Ion-exchange methods

- Exchange ions causing hardness with non-hardness causing ions
- Reversible – occur between solid and liquid phase
- Common ion-exchangers used for water softening
  i. Natural and synthetic zeolites
  ii. Carbonaceous ion-exchangers
  iii. Synthetic resins

Zeolite or Permutit process

- Zeolite – $Na_2O.Al_2O_3.xSiO_2.yH_2O$ (x = 2-10 and y = 2-6)
- Zeolite exchange Na^+ with hardness-producing ions in water. Thus find application in softening of water.

Zeolite

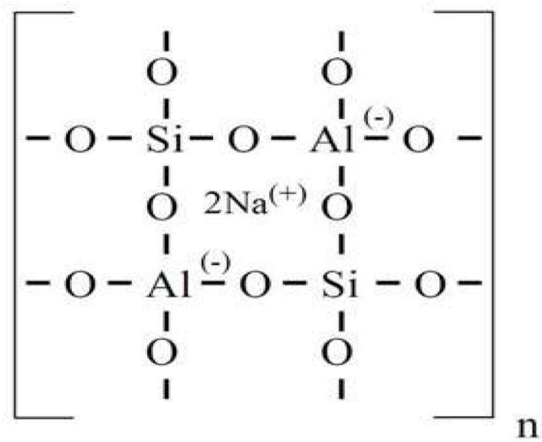
Natural

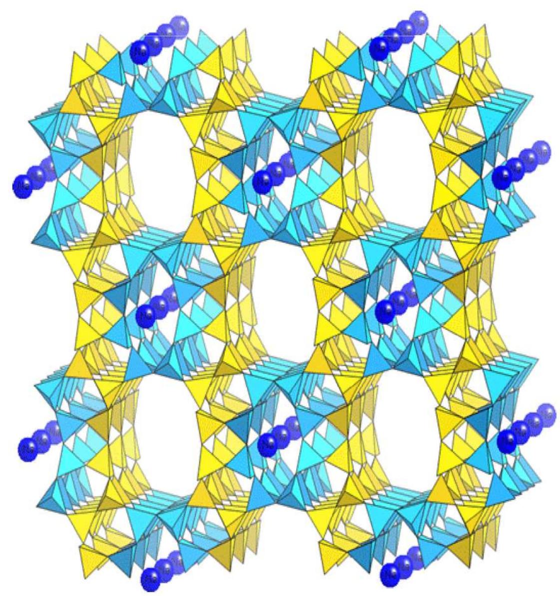
- Non-porous
- Eg. Natrolite $Na_2O.Al_2O_3.3SiO_2.2H_2O$
- Thomsonite Na_2O $CaO.Al_2O_3.2SiO_2.2.5H_2O$
- Harmotome BaO $K_2O.Al_2O_3.5SiO_2.5H_2O$

Synthetic

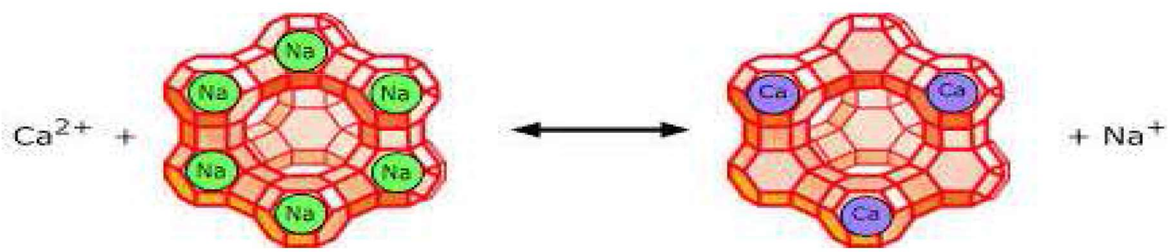
- Porous
- Have higher exchange capacity per unit
- Weight than natural zeolite
- Prepared by heating sodium silicate and aluminium hydroxide

- Zeolite - microporous solid
- Pores of zeolite can accommodate wide variety cations Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} etc. Cations are loosely held and can readily be exchanged for others in a contact solution.
- Natural mineral – aluminosilicate - $Na_x[(AlO_2)_x(SiO_2)_y]_x\ zH_2O$.
- Insoluble in water
- The word 'Zeolite' derived from Greek 'zeo' – boiling 'lithios' – stone. This word was coined by Cornstedt in 1736.
- Natural zeolite is not pure. Pores filled by minerals, metals, quartz and other zeolites.
- Zeolites – also produced industrially in large scale (pure and uniform pores)





- Softening of water - hard water percolate at specified rate through a zeolite bed.
- Hardness causing ions (Ca^{2+}, Mg^{2+}, etc.,) retained by zeolite as CaZe and MgZe. Equivalent of Na^+ is released
- Fe and Mn present in water also get removed.
- Fe and Mn bound tightly to zeolite such that it cannot be easily exchanged for Na^+ during regeneration.



$$Na_2Ze + \begin{matrix} Ca(HCO_3)_2 \\ Mg(HCO_3)_2 \end{matrix} \longrightarrow \begin{matrix} CaZe \\ MgZe \end{matrix} + 2NaHCO_3$$

$$Na_2Ze + \begin{matrix} MgCl_2, MgSO_4 \\ CaCl_2, CaSO_4 \end{matrix} \longrightarrow \begin{matrix} MgZe \\ CaZe \end{matrix} + 2NaCl, Na_2SO_4$$

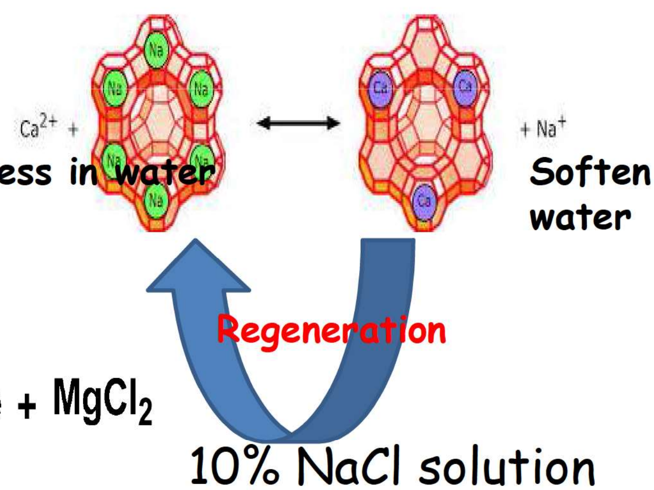
$$Na_2Ze + \begin{matrix} Fe(HCO_3)_2 \\ Mn(HCO_3)_2 \end{matrix} \longrightarrow \begin{matrix} FeZe \\ MnZe \end{matrix} + 2NaHCO_3$$

Regeneration of Zeolite

- When zeolite get exhausted i.e Na_2Ze become CaZe or MgZe it stops softening water.
- Regeneration of CaZe or MgZe to NaZe with 10% NaCl solution.
- Regeneration of zeolite can also be achieved with $NaNO_3$, Na_2SO_4, KCl, KNO_3.
- Regenerated zeolite can be used again for softening of water.

Steps involved in regeneration

- Back washing
- Treating with brine solution
- Rinsing before use



$$MgZe + sat.NaCl \longrightarrow Na_2Ze + MgCl_2$$

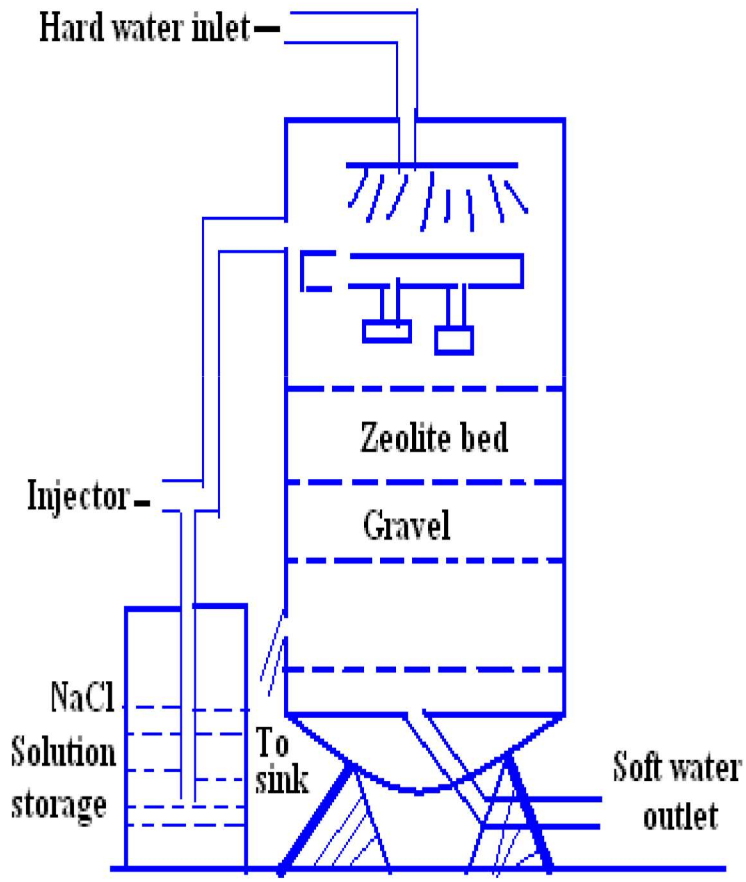
Exhausted Zeolite

$$CaZe + sat.NaCl \longrightarrow Na_2Ze + CaCl_2$$

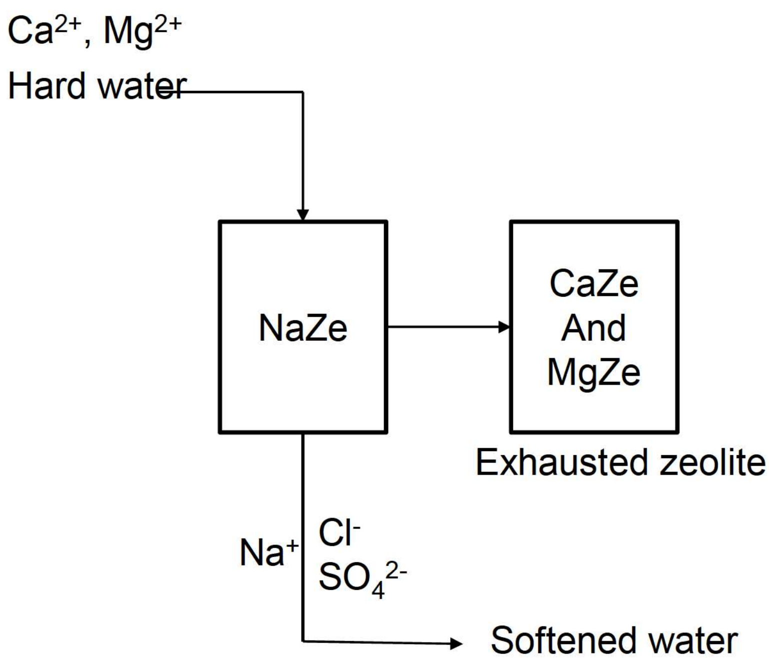
Exhausted Zeolite

Zeolite water softener

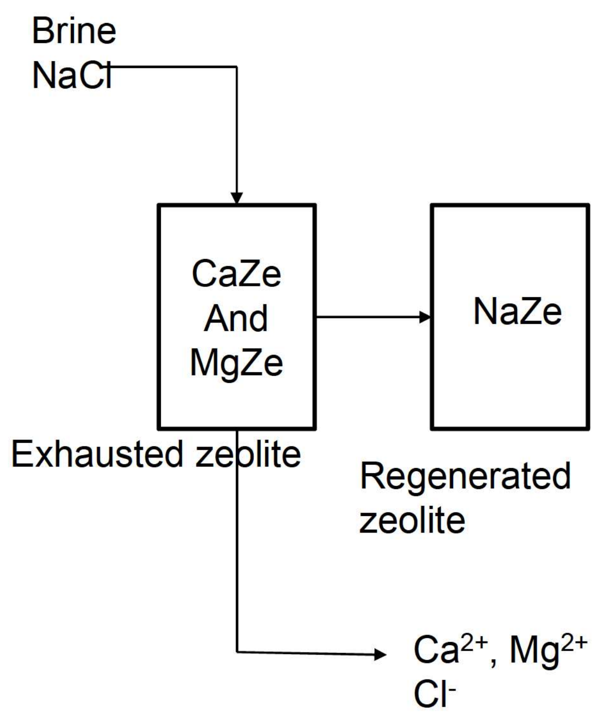
- Made in both pressure and gravity type and both the types are available in automatic, semi-automatic and manually operated design.
- Hard water percolate at specified rate through zeolite bed.
- Ca^{2+} and Mg^{2+} ions are retained by zeolite bed and equivalent of Na^{+} is liberated.
- Resulted water is free from Ca^{2+} and Mg^{2+} i.e soft water



Softening cycle



Regeneration cycle



Limitation of zeolite process

- Supply water should be free from turbid and suspended matter. Otherwise pores will be clogged and rate of softening
- Supply water should be free from Mn^{2+} and Fe^{2+} because it will bind tightly to zeolites which cannot be easily regenerated.
- pH of water supplied should be neutral i.e 7. Acidic or alkaline water may attack Zeolite.
- Hot water should not be used as the zeolite tends to dissolve in it.

- **Disadvantages of zeolite process**
  - Treated water contains more sodium salts than in L-S process.
  - The method only replaces Ca^{2+} and Mg^{2+} ions by Na^{+} ions but leaves ions such as HCO_3^-, CO_3^{2-} in the softened water.

$$NaHCO_3 \longrightarrow \underbrace{NaOH}_{\text{Caustic embrittlement}} + CO_2$$

Advantages of zeolite process

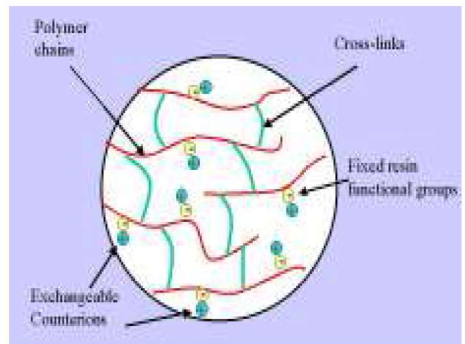
- Produces water of residual hardness 10 ppm.
- Equipment is compact.
- No danger of sludge formation in treated water.
- Unlike L-S there is no 'after deposition' problem
- Clean process
- Less time for softening
- Need less skill for maintenance and operation.
- Process adjust itself for hardness of incoming water.
- It can work under pressure. Hence, it can be installed in the water supply line itself avoiding double pumping.

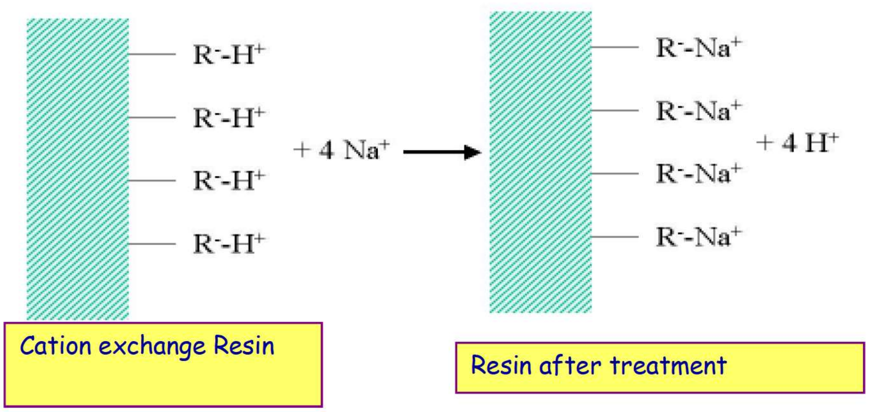
Comparison of zeolite and L-S process

Zeolite process	L-S process
Residual hardness of 10-15 ppm in water	Residual hardness of 15-50 ppm in water
Cost of plant and material is higher	Capital cost is lower
Operation expenses are lower	Operation expenses are higher
Compact	Need more space
Water to be softened must be free from acidity, alkalinity and turbidity.	There are no such limitation
Can operate under pressure	It cannot operate under pressure
No problem of settling, coagulation, filtration and removal of ppt	Difficulty in settling, coagulation, filtration and removal of ppt
Only treated water has to be checked	Frequent control and adjustment of reagent is needed
Treated-water has more dissolved solids	Treated-water has less dissolved solids
Adjust itself to water of different hardness	Reagent dose must be adjusted for water of different hardness

Carbonaceous ion-exchangers

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a microporous structure, and the functional groups attached to the chain is responsible for the "ion-exchange" properties.





In general the resins containing acidic functional groups (-COOH, -SO_3H etc) are capable of exchanging their H^+ ions with other cations, which comes in their contact; whereas those containing basic functional groups (-NH_2, =NH as hydrochlorides) are capable of exchanging their anions with other ions, which comes in their contact.

Properties of good ion-exchanger

For effective water treatment, ion exchanger should possess the following properties

- Should be non-toxic
- Should possess a high ion-exchange capacity
- Should be physically durable
- Should be resistant to chemical attack
- Should be cheap and commonly available
- Regeneration should be easy and economic
- Should have large surface area - ion-exchange is surface phenomenon.

Structure

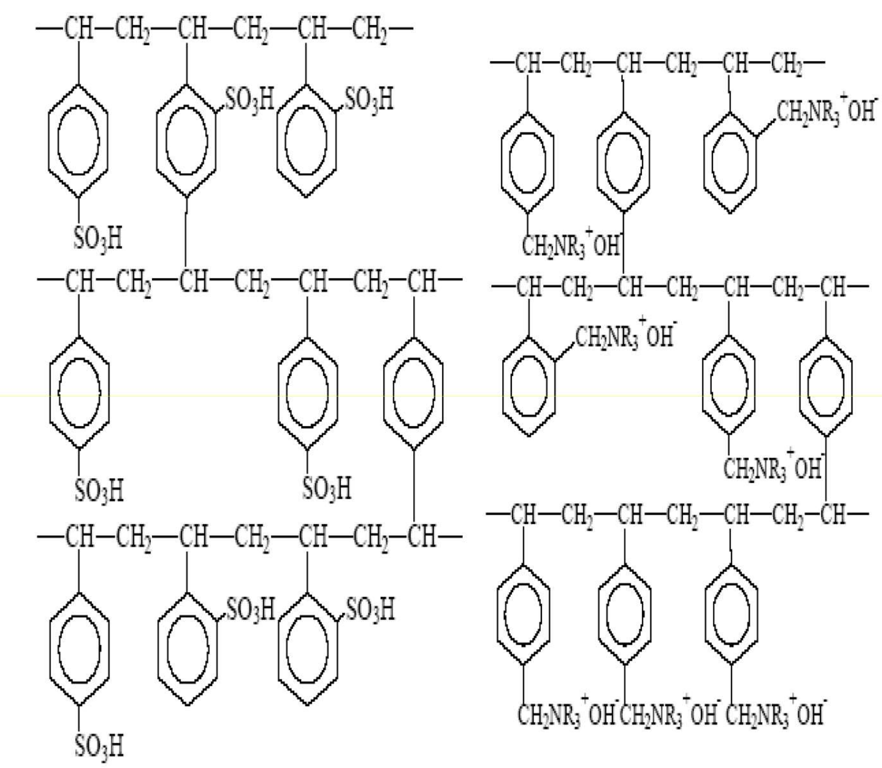
<u>Types</u>

1. Cation exchange resin (RH^+) –

   Strongly acidic ($SO_3^-H^+$) and weakly acidic (COO^-H^+) cation exchange resins

2. Anion Exchange resin (ROH^-) –

   Strongly basic ($R_4N^+OH^-$) and weakly basic ($RNH_2^+OH^-$) anion exchange resins

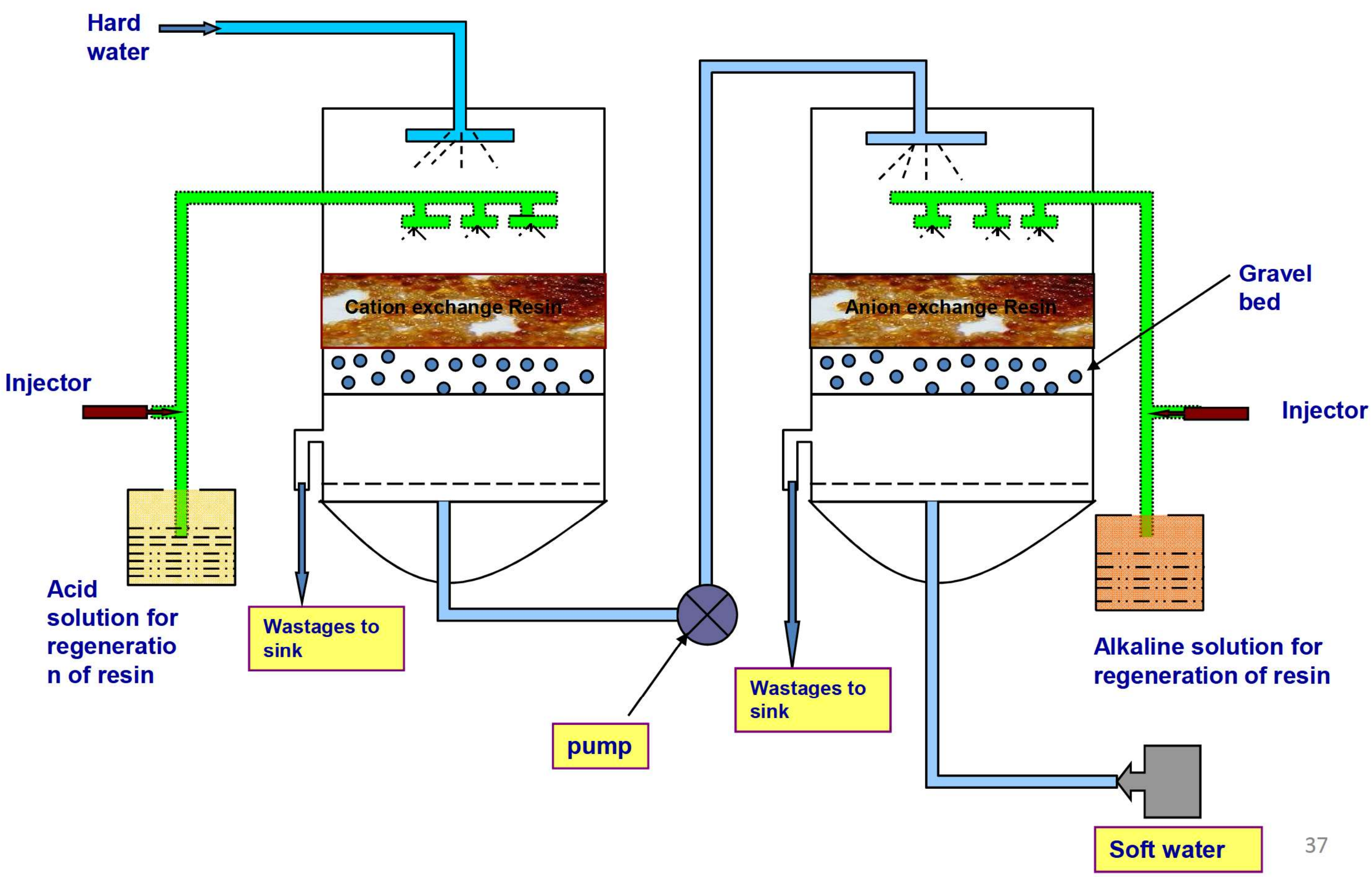


A strongly acidic sulphonated polystyrene cation exchange resin

A strongly basic quaternary ammonion anion exchange resin

R = CH_3

Ion exchange purifier or softener



Process or Ion-exchange mechanism involved in water softening

Reactions occurring at Cation exchange resin

$$2\ RH^+ + Ca^{2+}\ (\text{hard water}) \longrightarrow R_2Ca^{2+} + 2\ H^+$$

$$2\ RH^+ + Mg^{2+}\ (\text{hard water}) \longrightarrow R_2Mg^{2+} + 2\ H^+$$

Reactions occurring at Anion exchange resin

$$2\ ROH- + SO_4^{2-}\ (\text{hard water}) \longrightarrow R_2SO_4^{2-} + 2\ OH^-$$

$$2\ ROH^- + Cl^-\ (\text{hard water}) \longrightarrow R_2Cl^- + 2\ OH^-$$

At the end of the process

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

Regeneration of ion exchange resins

Regeneration of Cation exchange resin

$$R_2Ca^{2+} + 2H^+ \text{ (dil. HCl (or) } H_2SO_4) \longrightarrow 2\,RH^+ + Ca^{2+}$$

$(CaCl_2$, washings)

Regeneration of Anion exchange resin

$$R_2SO_4^{2-} + 2OH^- \text{ (dil. NaOH)} \longrightarrow 2\,ROH^- + SO_4^{2-}$$

$(Na_2SO_4$, washings)

Advantages

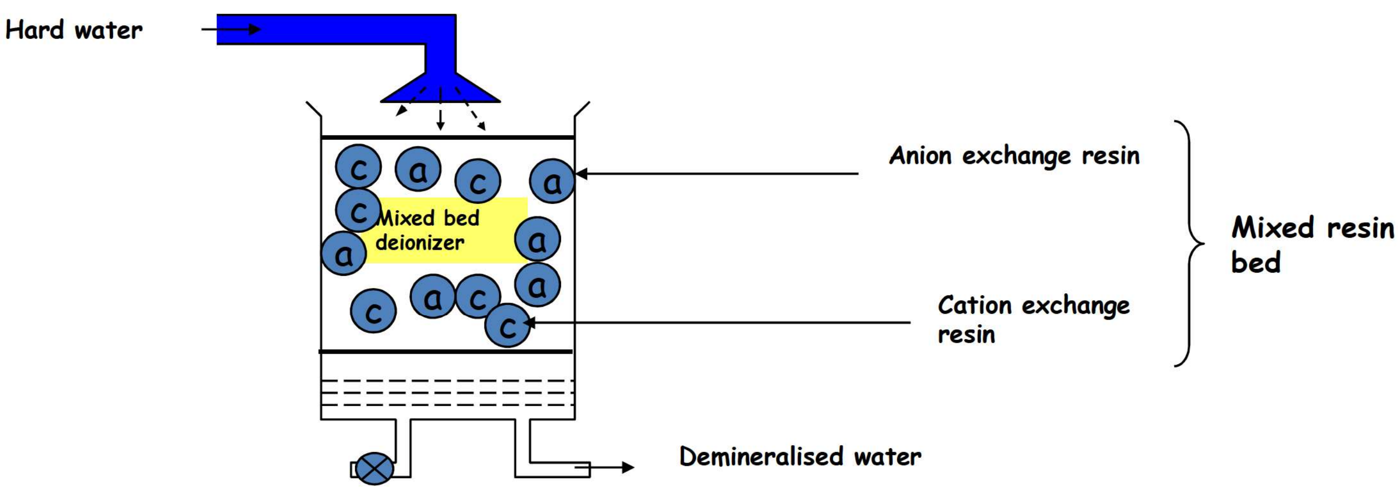
1. The process can be used to soften highly acidic or alkaline waters
2. It produces water of very low hardness of 1-2ppm. So the treated waters by this method can be used in high pressure boilers

Disadvantages

1. The setup is costly and it uses costly chemicals
2. The water should not be turbid and the turbidity level should not be more than 10ppm

Softening of water by Mixed Bed deioniser

1. It is a single cylindrical chamber containing a mixture of anion and cation exchange resins bed
2. When the hard water is passed through this bed slowly the cations and anioins of the hard water comes in to contact with the two kind of resins many number of times
3. Hence, it is equivalent to passing the hard water many number of times through a series of cation and anion exchange resins.
4. The soft water from this method contains less than 1ppm of dissolved salts and hence more suitable for boilers



Regeneration of mixed bed deionizer

1. When the bed (resins) are exhausted or cease to soften the water, the mixed bed is back washed by forcing the water from the bottom in the upward direction
2. Then the light weight anion exchanger move to the top and forms a upper layer above the heavier cation exchanger
3. Then the anion exchanger is regenerated by passing caustic soda solution (NaOH) from the top and then rinsed with pure water
4. The lower cation exchanger bed is then washed with dil.H_2SO_4 solution and then rinsed.
5. The two beds are then mixed again by forcing compressed air to mix both and the resins are now ready for use