Softening of Water: The process whereby we remove or reduce the hardness of water, irrespective of whether it is temporary or permanent is termed as 'softening of water.'

The hardness causing salts can be removed from water by following two ways.

ⓐ External treatment, and

ⓑ Internal treatment.

The external treatment of water is carried out before its entry into the boiler. This treatment prevents boiler problems. It can be done by Lime-soda, Zeolite or ion exchange processes.

In contrast, the internal treatment of boiler feed water refers to the conditioning of water in the boiler itself by addition of chemicals. It can be done by colloidal, phosphate, calgon and carbonate conditioning.

8.2 Zeolite or Permutit Process

Zeolites are naturally occurring hydrated sodium alumino silicate minerals (like $Na_2O . Al_2O_3 . x SiO_2 . y H_2O$ where $x = 2 - 10$ & $y = 2 - 6$) capable of exchanging reversibly its sodium ions for hardness-producing ions in water.

Zeolites are also known as *permutits* and in Greek it means 'boiling stone'.

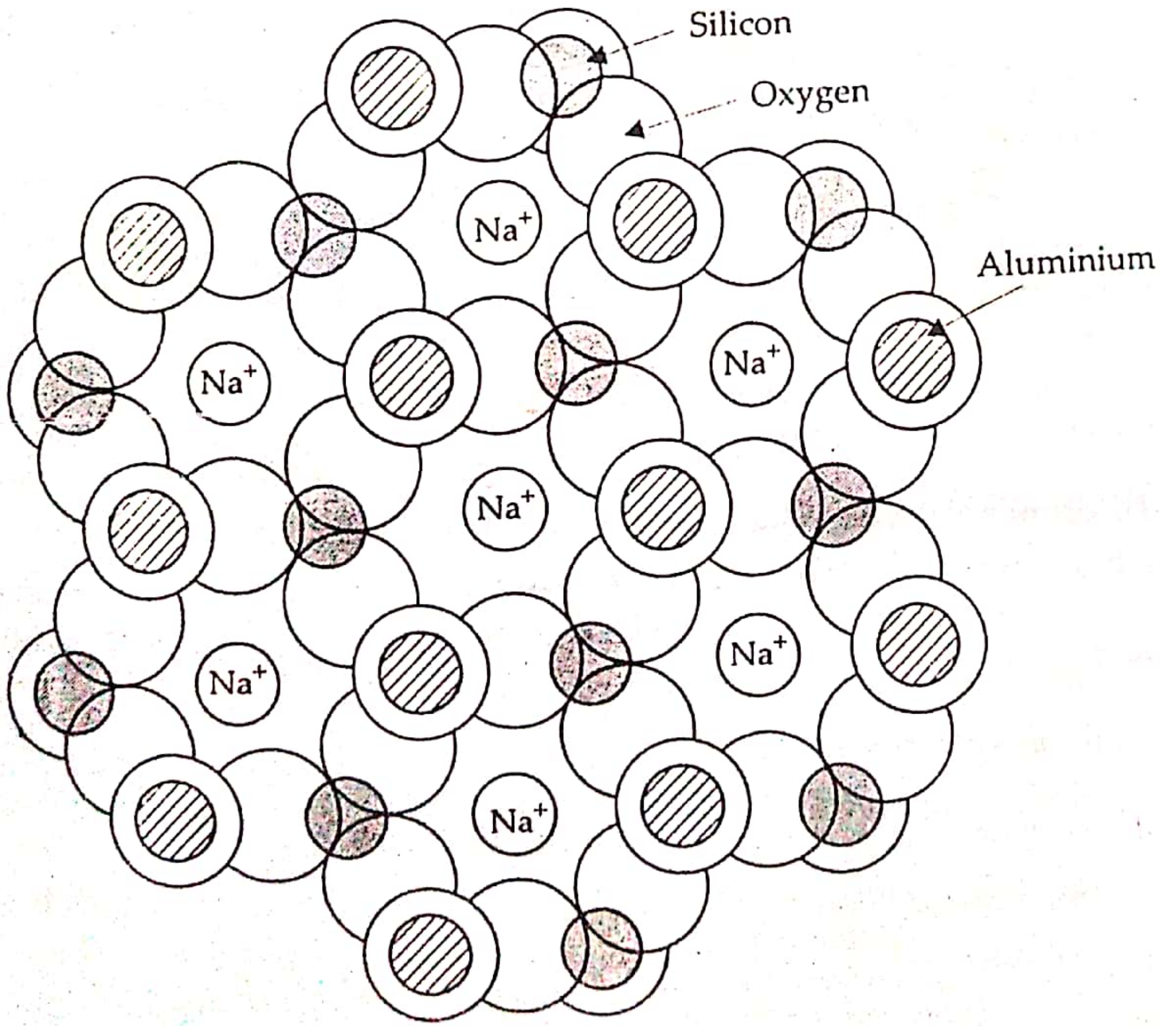


Fig. 3. Structure of a naturally occuring zeolite, $NaAlSiO_4$. The sodium ions are loosely held in holes in the lattice.

A zeolite crystal can be considered to result from the linking of several SiO_4 tetrahedra, each oxygen of a tetrahedron being shared with an adjacent one. The empirical formula is thus $(SiO_2)_n$. However, some of the Si^{4+} ions may be isomorphostly replaced by Al^{3+} **ions** and in order to balance the charges an extra positive-ion such as Na^+ and K^+ must also be incorporated for every Al^{3+} introduced. The *linking of these tetrahedra results in an open structure with cavities.* The porous nature of the structure permits free movement of water molecules and ions.

Zeolites are of two *types viz.* natural and synthetic.

(*i*) *Natural zeolites* are non-porous, amorphous and durable for example, natrolite, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$.

(*ii*) *Synthetic zeolites* are porous and possess a gel structure. They are prepared by heating together sodium carbonate (Na_2CO_3), alumina (Al_2O_3) and silica (SiO_2).

Synthetic zeolites possess higher exchange capacity per unit weight compared to natural zeolites.

Process. For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, housed in a cylindrical unit, see Fig. 4.

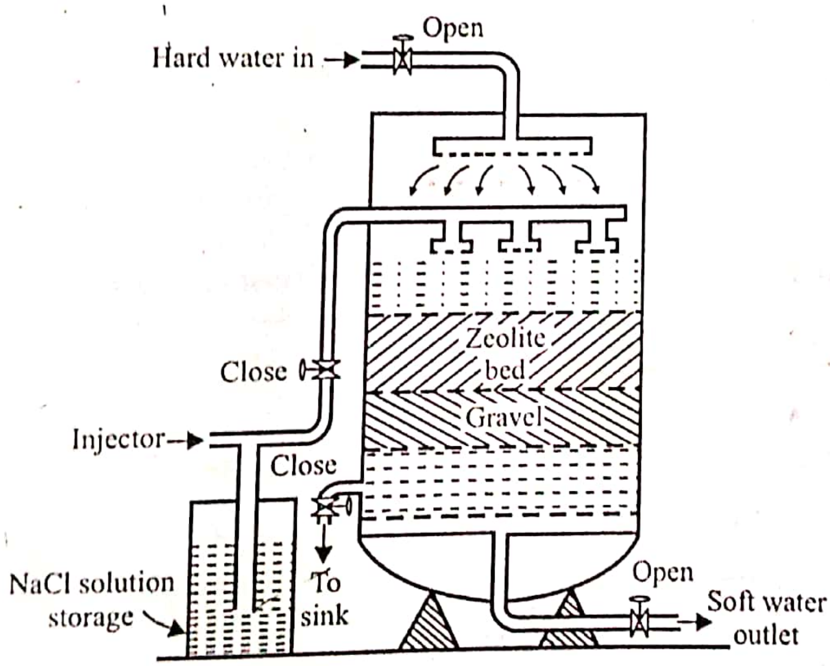


Fig. 4. Zeolite softener.

Zeolite holds sodium ions loosely and can be simply represented as Na_2Ze where Ze represents insoluble radical frame work.

The hardness-causing ions (Ca^{2+}, Mg^{2+}, etc.) are retained by the zeolite as CaZe and MgZe respectively, while the outgoing water contains sodium salts. In the process, the water becomes free from Ca^{2+} & Mg^{2+}, the main hardness producing cations.

Reactions taking place during the softening process are :

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

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

Regeneration. After some time, the zeolite is completely converted into calcium and magnesium zeolites. Eventually, the bed ceases to soften water, *i.e.*, it gets exhausted. At this stage, the supply of hard water is stopped and the exhausted zeolite is reclaimed by treating the bed with a concentrated sodium chloride (brine) solution when the following reactions take place.

$$\underset{\text{Exhausted zeolite}}{CaZe \text{ (or } MgZe)} + \underset{\text{Brine}}{2\,NaCl} \longrightarrow \underset{\text{Reclaimed zeolite}}{Na_2Ze} + \underset{\text{Washings}}{CaCl_2 \text{ (or } MgCl_2)}$$

Limitations of zeolite process

(1) If the supplied water is turbid, the suspended matter must be removed (by coagulation, filteration, etc.) before the water is fed to the zeolite bed. Otherwise the pores of the zeolite bed will get clogged by the turbidity, thereby making it inactive.

(2) If water contains large quantities of Mn^{2+} and Fe^{2+}, they must be removed first because these ions produce maganese and iron zeolites, which are very difficult to be regenerated.

(3) Mineral acids, if present in water, destroy the zeolite bed and hence they must be neutralized with soda in advance, before feeding the water into the zeolite bed.

(4) The water to be softened should not be hot as the zeolite tends to dissolve in it.

(5) Anions are not removed by this process. Thus the bicarbonates present in hard water get converted to $NaHCO_3$ which goes into soft water effluent. If it is used as boiler feed, under the boiler conditions $NaHCO_3$ dissociates to

$$NaHCO_3 \longrightarrow NaOH + CO_2$$

Both the products are not desirable. Since NaOH may lead to caustic embrittlement and CO_2 makes the condensed water acidic and corrosive. Thus it is desirable to remove temporary hardness before subjecting the raw water to zeolite process.

(6) Compared to ion-exchange process, water treated by the zeolite process contains 25% more dissolved solids. Moreover, the higher cost of the plant and materials are also limiting factors.

Advantages of zeolite process

(*i*) The hardness is nearly completely removed and water of about 10 ppm hardness is produced.

(*ii*) The equipment used is compact and occupies less space.

(*iii*) It is quite clean and rapid process which requires less time for softening.

(*iv*) For maintenance as well as operations, less skill is needed.

(*v*) Impurities are not precipitated, so there is no danger of sludge formation.

8.3 Demineralization or Deionization by Ion-exchange Process

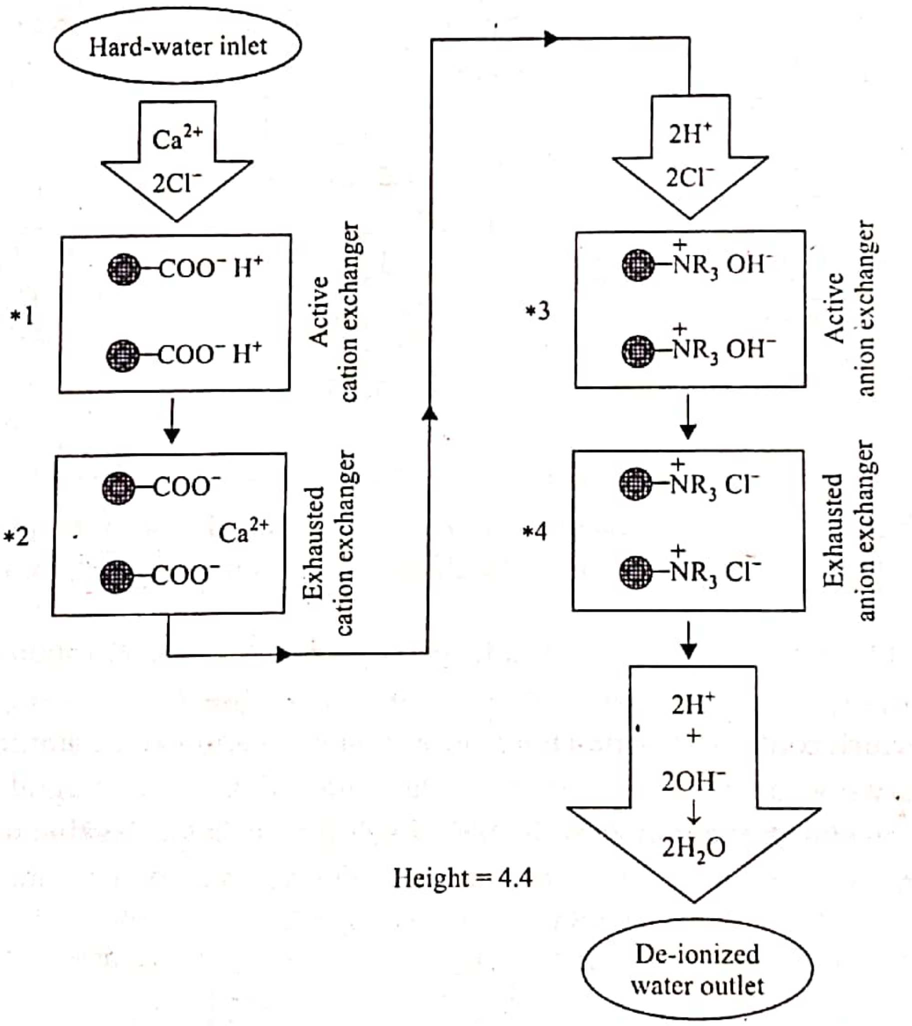
Ion exchange is a process by which ions held on a porous, essentially insoluble solid are exchanged for ions in solution that is brought in contact with it.

Ion-exchange resins are insoluble, cross-linked, high molecular weight, organic polymers with a porous structure, and the *"functional groups"* attached to the chains are responsible for the *ion-exchange properties*.

Process. The hard water is first passed through cation exchange column Fig. 8, when all the cations like Ca^{2+}, Mg^{2+}, etc. are removed (taken up by the resin) from it, and equivalent amount of H^+ ions are released from this column to water.

Thus

$$\underset{\text{Solids}}{2\,RCOO^-H^+} + \underset{\text{Solution}}{Ca^{2+}} \rightleftharpoons \underset{\text{Solid}}{(RCOO^-)_2\,Ca^{2+}} + \underset{\text{Solution}}{2\,H^+}$$



*1. Styrene-divinyl benzene copolymer after functionalization with carboxylic acid groups becomes cation exchange resin with exchangeable H^+ ions.

*2. The Ca^{2+} ions from the hard water replace the H^+ ions in the cation-exchanger, and de-cationized water is obtained.

*3. Styrene-divinyl benzene copolymer after functionalization with quaternary ammonium hydroxide becomes anion exchange resin with exchangeable OH^- ions.

*4. The Cl^- ions from the de-cationized water replace the OH^- ions in the anion- exchanger.

Fig. 8. Illustration of the de-ionization process using ion-exchange resins.

After passing through cation exchange column, the hard water is passed through anion exchange column, when all the anions like SO_4^{2-}, Cl^-, etc. present in the water are removed (taken up by resin) and equivalent amount of OH^- ions are released from this column to water.

Thus : $\underset{\text{Solid}}{[R-\overset{\oplus}{N}(CH_3)_3]OH^-} + \underset{\text{Solution}}{Cl^-} \rightleftharpoons \underset{\text{Solid}}{[R-\overset{+}{N}(CH_3)_3]Cl^-} + \underset{\text{Solution}}{OH^-}$

H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water 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, is known as ***deionized*** or ***demineralized water***, and is also free from acidity or alkalinity. Thus it is as pure as distilled water.

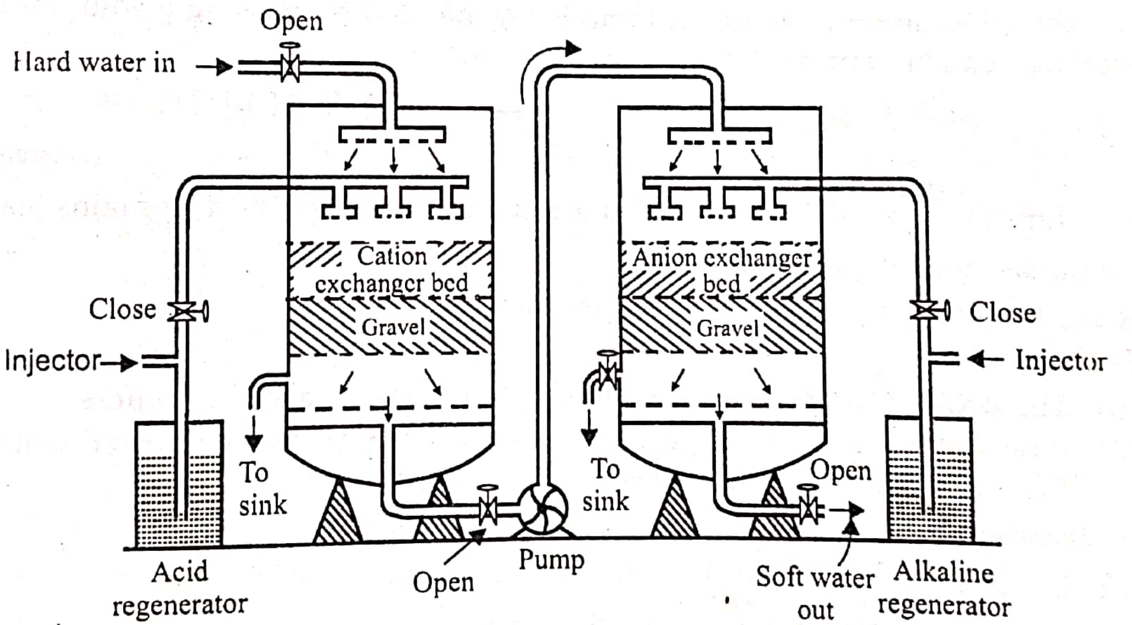


Fig. 9. Demineralization of water.

For deionization, water is first passed through the cation exchanger and then through the anion exchanger.

This is because cation exchangers are easily attacked by alkalis, whereas all types of ion-exchangers are not attacked by acids.

When water is first passed through a cation exchanger, salts present in water are converted into corresponding acids, which on passing through an anion exchanger do not harm it and finally get converted into pure water.

If reverse sequence is used, then on passing water through anion-exchanger, alkali is produced which harms the cation-exchanger in subsequent step. Thus, such a sequence is usually avoided.

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. H_2SO_4. The regeneration can be represented as :

$$(RSO_3^-)_2 M^{2+} + 2H^+ \longrightarrow 2RSO_3^-H^+ + \underset{\text{(washing)}}{M^{2+}}$$

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

$$[RN^+(CH_3)_3]_2 A^{2-} + 2OH^- \longrightarrow 2\,[RN^+(CH_3)_3]\,OH^- + \underset{\text{(Washing)}}{A^{2-}}$$

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

The regenerated ion exchange resins are then used again.

Advantages

(*i*) The process can be used to soften highly acidic or alkaline waters.

(*ii*) It produces water of very low hardness (say 2 ppm). So, the treated water is very good for use in high pressure boilers.

Disadvantages

(*i*) Capital cost is high since chemical and equipment both are costly.

(*ii*) If water contains turbidity then the efficiency of the process is reduced.