

before put to use. *The process of removing hardness-producing salts from water, is known as softening of water.* In industry, main three methods employed for softening of water are :

(1) Lime-soda process : In this method, the soluble calcium and magnesium salts in water are chemically converted into **insoluble compounds**, by adding calculated amounts of *lime* $[Ca(OH)_2]$ and *soda* $[Na_2CO_3]$. *Calcium carbonate* $[CaCO_3]$ and *magnesium hydroxide* $[Mg(OH)_2]$, so-precipitated, are filtered off.

Note : It may be pointed here that *the chemical reactions taking place during lime-soda treatment are rather slow.* Moreover, the precipitates formed, particularly of $CaCO_3$ and $Mg(OH)_2$, are fine and they tend to produce a super-saturated solution. This eventually results in "after deposition", later in the pipes and boiler tubes, producing sludges. These in-turn decrease the effective diameters of pipes, clog tubes and valves, cause their corrosion, etc. Consequently, these drawbacks partly offsets the purpose of water softening. To overcome these drawbacks, the following arrangements are made :

(i) *Thorough mixing* of the chemicals and water is carried out. (ii) *Proper time for completion of reactions, these, is given.* Alternatively, means are adopted for accelerating the reaction (e.g., by using hot lime-soda method). (iii) Substances that bring down the fine particles of precipitates called accelerators (like activated charcoal) are added. (iv) Substances that help in the formation of coarse precipitates are added. These are called coagulants or flocculents, e.g., alum. (v) Suitable sedimentation chamber is provided before final filtration.

Calculation of lime-soda requirement.

Constituent	Reaction	Need
Ca^{2+} (Perm. Ca)	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	S
Mg^{2+} (Perm. Mg)	$\text{Mg}^{2+} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Mg}(\text{OH})_2 + \text{Ca}^{2+}$	
	$\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
HCO_3^- (e.g., NaHCO_3)	$2\text{HCO}_3^- + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_3^{2-}$	L - S
$\text{Ca}(\text{HCO}_3)_2$ (Temp. Ca)	$\text{Ca}(\text{HCO}_3)_2 + \text{Ca}(\text{OH})_2 \longrightarrow 2\text{CaCO}_3 + 2\text{H}_2\text{O}$	L
$\text{Mg}(\text{HCO}_3)_2$ (Temp. Mg)	$\text{Mg}(\text{HCO}_3)_2 + 2\text{Ca}(\text{OH})_2 \longrightarrow$ $2\text{CaCO}_3 + \text{Mg}(\text{OH})_2 + 2\text{H}_2\text{O}$	2L
CO_2	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	L
H^+ (free acids, HCl, H_2SO_4 , etc.)	$2\text{H}^+ + \text{Ca}(\text{OH})_2 \longrightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
Coagulants : FeSO_4	$\text{Fe}^{2+} + \text{Ca}(\text{OH})_2 \longrightarrow \text{Fe}(\text{OH})_2 + \text{Ca}^{2+}$ $2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} + \text{O}_2 \longrightarrow 2\text{Fe}(\text{OH})_3$ $\text{Ca}^{2+} + \text{Na}_2\text{CO}_3 \longrightarrow \text{CaCO}_3 + 2\text{Na}^+$	L + S
$\text{Al}_2(\text{SO}_4)_3$	$2\text{Al}^{3+} + 3\text{Ca}(\text{OH})_2 \longrightarrow 2\text{Al}(\text{OH})_3 + 3\text{Ca}^{2+}$ $3\text{Ca}^{2+} + 2\text{Na}_2\text{CO}_3 \longrightarrow 3\text{CaCO}_3 + 6\text{Na}^+$	L + S
NaAlO_2	$\text{NaAlO}_2 + \text{H}_2\text{O} \longrightarrow \text{Al}(\text{OH})_3 + \text{NaOH}$ 2NaOH is eq to $\text{Ca}(\text{OH})_2$	-L

Notes : (1) If $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$ are considered as ions ($\text{Ca}^{2+} + 2\text{HCO}_3^-$) and ($\text{Mg}^{2+} + 2\text{HCO}_3^-$) respectively, then calculation results will be same.

(2) Equivalent weight of NaAlO_2 is equal to its molar mass.

(3) If treated water contains OH^- and CO_3^{2-} ions, then these are formed from excess eq each of $\text{Ca}(\text{OH})_2$ plus Na_2CO_3 and Na_2CO_3 respectively. So these excess amounts should be added to the calculations.

(4) When the impurities are given as CaCO_3 and/or MgCO_3 , these should be considered due to bicarbonates of calcium and/or magnesium respectively.

(5) Substances like NaCl , KCl , Na_2SO_4 , SiO_2 , Fe_2O_3 , etc. do not impart any hardness and, therefore, these do not consume any lime or soda. These should not be taken into consideration for calculating the lime and soda requirements.

Now 100 parts by mass of CaCO_3 are equivalent to |: (i) 74 parts of $\text{Ca}(\text{OH})_2$, and (ii) 106 parts of Na_2CO_3 .

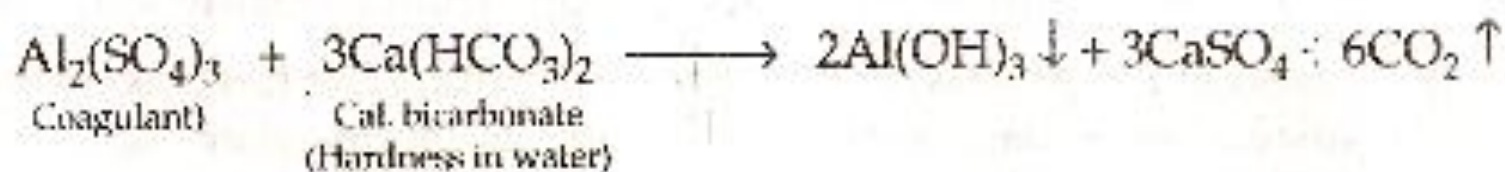
\therefore Lime requirement for softening

$$= \frac{74}{100} \left[\begin{array}{l} \text{Temp. Ca}^{2+} + 2 \times \text{Temp. Mg}^{2+} + \text{Perm. (Mg}^{2+} + \text{Fe}^{2+} + \text{Al}^{3+}) \\ + \text{CO}_2 + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) + \text{HCO}_3^- - \text{NaAlO}_2 \\ \text{all in terms of CaCO}_3 \text{ eq} \end{array} \right]$$

\therefore Soda requirement for softening

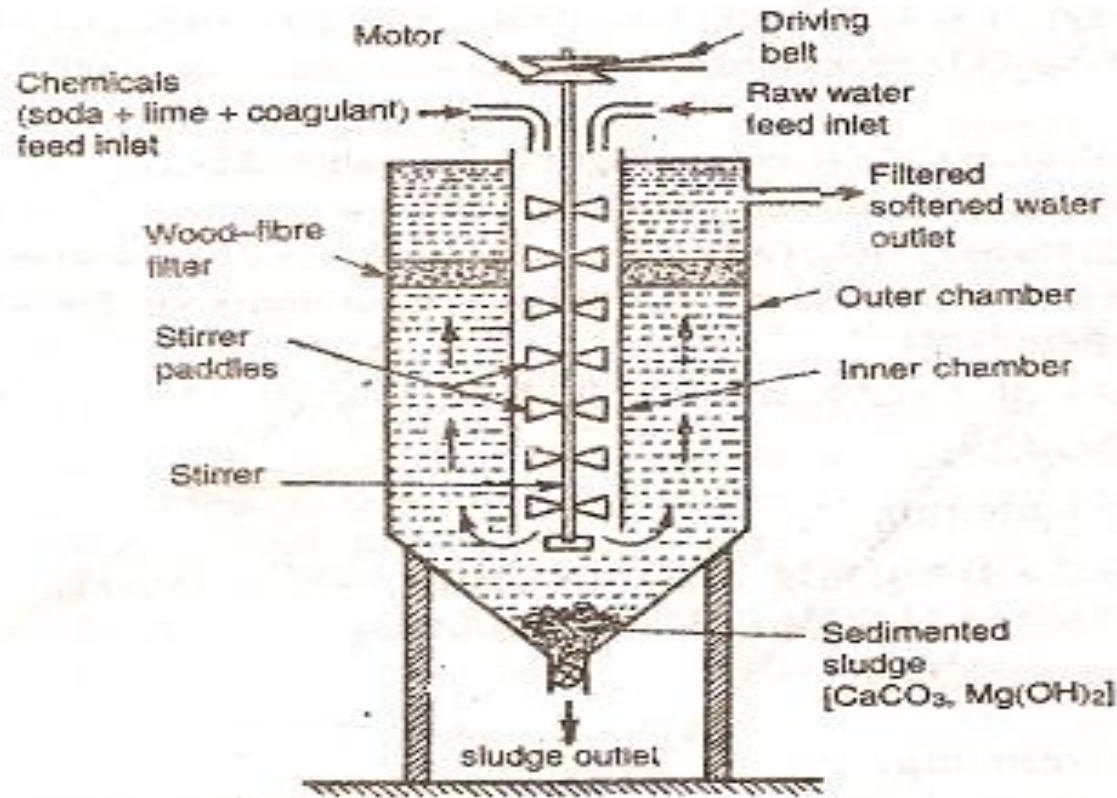
$$= \frac{106}{100} \left[\begin{array}{l} \text{Perm. (Ca}^{2+} + \text{Mg}^{2+} + \text{Al}^3 + \text{Fe}^{2+}) + \text{H}^+ (\text{HCl or H}_2\text{SO}_4) - \text{HCO}_3^- \\ \text{all in terms of CaCO}_3 \text{ eq} \end{array} \right]$$

(i) **Cold lime-soda process** ; In this method, calculated quantity of chemical (lime and soda) are mixed with water at room temperature. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and cannot be filtered easily. Consequently, it is essential to add small amounts of coagulants (like alum, aluminium sulphate, sodium aluminate, etc.), which hydrolyse to flocculent, gelatinous precipitate of aluminium hydroxide, and entraps the fine precipitates. Use of sodium aluminate as coagulant also helps the removal of silica as well as oil, if present in water. Cold L-S process provides water, containing a residual hardness of 50 to 60 ppm.



Method : Raw water and calculated quantities of chemicals (lime + soda + coagulant) are fed from the top into the inner vertical circular chamber, fitted with a vertical rotating shaft carrying a number of paddles. As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, whereby softening of water takes place. As the softened water comes into the outer co-axial chamber, it rises upwards. The heavy sludge (or precipitated floc) settles down in the outer chamber by the time the softened water reaches up. The softened water

complete removal of sludge. Filtered soft water finally flows out continuously through the outlet at the top (see Fig.) Sludge settling at the bottom of the outer chamber is drawn off occasionally.



. Continuous cold lime-soda softener.

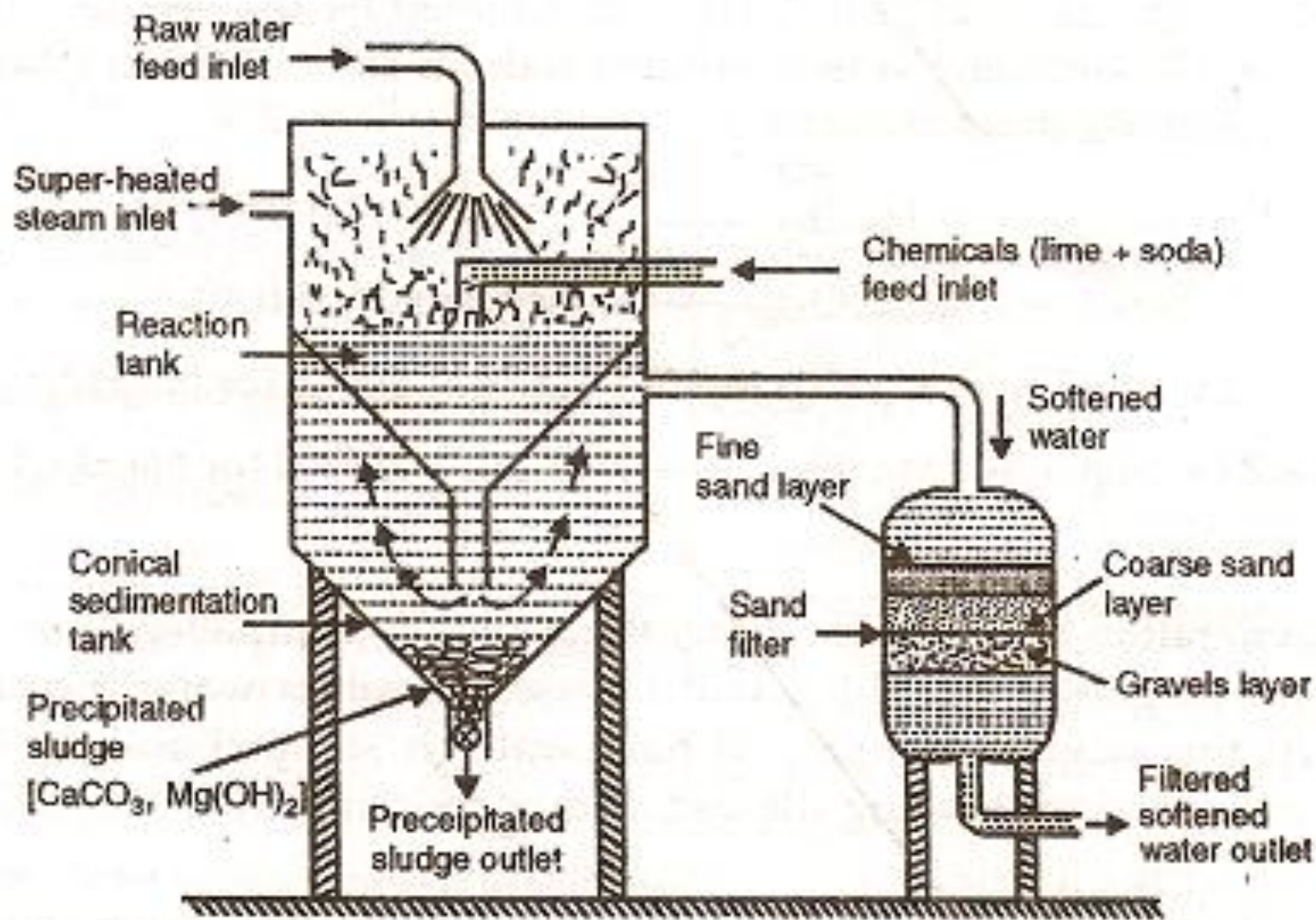
(ii) **Hot lime-soda process** involves in treating water with softening chemicals at a temperature of 80 to 150°C . Since hot process is operated at a temperature close to the boiling point of the solution, so : (a) the reaction proceeds faster ; (b) the softening capacity of hot process is increased to many fold ; (c) the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed ; (d) much of the 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, and (f) hot lime-soda process produces water of comparatively lower residual hardness of 15 to 30 ppm.

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Hot lime-soda plant consists essentially (see Fig.) of three parts: (a) a 'reaction tank' in which raw water, chemicals and steam are thoroughly mixed ; (b) a "conical sedimentation vessel" in which sludge settles down, and (c) a "sand filter" which ensures complete removal of sludge from the softened water.

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 needed. (iii) The process increases the pH value of the treated-water, thereby corrosion of the distribution pipes is reduced. (iv) Besides the removal of hardness, the quantity of minerals in the water are reduced. (v) To certain extent, iron and manganese are also removed from the water. (vi) Due to alkaline nature of treated-water, amount of pathogenic bacterias in water is considerably reduced.

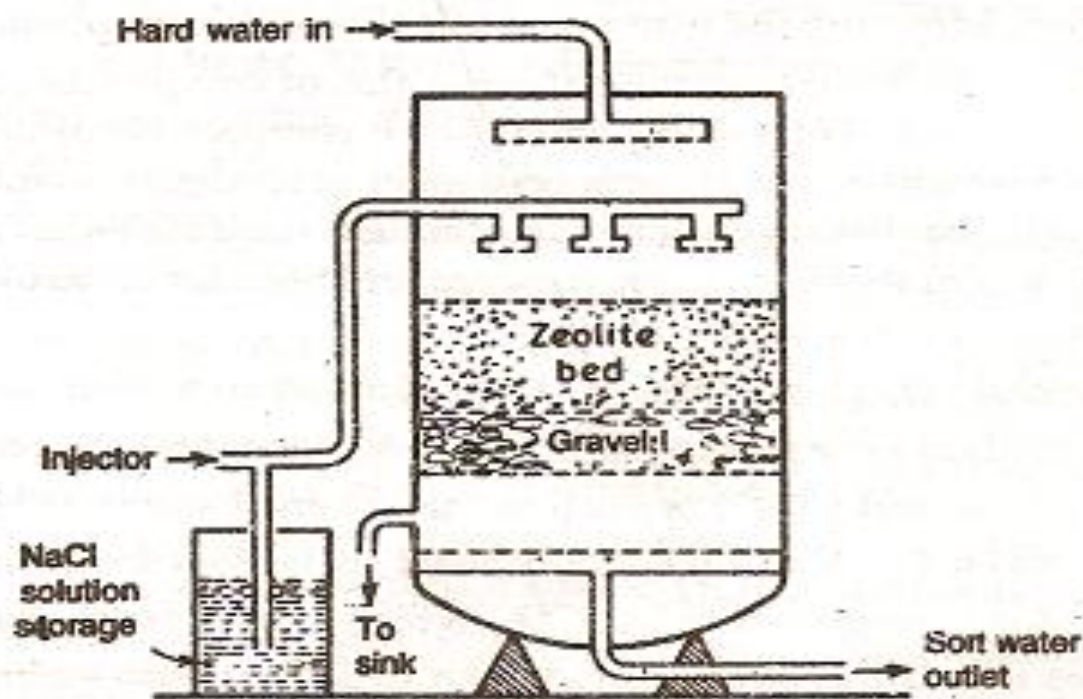
Disadvantage of L-S process : (i) For efficient and economical softening, careful operation and skilled supervision is required. (ii) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city. (iii) This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



Continuous hot lime-soda softener.

(2) **Zeolite or permutit process** : Chemical structure of sodium zeolite may be represented as: $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y \text{H}_2\text{O}$ where $x = 2 - 10$ and $y = 2 - 6$. Zeolite is hydrated sodium aluminosilicate, capable of exchanging reversibly its sodium ions for hardness-producing ions in water. Zeolites are also known as permutits. Zeolites are of two types : (i) *Natural zeolites* are non-porous. For example, natrolite, $\text{Na}_2\text{O} \cdot \text{Al}_3\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. (ii) *Synthetic zeolites* are porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash. Such zeolites possess higher exchange capacity per unit weight than natural zeolites.

Process : For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder (see Fig.). The



. Zeolite softener.

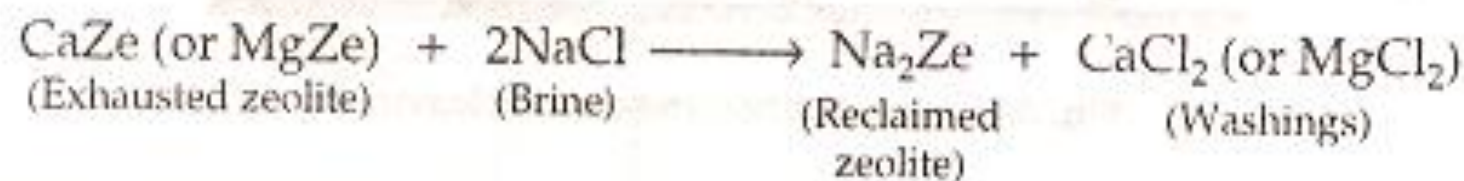
hardness-causing ions (Ca^{2+} , Mg^{2+} , etc.) are retained by the zeolite as CaZe and MgZe ; while the outgoing water contains sodium salts. Reactions taking place during the softening process are :



(Zeolite)

(Hardness)

Regeneration : After some time, the zeolite is completely converted into calcium and magnesium zeolites and it 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 (10%) brine (NaCl) solution.



The washings (containing CaCl_2 and MgCl_2) are led to drain and the regenerated zeolite bed thus-obtained is used again for softening purpose.

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

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

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

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 lime-soda process. (2) The method 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 $NaHCO_3$, Na_2CO_3 , etc.) is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2 , which causes corrosion ; and sodium carbonate hydrolyses to sodium hydroxide, which causes caustic embrittlement. (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.