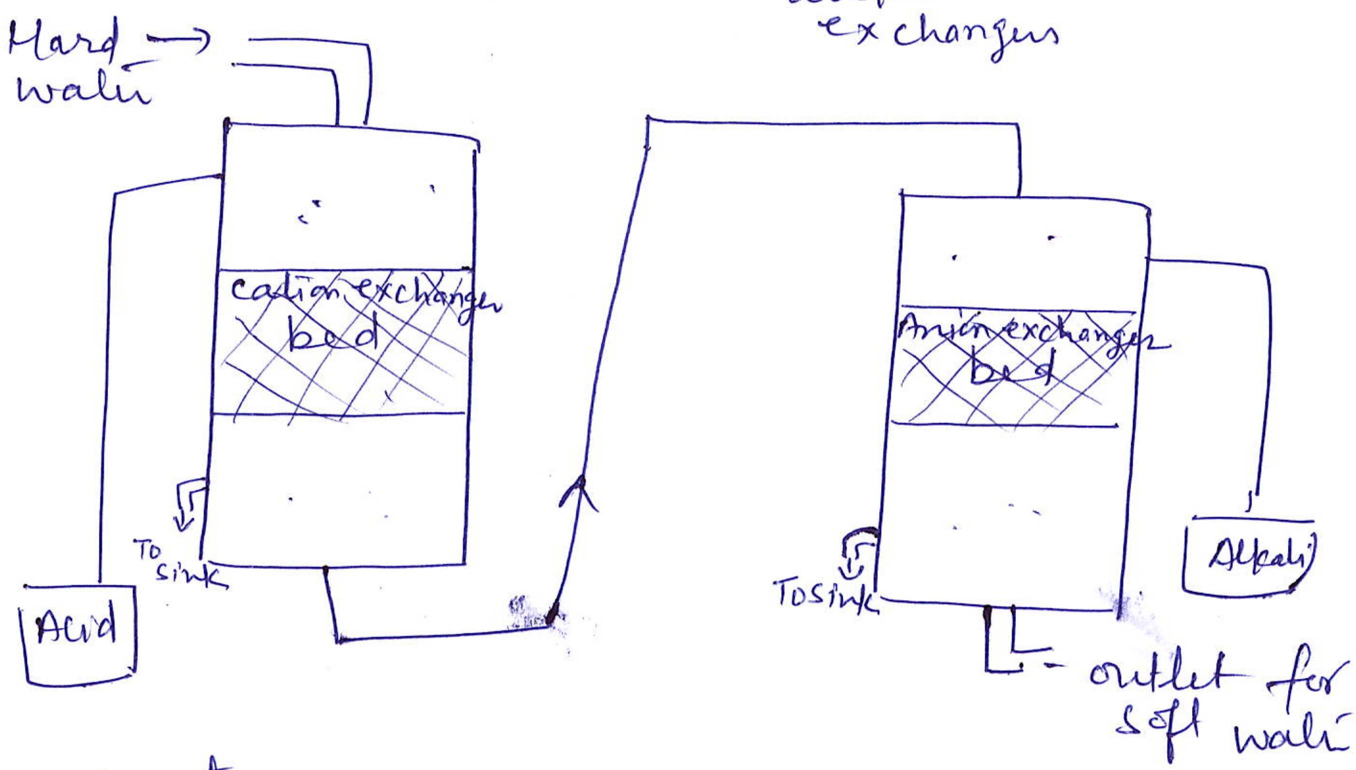
Therefore water obtained from this process is free from all cations and anions and the water is known as deionised or demineralised water

Regeneration :- As the cation and anion exchangers are used continuously they loose their ion exchanging capacity and become exhausted.

The reclaimation of Ion exchanging capacity of exhausted cation and anion exchangers by treating it with a solution of dil HCl / H_2SO_4 and dil NaOH respectively is known as Regeneration.

$$\underset{\text{Exhausted cation}}{R_2Ca^{++}} + \underset{\text{from acid}}{2H^+} \rightarrow \underset{\text{Regenerated cation exchanger}}{2RH^+} + \underset{\text{washings}}{Ca^{++}}$$

$$\underset{\text{Exhausted anion}}{R_2SO_4^{--}} + \underset{\text{from alkali}}{2OH^-} \rightarrow \underset{\text{Regenerated anion exchanger}}{2ROH^-} + \underset{\text{washings}}{SO_4^{--}}$$



Advantage :- ① The process can be used to soften highly acidic or alkaline waters

② It produces water of very low hardness (2ppm) so the treated water is very good for use in high pressure boilers.

Disadvantages :- ① The cost of plant and equipment is very high.

② If water contains turbidity then efficiency of the process is reduced.

Note :- During the process water will be passed first through cation exchanger then anion exchanger because water which comes from cation exchangers is slightly acidic in nature and it will not affect the anion resin but if reverse happens then alkaline water will destroy the cation exchangers.

Lime - Soda process :- Chemically Convert all the soluble hardness causing substance into Insoluble precipitates which are then removed by settling and filteration.

In this process, calculated amount of lime ($Ca(OH)_2$) and soda (Na_2CO_3) are added to hard water which react with the calcium and magnesium salts so as to form Insoluble precipitates of $CaCO_3$ and $Mg(OH)_2$

Reaction with lime

(a) Removal of temporary hardness

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

$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow MgCO_3 + CaCO_3\downarrow + 2H_2O$$

$$MgCO_3 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow$$

(b) Removal of Permanent Mg hardness

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

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

(c) Removal of dissolved CO_2 and H_2S

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

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

(d) Removal of dissolved Iron and Aluminium salts

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

$$2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2Fe(OH)_3 \downarrow$$

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

(e) Removal of free mineral acid

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

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

(f) Reaction with $NaHCO_3$

$$2NaHCO_3 + Ca(OH)_2 \rightarrow Na_2CO_3 + CaCO_3 \downarrow + 2H_2O$$

Reaction with soda

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

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

Calculation of the amount of lime & soda required

- Lime requirment =

$$\frac{74}{100}\left[2 \times \text{Temp. Mg} + \text{Temp. Ca} + \text{Permanent Mg} + \text{salt of Fe+Al}\right) + CO_2 + HCl + H_2SO_4 + HCO_3^- - NaAlO_2 \text{ all in terms of } CaCO_3 \text{ equivalent}$$

$$\text{Soda requirement} = \frac{106}{100}\left(\text{Perm. Ca} + \text{Perm. Mg} + \text{Salt of Fe} + \text{Al}) + \text{HCl} + H_2SO_4 - HCO_3^- \text{ all in terms of } CaCO_3 \text{ equivalent}\right] \times \text{Vol. of } H_2O \times \frac{100}{\%\ \text{purity}} \text{ mg}$$

Example :- Calculate the quantity of lime 74% pure and soda 90% pure required for softening 50,000 litres of water containing -

$Mg(HCO_3)_2 = 50\ mg/L$ $\quad Ca(HCO_3)_2 = 81\ mg/L$ $\quad MgCl_2 = 6\ mg/L$

$HCl = 73\ mg/L$ $\quad CO_2 = 44\ mg/L$ $\quad Al_2(SO_4)_3 = 57\ mg/L$

Solution :- Conversion into $CaCO_3$ Equivalents

$$Mg(HCO_3)_2 = \frac{50 \times 50}{73} = 34.26\ ppm$$

$$Ca(HCO_3)_2 = \frac{81 \times 50}{81} = 50\ ppm$$

$$MgCl_2 = \frac{6 \times 50}{47.5} = 6.31\ ppm$$

$$CO_2 = \frac{44 \times 50}{22} = 100\ ppm$$

$$HCl = \frac{73 \times 50}{36.5} = 100\ ppm$$

$$Al_2(SO_4)_3 = \frac{57 \times 50}{57} = 50\ ppm$$

$$\text{Lime requirement} = \frac{74}{100}\left(Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + Al_2(SO_4)_3 + MgCl_2 + CO_2 + HCl \text{ as } CaCO_3 \text{ eq.}\right) \times \frac{100}{\%\ \text{purity}} \times \frac{\text{Vol. of } H_2O}{10^6} \text{ kg}$$

$= \frac{74}{100}\left(50 + 2 \times 34.26 + 50 + 6.31 + 100 + 100\right] \times \frac{100}{74} \times \frac{50,000}{106}$ kg

$= 18.74$ kg

soda requirement $= \frac{106}{100}\left(MgCl_2 + Al_2(SO_4)_3 + HCl \text{ as CaCO}_3\text{eq.}\right] \times \frac{100}{\text{\% purity}} \times \frac{\text{Vol of the}}{106}$ kg

$= \frac{106}{100}\left(6.31 + 50 + 100\right) \times \frac{100}{90} \times \frac{50,000}{106}$ kg

$= 9.20$ kg

Lime requirement $= 18.74$ kg

Soda requirement $= 9.20$ kg

Q. A water sample has the following analysis. Calculate temp., Permanent hardness in °Cl. (18)

$Mg(HCO_3)_2 = 83$ mg/L

$Ca(HCO_3)_2 = 134$ mg/L

$CaSO_4 = 124$ mg/L

$MgCl_2 = 84$ mg/L

$CaCl_2 = 94$ mg/L

$NaCl = 50$ mg/L Does not produce hardness

Soln.

$Mg(HCO_3)_2 = \frac{83 \times 50}{73} = 56.8$ mg/L

$Ca(HCO_3)_2 = \frac{134 \times 50}{81} = 82.7$ mg/L

$CaSO_4 = \frac{124 \times 50}{68} = 91.2$ mg/L

$MgCl_2 = \frac{84 \times 50}{47.5} = 88.4$ mg/L

$CaCl_2 = \frac{94 \times 50}{55.5} = 84.7$ mg/L

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

$= 82.7 + 56.8$

$= 139.5$ mg/L $= 139.5 \times .07$ °Cl

$= 9.77$ °Cl

Permanent hardness $= CaSO_4 + MgCl_2 + CaCl_2$

$= 91.2 + 88.4 + 88.7$

$= 264.3$ mg/L $= 264.3 \times .07 = 18.50$ °Cl

Q. calculate the quantity of lime & soda required for softening 50,000 litres of water containing the following salts per litres.

$$Ca(HCO_3)_2 = \frac{9.2 \times 50}{81} = 5.68 \text{ mg/L}$$

$$Mg(HCO_3)_2 = \frac{7.9 \times 50}{73} = 5.41 \text{ mg/L}$$

$$CaSO_4 = \frac{15.3 \times 50}{68} = 11.25 \text{ mg/L}$$

$$MgSO_4 = \frac{15 \times 50}{60} = 12.5 \text{ mg/L}$$

$$MgCl_2 = \frac{3.0 \times 50}{47.5} = 3.16 \text{ mg/L}$$

Lime requirement $= \frac{74}{100}\left(Ca(HCO_3)_2 + 2 \times Mg(HCO_3)_2 + MgSO_4 + MgCl_2\right) \times$ all in terms of $CaCO_3$ eq. vol. of H_2O

$$\frac{74}{100}\left(5.68 + 2 \times 5.41 + 12.5 + 3.16\right) = 23.39 \text{ mg/L}$$

$$= 23.39 \times 50{,}000 = 1170 \text{ g} = 1.17 \text{ kg}$$

Soda Requirement $= \frac{106}{100}\left(CaSO_4 + MgSO_4 + MgCl_2\right)$ all in terms of $CaCO_3$ eq.

$$= \frac{106}{100}\left(11.25 + 12.5 + 3.16\right) \times 50{,}000$$

$$= 14.26 = 1.426$$

Types of lime-soda process:- Lime-soda process are of two types-

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

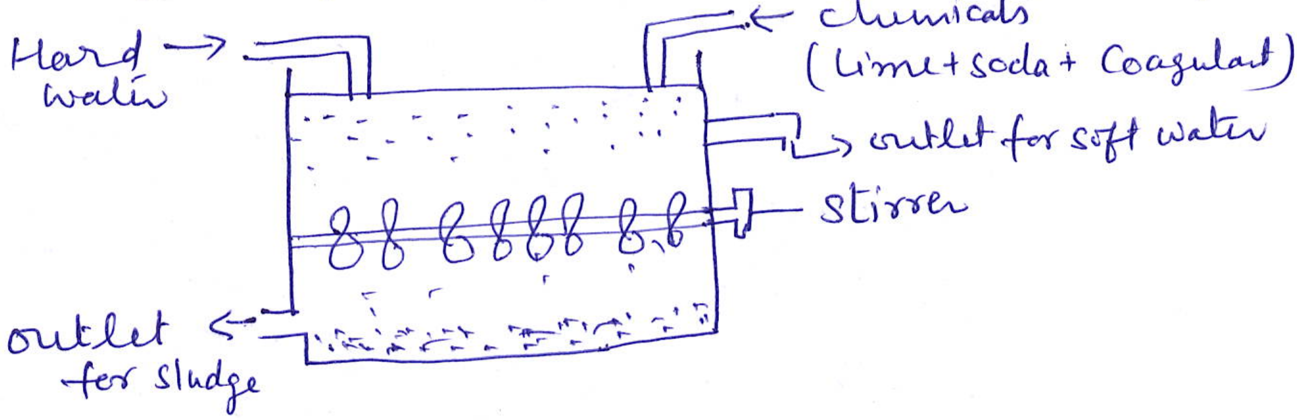
Cold lime-soda process :- In this process calculated amount of lime and soda are mixed with hard water at room temperature. Since the precipitates formed are finely divided they remain suspended in water and do not settle down easily. Therefore They can't be filtered easily. Hence it is necessary to add a small amount of Coagulant like aluminium sulphate, sodium aluminate or alums etc. These get hydrolysed to form gelatinous ppt of $Al(OH)_3$ which entraps the finely suspended particles of $CaCO_3$ and $Mg(OH)_2$. Therefore Coagulants help in the formation of coarse ppt.

There are two types of softeners used for softening water by this process

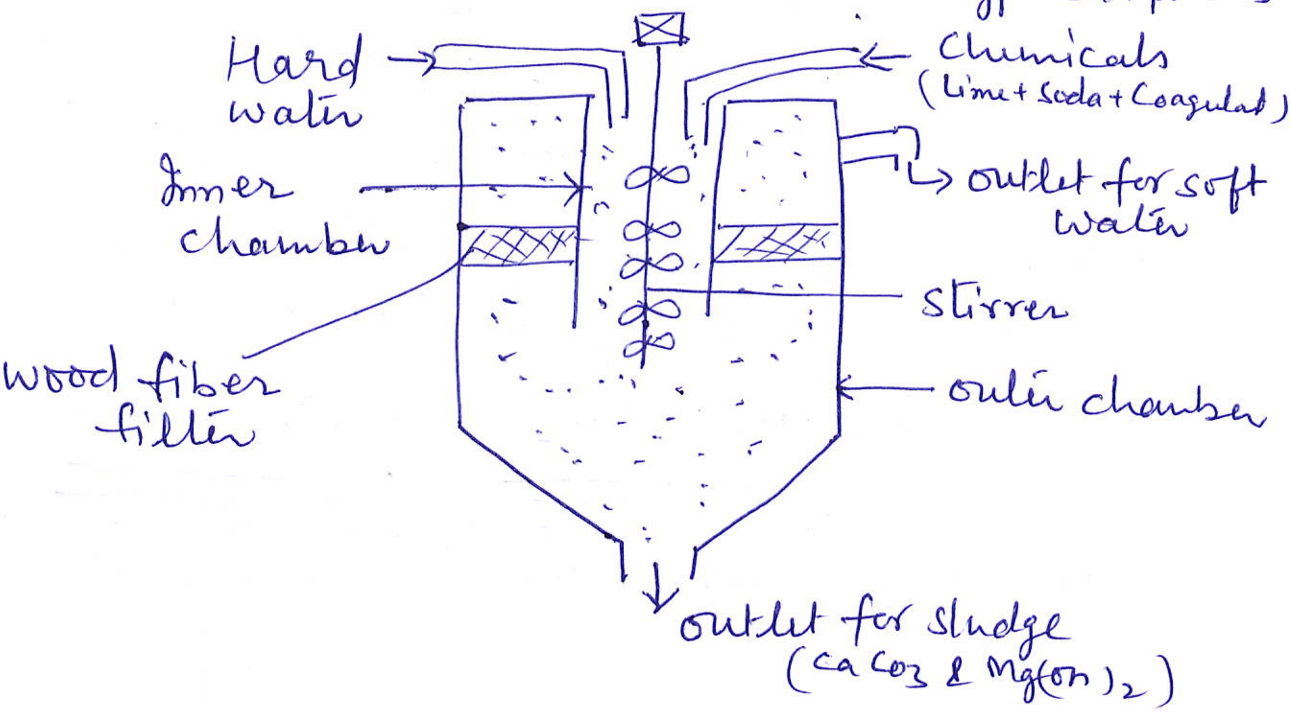
(a) Intermittent type (Batch process) :- Intermittent consists of a pair of tanks. Each tank is used in turn for softening of water.

Each tank is provided with inlets for raw water and chemicals, outlets for softened water and sludge, and a mechanical stirrer. Raw water and the calculated quantities of lime and soda are allowed to run in simultaneously and stirring is started.

Stirring is stopped, when the reaction is complete and the sludge formed is allowed to settle. The sludge formed in the tank is removed through the outlet and clear softened water is collected through a float pipe and filtered by filtering unit.



(2) Continuous cold lime-soda process :- Conventional type cold process



This is a continuous process inwhich the hard water and the chemicals in calculated amount are continuously fed from the top into an inner chamber at room teperature. As the hard water and chemicals flow down the chamber a continuous mixing takes place due to vigrous stirring. softening of water takes place in the inner chamber and ppt (sludge) settles down at the bottom in the outer chamber. The soften water goes upwards in the outer chamber where it passes through a filtering media (made up of wood fibres) to ensure the complete removal of sludge. filtered soft water finally comes out continuously through the outlet

Hot - lime soda process :- In this process hard water is treated with chemicals at temperature of 80 - 150°C. Since the reaction takes place at higher temperature, no Coagulant is needed in this process.

The softener may be of (1) Intermittent
(2) Continuous

(1) Intermittent type Hot - lime soda process :- Hot lime - soda intermittent type softener is similar to the Intermittent cold. lime soda process except that heating coils are intalled in it for heating.

② Continuous type lime-soda process :- This softener consist of the following three parts-

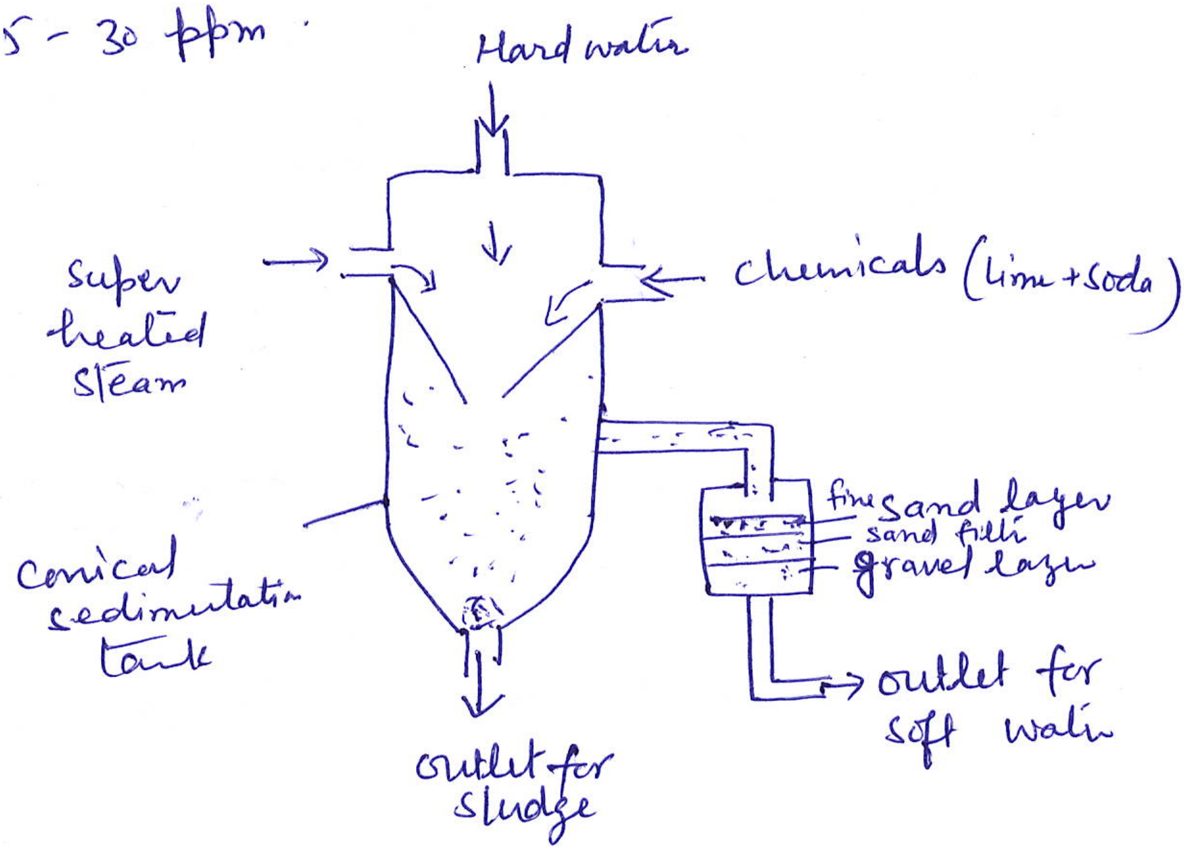
a) Reaction tank ⓑ sedimentation tank ⓒ Sand filter

a) Reaction tank :- Raw water and chemicals are added in this tank through two different inlets. Tank is also provided with an additional inlet for steam.

b) Sedimentation tank :- The sedimentation of sludge takes place in a conical sedimentation tank

c) Sand filter :- Sand filter ensure the complete removal of sludge from the clear and softened water from the sedimentation tank.

water thus obtained has the residual hardness 15 - 30 ppm.



Advantage of Lime-soda process:-

(1) Lime-soda process is very economical
(2) Lesser amount of coagulant are required
(3) The alkaline nature of Treated water reduces the amount of pathogenic bacteria in water to a Considerable extent

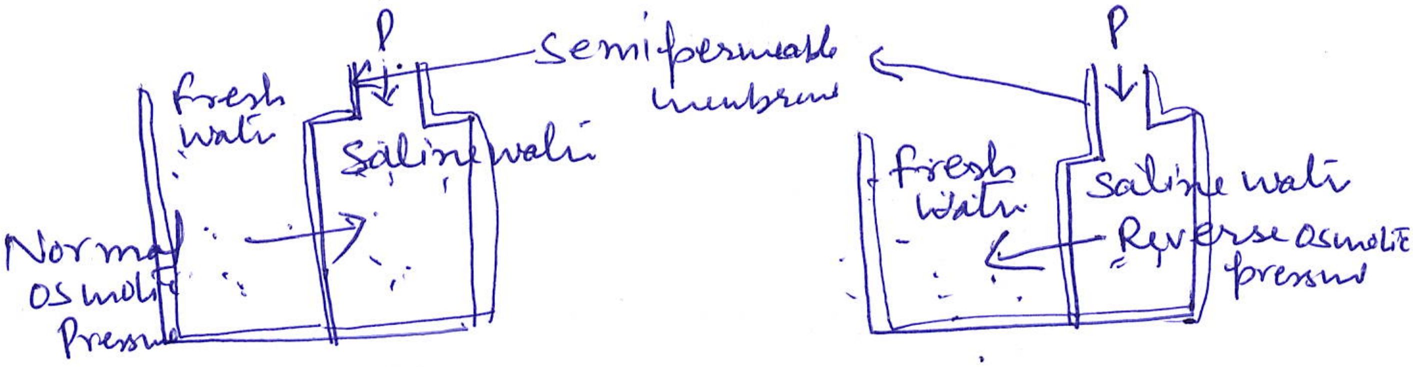
Disadvantages of lime-soda process:

(1) Disposal of large amount of sludge is a problem
(2) Treated water removes hardness only upto 15 ppm which are not ideal for boilers

Difference b/w Cold & Hot lime-soda process

Cold-lime soda process	Hot lime-soda process
1. calculated amount of lime and soda is mixed at room temperature	This is done at elevated temp. (80 - 150°)
(2) It is slow process	fast process
(3) The ppt formed are finely divided and can't settle easily and hence filtration is not easy	ppt formed like sludge settle down easily & hence filteration is easy
(4) Use of coagulant is must	Coagulants are not required
(5) Dissolved gases are not removed	Dissolved gases are removed
(6) softened water has residual hardness around 60 PPm	Residual hardness is about 15 - 30 ppm

Reverse osmosis :- The flow of solvent but not the solute from a region of low concentration to high concentration when the two solutions of diffent concentration are separated by a semipermeable membrane is known as osmosis.



If a hydrostatic Pressure in excess of osmotic pressure is applied to the higher concentration side the flow of solvent gets reversed and this process is known reverse osmosis
Therefore in reverse osmosis the solvent is forced to move from concentrated soln. to dilute soln. across the semipermeable membrane.

Advantage of reverse osmosis :-

1. Semipermeable membrane is durable & can be easily replaced within few minutes
2. No phase change takes place during the process
3. The process is promising for the future it requires extremely low energy for consumption.

Water softening Techniques :- Internal Treatment of Boiler feed water

The Treatment of raw water inside the boiler is known as Internal Treatment.

Internal Treatment methods are -

i) Colloidal Conditioning :- Scale formation can be reduced by adding colloidal substances like Kerosene tanin, glue, agar etc. to the boiler water. These substances act as Protective Coatings. They surround the minute particles of scale forming salts and prevent their coalescence & coagulation. Hence, the salt remains as loose, non sticky deposits in the form of sludges which can be removed by simple blow-down operation. This process is suitable for low-pressure boilers.

ii) Carbonate Conditioning :- In this process Na_2CO_3 is added to boiler water due to which the main scale forming salt $CaSO_4$ gets converted into $CaCO_3$ and ppt out in the form of loose sludge which can be removed by blow down operation

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

Carbonate conditioning is not suitable for high pressure boiler because CO_3^{-} ions undergo hydrolysis to form OH^{-} ions.

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

$$HCO_3^{-} + H_2O \longrightarrow H_2O + CO_2 + OH^{-}$$

iii) Phosphate Conditioning :- Scale formation is prevented by addition of sodium phosphate which react with calcium and magnesium salts giving non-adherent and soft sludge of Calcium & magnesium phosphate respectively. (low pressure boilers)

$3MgCl_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2\downarrow + 6NaCl$

$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$

(4) <u>Calgon conditioning</u> :- Calgon is sodium hexa meta phosphate $Na_2[Na_4(PO_3)_6]$
It is extensively used in Internal Treatment and prevent the ~~scale~~ scale and sludge formation by converting scale forming impurity like $CaSO_4$ to highly soluble complex

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

$$\underset{\text{Scale forming Salt}}{2CaSO_4} + [Na_4(PO_3)_6] \longrightarrow \underset{\text{soluble complex}}{[Ca_2(PO_3)_6]^{--}} + 2Na_2SO_4$$

At high temp. and Pressure

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

Sodium orthophosphate

$$Na_2P_2O_7 + 2CaSO_4 \longrightarrow Ca_2P_2O_7 + Na_2SO_4$$

sludge blow down operation
Calcium orthophosphate