Engineering Chemistry

F. Y. B. Tech.

Lecture – [7-11]

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Softening Methods

1. Lime-Soda Method
2. Zeolite Softener method
3. Ion Exchange Method

1. Lime-Soda Method

- In this method, calculated quantity of Lime [$Ca(OH)_2$] and Soda [Na_2CO_3] mixture is added to hard water.
- Precipitates of $CaCO_3$ and $Mg(OH)_2$ are formed due to reactions of hardness causing salts with lime and soda.
- These precipitates gets settled down in the form of sludge.
- This settling of precipitates is faster in hot lime soda method compared to cold Lime soda method.
- Hence for quick settling of particles of $CaCO_3$ and $Mg(OH)_2$, coagulants such as Alum [$Al_2(SO_4)_3$], sodium meta aluminate [$NaAlO_2$], or $FeSO_4$ could be used in cold lime soda method.

Constituent	Reaction	Need
Ca^{2+} (Perm. Ca)	$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	S
Mg^{2+} (Perm. Mg)	$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2 + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
HCO_3^- (e.g., $NaHCO_3$)	$2HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O + CO_3^{2-}$	L − S
$Ca(HCO_3)_2$ (Temp. Ca)	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2H_2O$	L
$Mg(HCO_3)_2$ (Temp. Mg)	$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$	2L
CO_2	$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$	L
H^+ (free acids HCl,	$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
Coagulants : $FeSO_4$	$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2 + Ca^{2+}$ $2Fe(OH)_2 + H_2O + O_2 \longrightarrow 2Fe(OH)_3$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+$	L + S
$Al_2(SO_4)_3$	$2Al^{3+} + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3Ca^{2+}$ $3Ca^{2+} + 2Na_2CO_3 \longrightarrow 3CaCO_3 + 6Na^+$	L + S
$NaAlO_2$	$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 + NaOH$	−L

From the above table it can be seen that 100 parts by mass of $CaCO_3$ are equivalent to 74 parts of $Ca(OH)_2$ and 106 parts of Na_2CO_3.

Lime requirement for softening

$$= \frac{74}{100}\left[\begin{array}{c}\text{Temp. } Ca^{2+} + 2 \times \text{Temp. } Mg^{2+} + \text{Perm. } (Mg^{2+} + Fe^{2+} + Al^{3+}) \\ + CO_2 + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^- - NaAlO_2 \\ \text{all in terms of } CaCO_3 \text{ eq.}\end{array}\right] \times \frac{\text{Volume of water}}{10^6} \times \frac{100}{\%\text{Purity}} \text{ Kg}$$

And Soda requirement for softening

$$= \frac{106}{100}\left[\begin{array}{c}\text{Perm. } (Ca^{2+} + Mg^{2+} + Al^{3+} + Fe^{2+}) + H^+ (HCl \text{ or } H_2SO_4) - HCO_3^- \\ \text{all in terms of } CaCO_3 \text{ eq.}\end{array}\right] \times \frac{\text{volume of water}}{10^6} \times \frac{100}{\%\text{Purity}} \text{ kg}$$

There are two types of lime-soda process.

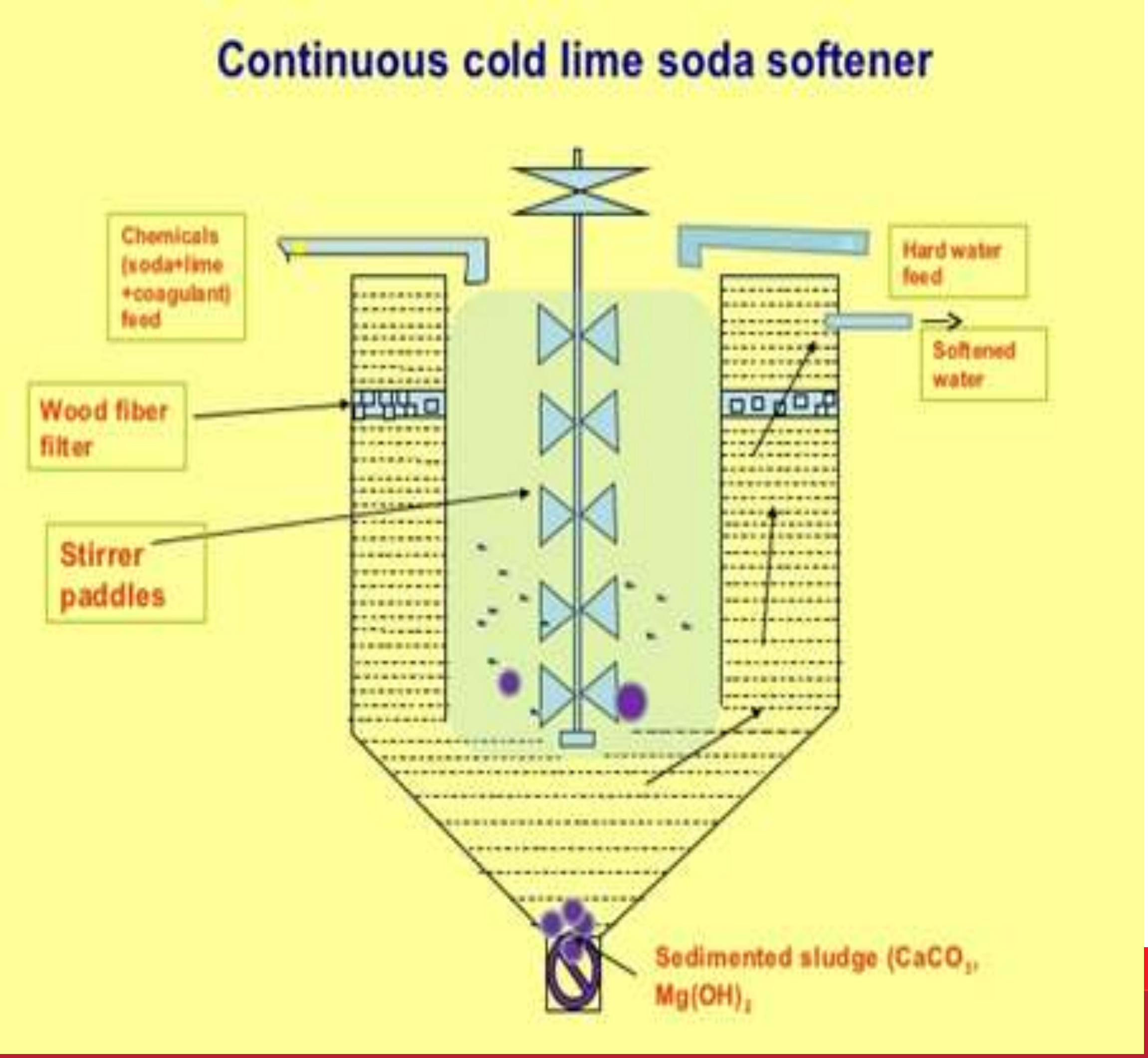
(1) Cold lime-soda process

and (2) Hot lime-soda process

A. Cold Lime-Soda Method

- In cold lime-soda method, hard water is treated with mixture of lime, soda and coagulants at room temperature about 25-30 ^{0}C.
- **Inner cylindrical reaction tank** equipped with stirrer, which ensures complete mixing of lime, soda and coagulants with hard water.
- In **outer conical sedimentation vessel**, sludge settles down
- **Wood fiber filters** ensures the complete removal of sludge particles from softened water.

Cold Lime-Soda Method



1. Carried out at 25 ^{0}C to 30 ^{0}C
2. Coagulants required
3. Stirring is essential as the reaction is operated at low temperature
4. Slow process
5. Dissolved gases are not removed
6. Filtration is not easy
7. Residual hardness is 50-60 ppm
8. Low softening capacity

B. Hot Lime-Soda Method

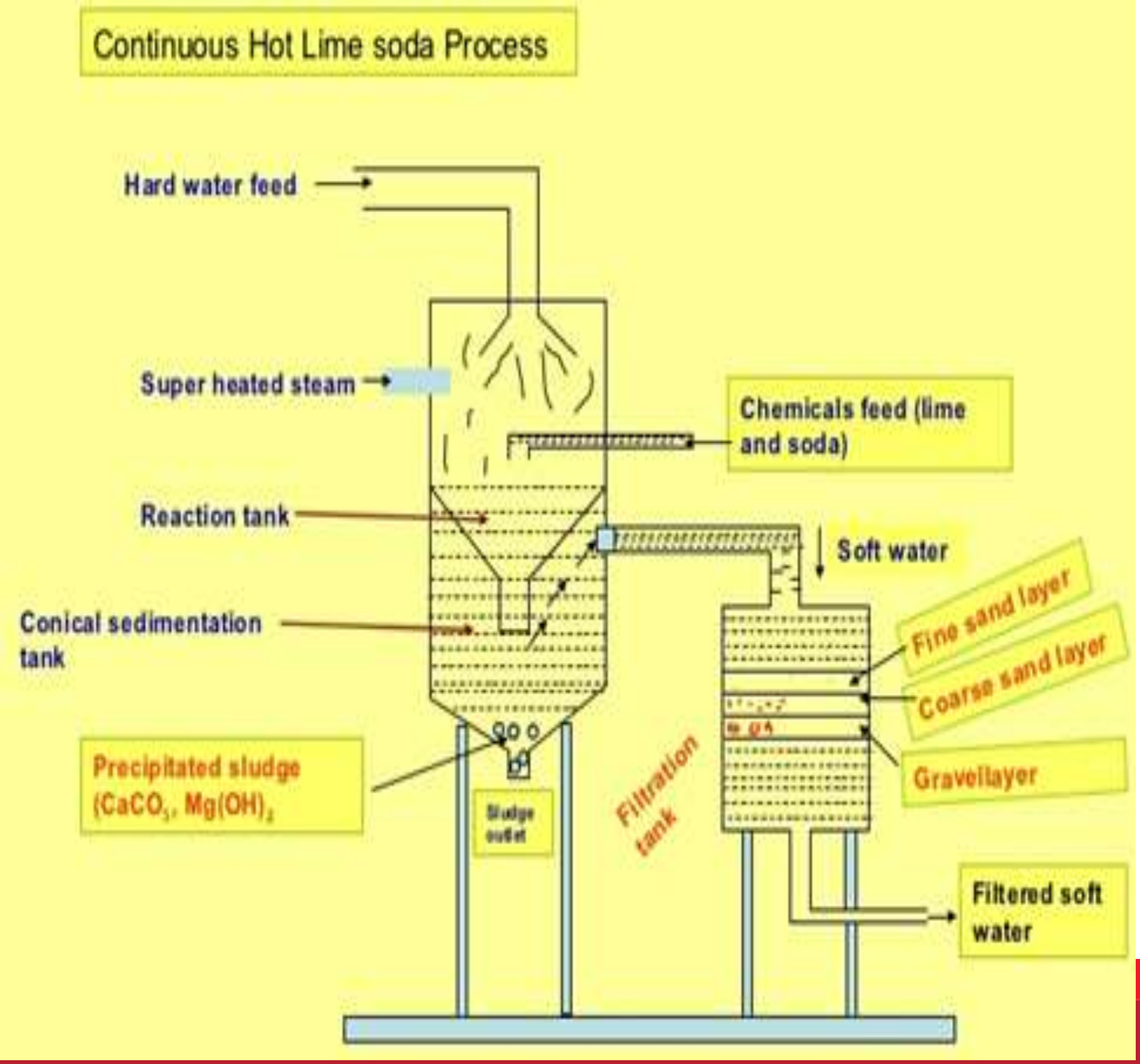
In Hot lime-soda process hard water is treated with soda and lime at 94-100°C
Hot lime-soda plant essentially consists of three parts

→ A 'Reaction tank' in which raw water, chemicals and steam are thoroughly mixed.

→ A 'Conical sedimentation vessel' in which sludge settles down, and

→ A 'sand filter' which ensures complete removal of sludge from the softened water.

Hot Lime-Soda Method



1. Carried out at 95 ^{0}C to 100 ^{0}C
2. Coagulants are not required
3. Stirring is not essential as the reaction is operated at high temperature
4. Fast process
5. Dissolved gases gets removed due to high temperature
6. Filtration is easy, hence sand filter is sufficient
7. Residual hardness is 15-30 ppm
8. High softening capacity

Advantages of hot lime-soda method over cold lime-soda method

- Economical process
- pH value of softened water is high (Decrease corrosion)
- Alkaline nature of treated water reduces pathogens, bacteria in water
- Fe (II) and Mn (II) can also be removed to certain extent

Disadvantages of Lime-soda method

- Softened water is 50 ppm hardness in cold lime-soda method and 15-30 ppm hardness in hot lime-soda method.
- Such water can not be used in high pressure boilers
- Disposal of large quantity of sludge is a big problem

2. Zeolite Softener method

- Sodium-Zeolites which are hydrated sodium alumino silicates, capable of exchanging their sodium ions with hardness producing ions are used.
- Chemically sodium zeolites are $Na_2O.Al_2O_3.xSiO_2.yH_2O$

  (Where, x= 2-10 & y= 2-6).

Principle: hard water passed over zeolite, it exchanges its own sodium ions with hardness causing ions.

$2Na^+$ ions are generally exchanged with each bivalent hardness producing ions.

Process

- For **softening,** hard water is passed over zeolite bed at specific rate
- The hardness causing ions will be retained on zeolite and they are exchanged with equivalent sodium ions
- After certain usage zeolite gets exhausted as all the sodium ions got exchanged
- Such exhausted zeolite is **regenerated by passing 10 % brine** solution over it
- This regenerates the zeolite by replacing hardness causing ions with Na^+ ions to become Na-zeolite
- Hence softening and regeneration are exactly opposite reactions

Reactions

- **Softening:**

For softening of hard water, it is passed over sodium zeolite bed. Exchange of hardness causing ions takes place with sodium ions present on zeolite. The following reactions takes place.

$$CaCl_2 + Na_2Ze \longrightarrow CaZe + 2NaCl$$

$$MgSO_4 + Na_2Ze \longrightarrow MgZe + Na_2SO_4$$

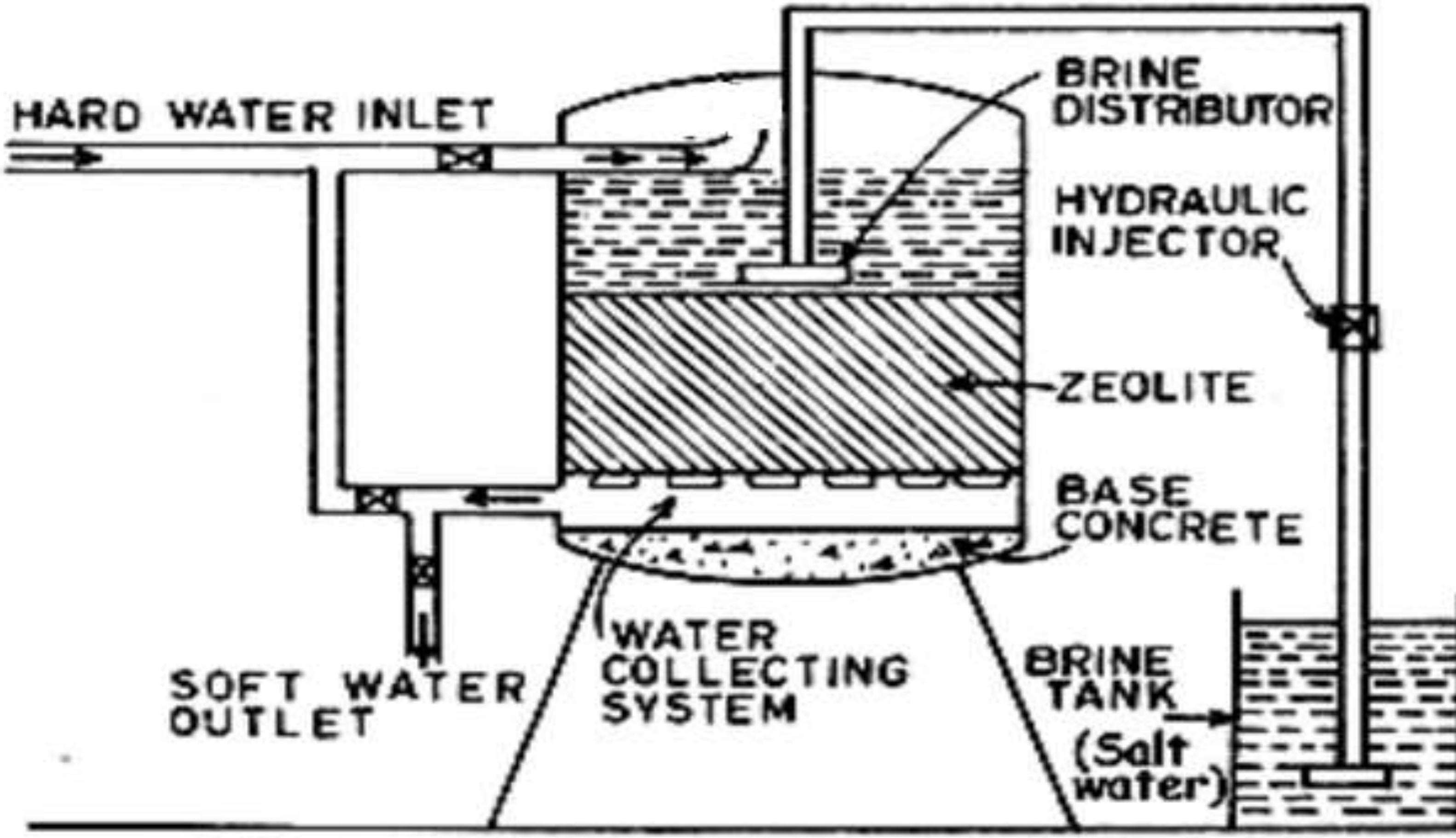
- **Regeneration:**

For regeneration of exhausted zeolite, 10 % brine solution is passed over used zeolite.

$$CaZe + 2NaCl \longrightarrow CaCl_2 + Na_2Ze$$

$$MgZe + 2NaCl \longrightarrow MgCl_2 + Na_2Ze$$

Zeolite water softener



Advantages

- Water obtained after treatment is about 10 ppm hardness
- No sludge formation is taking place
- Equipment is compact and easy in operation
- Equipment occupies less space and low in maintenance

Numerical

A zeolite softener was completely exhausted and was regenerated by passing 100 liters of NaCl solution containing 100 g/litre NaCl. How many liters of water of hardness 500 ppm can be softened by this softener ?

- **Solution:**

Limitations and Disadvantages of Zeolite softener method

Limitations

- Suspended impurities blocks the pores of zeolite
- Colored ions such as Fe^{3+} and Mn^{2+} forms strong bonds with zeolite hence can not be removed while regeneration from zeolite
- Mineral acids can destroy zeolite

Disadvantages

- The treated water is high in sodium salts
- Only cations could be removed leaving behind anions in water

3. Ion Exchange softener method (De-mineralization Process)

- Ion exchange resins are insoluble, cross-linked, long chain organic polymers with micro-porous structure. The functional groups attached to the chains are responsible for ion exchanging property.
- **Cation Exchanger resins (RH^+) :**

  Resins containing acidic functional groups (-COOH, $-SO_3H$ etc.) are capable of exchanging their H^+ ions with other cations in hard water.
- **Anion Exchanger resins (ROH^-) :**

  Resins containing basic functional groups ($-NH_2$-OH, =NH-OH, $-NMe_2$-OH etc.) are capable of exchanging their OH^- with other anions in hard water.

Process - Softening

- For **softening,** hard water is first passed over cations exchanger resin column at specific rate, which removes cations like Ca^{2+}, Mg^{2+} etc. from hard water.
- The hardness causing ions will be retained on cation exchanger resin and they are exchanged with equivalent amount of H^+ ions
- Further, the softened water from cation exchanger column is passed through anion exchanger column, which removes anions like, SO_4^{2-}, Cl^-, CO_3^{2-} etc. with equivalent amount of OH^- ions from the resin.
- H^+ and OH^- ions from resin columns combines to form water.

Softening

$$2\,RH^+ + CaCl_2 \rightarrow R_2Ca^{2+} + 2HCl$$

$$2\,RH^+ + MgSO_4 \rightarrow R_2Mg^{2+} + H_2SO_4$$

$$2\,ROH^- + 2Cl^- \rightarrow 2\,RCl^- + 2\,OH^-$$

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

Process - Regeneration

- After certain usage both cation and anion exchanger resins gets exhausted and they can not exchange any more cations or anions.
- Exhausted cation exchanger resin is regenerated by passing dil. HCl solution
- Exhausted anion exchanger resin is regenerated by passing dil. NaOH solution
- This regenerates both the resins making the method reusable.

Regeneration

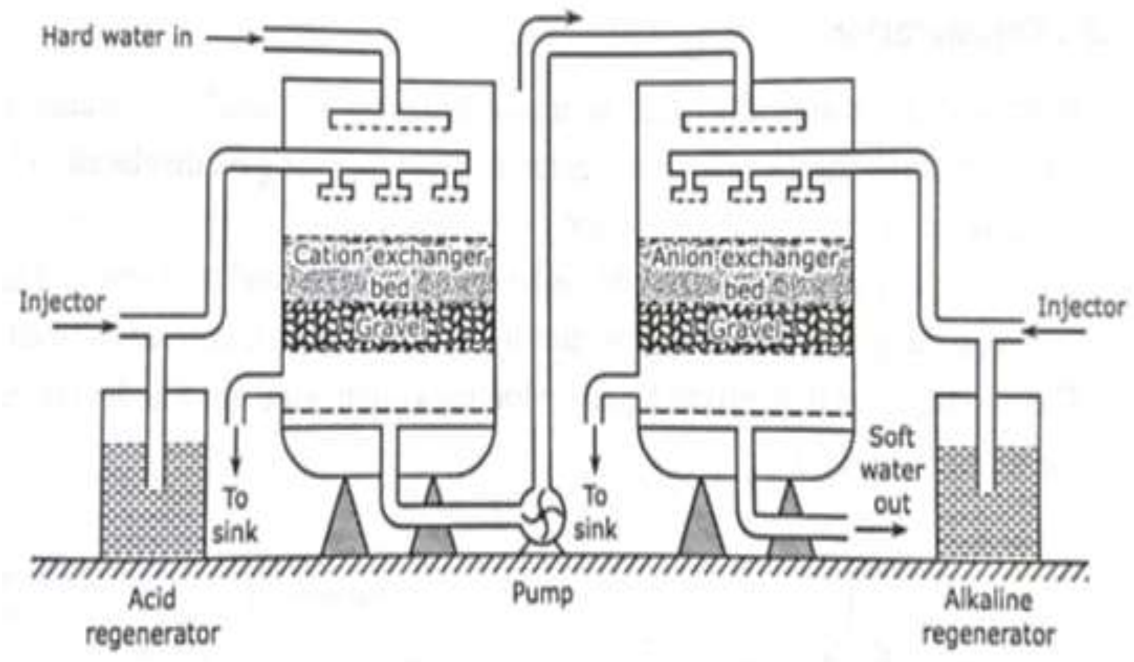
$$R_2Ca^{2+} + 2HCl \longrightarrow 2\,RH^{+} + CaCl_2$$

$$R_2Mg^{2+} + H_2SO_4 \longrightarrow 2\,RH^{+} + MgSO_4$$

$$R_2Cl^{-} + 2\,NaOH \longrightarrow 2\,ROH^{-} + 2NaCl$$

$$R_2SO_4^{2-} + 2\,NaOH \longrightarrow 2\,ROH^{-} + Na_2SO_4$$

Ion Exchange Softener



(Commercial plant)

Advantages

- The process can be used for highly acidic or alkaline water.
- It produces water of very low hardness (less than 2 ppm).
- Softened water can be used in steam generation boiler.

Disadvantages

- The equipment is costly and expensive resins are required.
- Turbid water could decrease the efficiency of the method. Hence turbidity need to be removed first by coagulation and then water could be passed over the resin.

Numerical

- **100000 L of hard water was softened by Ion exchange column. The exhausted cation exchanger resin column was regenerated by 200 L of 0.1 N HCL and anion exchanger resin column by 0.1 N NaOH. Calculate hardness of water sample in ppm.**

Solution:

100000 L of hard water is softened by 200 L of 0.1 N HCL/NaOH

Quantity of HCl used = 200 x 0.1 = 20 L eq. $CaCO_3$

If, 1 L of 1 N $CaCO_3$ = 50 gms

20 L of 1 N $CaCO_3$ = 50 x 20 gms

Therefore 100000 L water = 1000 g of $CaCO_3$

Hardness of 1 L water = 1000 x 1000/100000 = 10 ppm