HARDNESS OF WATER: Softening of Hard Water: Lime-Soda (LS) process

(ii) Hot lime soda process: It is operated at a temp. of 80 to 150°C.Since hot process is operated at a temp. close to the boiling point of the solution. Hence, (a) the reaction proceeds faster (b) the softening capacity of hot process is increased to many folds(c) the precipitate and sludge formed settle down rapidly and no coagulants required (d) much of dissolved gases such as CO_2 and air driven out of the water (e) viscosity of softened water is lower, so filtration of water becomes much easier. This in turn increases the filtering capacity of filters (f) hot lime soda process produces water of comparatively low residual hardness of **15 to 30 ppm**. Hot lime soda plant consists of three parts namely (i) a reaction tank-in which raw water, chemicals and steam are thoroughly mixed (ii) conical sedimentation vessel –in which sludge settle down (iii) sand filter-which ensures complete removal of sludge from the softened water.

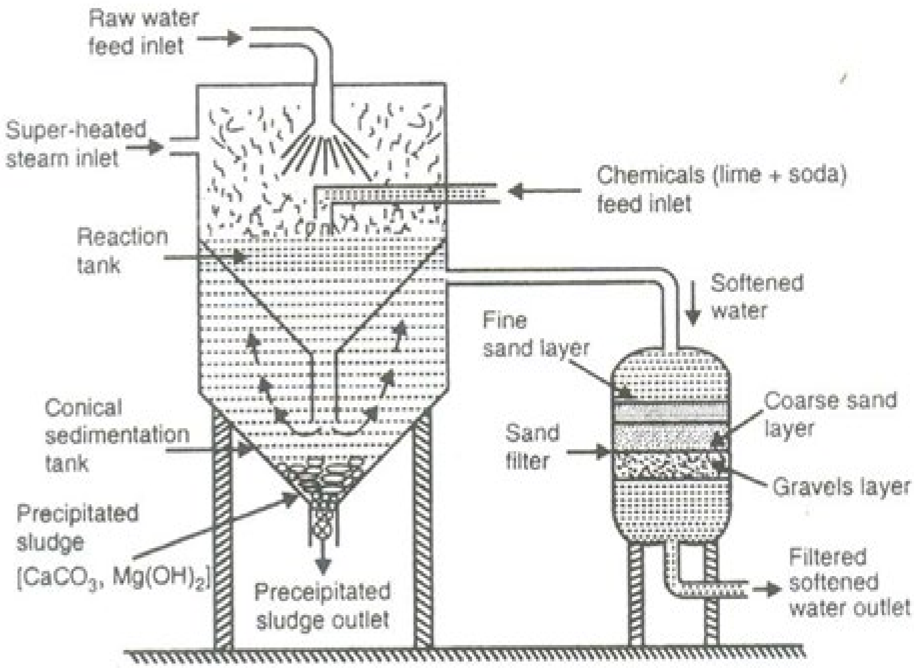

Fig. Hot lime-soda softener

Advantages of L-S process: (i) It is very economical. (ii) if this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be required. (iii) the process increases the pH value of treated water, thereby corrosion of distribution pipes is reduced. (iv) Besides, the removal of hardness, the quantity of minerals in water are reduced. (v) To certain extent, Fe and Mn are also removed from the water. (vi) Due to alkaline nature of treated water, amount of pathogenic bacteria in water is considerably reduced.

Disadvantages of L-S process: (i) For efficient and economical softening, careful operation and skilled supervision is required. (ii) Disposal of large amount of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low –lying areas of the city. (iii) This can remove hardness only up to **15 ppm**, which is not good for boilers.

(2) ZEOLITE OR PERMUTIT PROCESS: Chemical structure of sodium zeolite may be represented as $Na_2O.Al_2O_3.XSiO_2.Y,H_2O$ Where X=2-10, Y=2-6, expressed as Na_2Ze. Zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly its sodium ions with hardness producing ions in water. Zeolite are also known as permutits. Zeolites can be classified in to two types (i) **Natural zeolites**: are non-porous. For e.g., natrolite, $Na_2O.Al_2O_3.4SiO_2.2H_2O$ (ii) **Synthetic zeolites**: are porous and possess gel structure. They are prepared by heating together china clay, faldspar and soda ash. Such zeolites possess **higher exchange capacity** per unit weight than natural zeolites.

Zeolite Process: In this process hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions ($Ca^{2+,}$ Mg^{2+} etc.) are retained by zeolite as CaZe and MgZe: while outgoing water contains sodium salts. Reaction taking place during zeolite process are:

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

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

$Na_2Ze + CaCl_2$ (or $CaSO_4$) $\rightarrow CaZe + 2NaCl$ or Na_2SO_4

$Na_2Ze + MgCl_2$ (or $MgSO_4$) $\rightarrow MgZe + 2NaCl$ or Na_2SO4

(Zeolite) (Hardness)

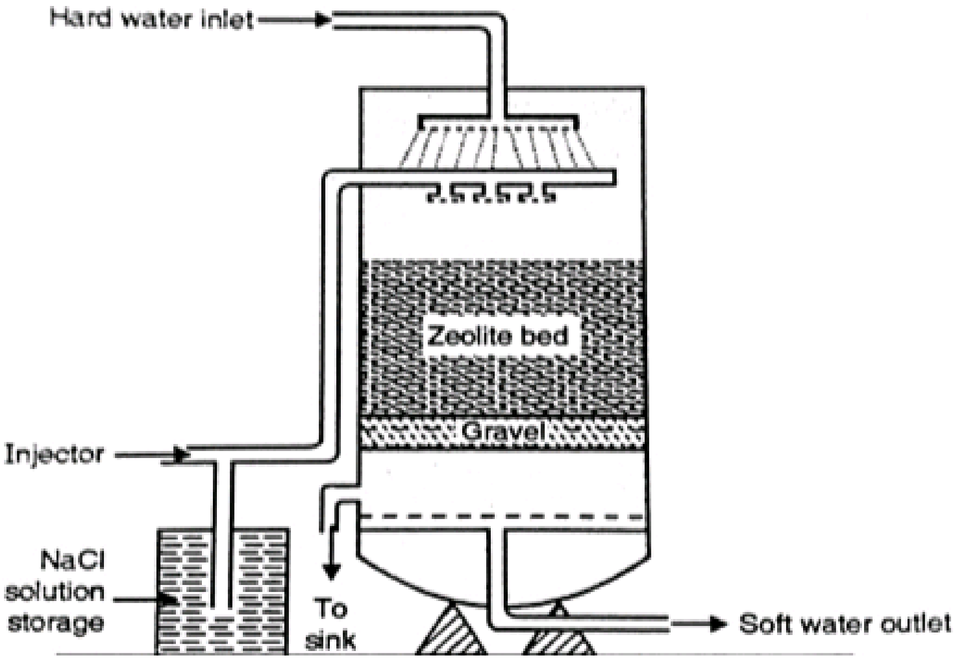

Fig. Zeolite water softener

Regeneration of zeolite: When zeolite is completely converted in to CaZe and MgZe and it ceases to soften water i.e.it gets exhausted. At this stage the supply of hard water is stopped and exhausted zeolite is reclaimed by treatment of zeolite bed with a Conc. 10% **brine (NaCl)** solution.

CaZe or MgZe + NaCl → Na_2Ze + $CaCl_2$ or $MgCl_2$

(Exhausted Zeolite) (Brine) (Reclaimed Zeolite) (Washing)

The washing containing $CaCl_2$ and $MgCl_2$ are led to drain and the regenerated zeolite bed thus obtained is used for softening purpose.

Limitations of Zeolite Process:

(1) If water is turbid, the suspended matter must be removed by coagulation or filtration before the water is admitted to zeolite bed, otherwise the turbidity will clog the pores of zeolite bed, thereby making it inactive.

(2) If water contains large quantities of colored ions such as Mn^{2+} and $Fe^{2+,}$ they must be removed first because these ions produce Mn and Fe zeolite, which cannot be easily regenerated.

(3) Mineral acids if present in water, destroy the zeolite bed. Therefore, they must be neutralized with soda before admitting the water to zeolite softening bed.

Advantages of zeolite process:

(1) It removes the hardness almost completely and water of about 10 ppm hardness is produced.

(2) The equipment used is compact occupying a small space.

(3) No impurities are precipitated so there is no danger of sludge formation in the treated water at a later stage.

(4) The process automatically adjusts itself for variation in hardness of incoming water.

(5) It is quite clean

(6) It requires less time for softening.

(7) It requires less skill for maintenance as well as operation.

Disadvantages of zeolite process:

(1) The treated water contains more sodium salts than in L-S process.

(2) The process only replaces Ca^{2+} and Mg^{2+} ions by Na+ ions but leaves all the acidic ions (like HCO_3^- and $CO_3^{2-)}$ as such in the softened water. When such softened water (containing $NaHCO_3$ and Na_2CO_3) is used in boilers for steam generation, $NaHCO_3$ decomposes producing CO_2, which causes corrosion and Na_2CO_3 hydrolyses to NaOH, which causes caustic

embrittlement. *Caustic Embrittlement is a type of boiler corrosion, caused by using highly alkaline water in the boiler. Caustic soda attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate. This causes embrittlement of boiler parts, particularly stressed parts like bends, joints, rivets etc. , causing even failure of boiler.*

(3) High turbidity water cannot be treated efficiently by this method because fine impurities get deposited on the zeolite bed, thereby creating problem for its working.

(3) ION EXCHANGE OR DE-IONIZATION OR DEMINERALIZATION PROCESS:

Ion exchange resins are insoluble, crossed linked, long chain organic polymers with a micropores structure and the "**functional groups**" attached to the chain are responsible for the ion exchanging properties. Resins containing acidic functional groups (-COOH, -SO_3H) are capable of exchanging their H^+ ions with other cations. While basic functional groups (-NH_2=NH as hydrochloride) are capable of exchanging their anions with other anions. Ion exchange resins may be classified as:

(i)Cation exchange resins (RH^+): are mainly styrene divinyl benzene copolymers, which on sulphonation or carboxylation become capable of exchange their H^+ ions with the cations in the water.

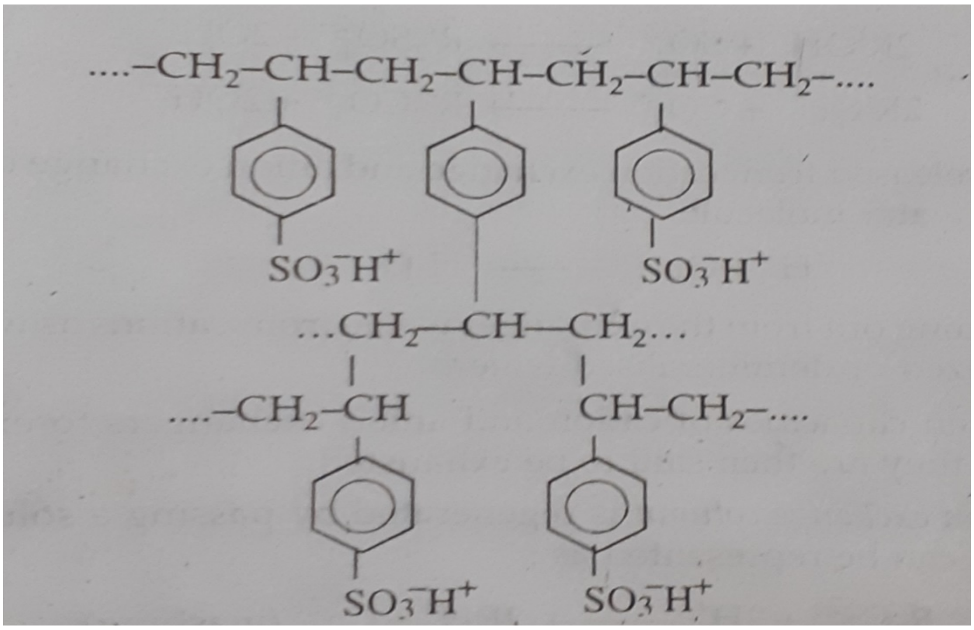

Fig: Acidic or Cation exchange resin (Sulphonate Form)

(ii)Anion exchange resins (R'OH): are styrene divinyl benzene or aniline formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium group as an integral part of the resin matrix. These, after treatment with Dil. NaOH solution, become capable to exchange their OH^- ions with anions in water.

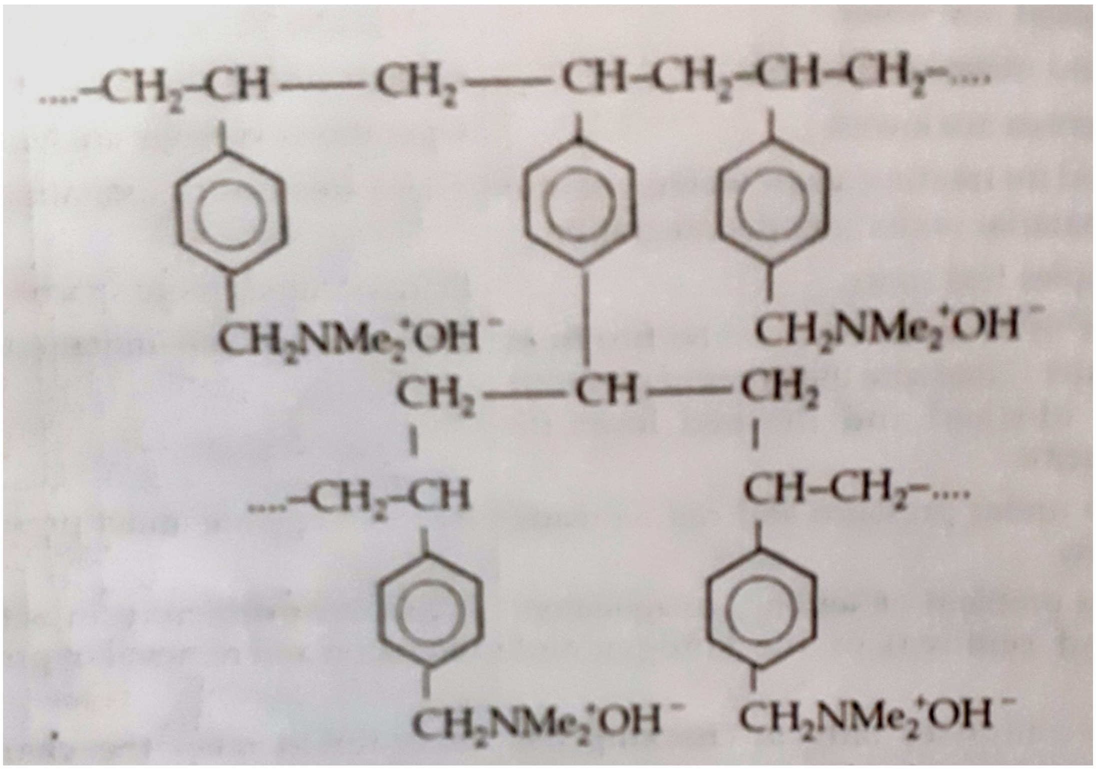

Fig: Basic or anion exchange resin (Hydroxide form)

Process: The hard water is passed first through cation exchange column which removes all cations like **Ca^{2+} and Mg^{2+}** from it and equivalent amount of H^+ ions are released from this column to water: Thus,

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

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

After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like **SO_4^{2-} , Cl^-** etc. present in water and equivalent amount of OH^- ions are released from this column to water. Thus:

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

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

$2R'OH- + CO_3^{2-} \rightarrow R'_2CO_3^{2-} + 2OH^-$

H^+ and OH^- ions (released from cation exchange and anion exchange column respectively) get combined to produce water molecule.

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

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

Regeneration: When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted.

The **exhausted cation exchange column** is regenerated by passing a solution of dil. **HCl** or dil.$\mathbf{H_2SO_4}$. The regeneration can be represented as:

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

The column is washed with deionized water and washing (which contains Ca^{2+}, Mg^{2+} etc. and Cl^- or SO_4^{2-}) is passed to sink or drain.

The **exhausted anion exchange column** is regenerated by passing a solution of dil. **NaOH**.The regeneration can be represented as:

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

The column is washed with deionized water and washing (which contains Na^+ and SO_{42-} or Cl^- ions) is passed to sink or drain.

The regenerated ion exchange resins are then used again.

Advantages: (1) The process can be used to soften highly acidic or basic waters (2) It produces water of very low hardness (say **2 ppm**) so it is very good for treating water for use in high pressure boilers.

Disadvantages: (1) The equipment is costly and more expensive chemicals are required. (2) If water contains turbidity, then the output of the process is reduced. The turbidity, must be below 10 ppm. If it is more, it has to be removed first by coagulation and filtration.

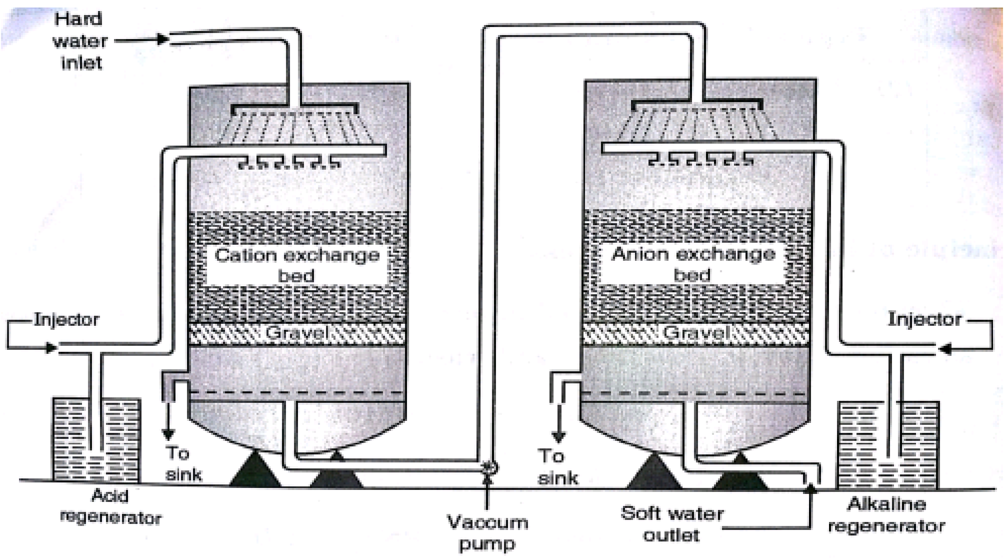

Fig: Demineralization of water