MANIPAL UNIVERSITY JAIPUR
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FIRST STATE PRIVATE UNIVERSITY IN RAJASTHAN
A+ NAAC ACCREDITED WITH GRADE
3.28 SCORE

B.TECH FIRST YEAR

ACADEMIC YEAR: 2024-2025

Course name: Engineering Chemistry

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Credits	:	4
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MANIPAL UNIVERSITY JAIPUR
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VISION
Global Leadership in Higher Education and Human Development

MISSION
• Be the most preferred University for innovative and interdisciplinary learning
• Foster academic, research and professional excellence in all domains
• Transform young minds into competent professionals with good human values

VALUES
Integrity, Transparency, Quality,
Team Work, Execution with Passion, Humane Touch

Water treatment technology. Introduction, Characteristics imparted by impurities in water, Hardness of water Degree of hardness. Determination of hardness by EDTA method. Numerical. problems. Softening of hard water: External treatment by lime soda process. Softening of hard water: Ion exchange method; Zeolite methods Softening of hard water, internal treatment by phosphate, Calgon condition and colloid conditioning. Numerical problems based on lime soda process.
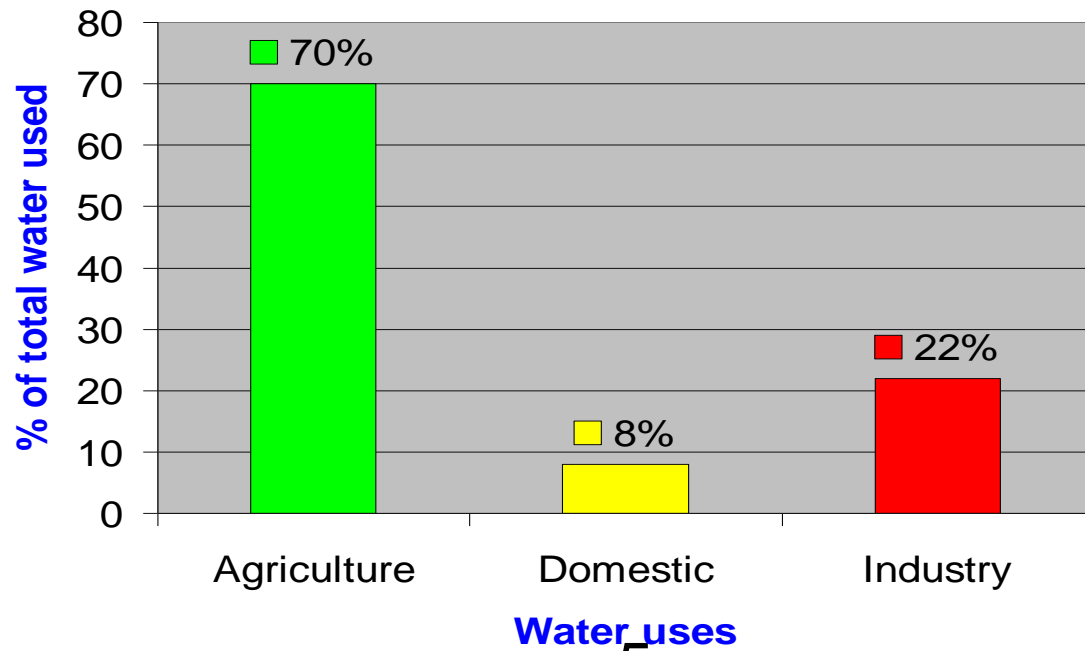
Water Technology:

➤ Introduction
➤ Characteristics imparted by impurities in water
➤ Hardness of water
➤ Degree of hardness

Water is one of the abundant commodities in nature, but is also the most misused one

Earth is a blue planet, 80% of our planet is covered by water.

But, 97.5% of it is locked in the oceans, which is too saline to drink and other uses.

2.4% water is trapped in polar ice caps and giant glaciers, from

which **only 1% water** is used by human for various development, industrial, agricultural and domestic purposes.

Agriculture

Domestic

Industry

% of total water used

70%

22%

8%

Agriculture   Domestic   Industry

Water uses

Sources of water

Surface Water:

 (i) Flowing water e.g. rivers and streams

In general river water contains dissolved minerals from soil such as chlorides, Sulphates, bicarbonates of sodium, calcium or magnesium, iron and organic matters derived from decomposition of plants, small particles of sand and rocks in suspensions.

(ii) Still waters e.g. lakes, ponds and reservoirs (Lowland surface drainage) Lake water has more constant chemical composition.

Underground Water: water from shallow and deep spring and wells

Rainwater: It is probably the purest form of natural water

Sea Water: It is probably the most impure form of natural water

Types of Impurities Present in water

Dissolved impurities:

(a) Inorganic salts e.g.
   (i) Cations: Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{+2}, Al^{+3}, Zn^{2+}, Cu^{2+}
   (ii) Anions: Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, F^-, NO_2^-
(b) Gases: CO_2, O_2, N_2, NH_3, H_2S
(c) Organic matter

Suspended impurities:

(a) Inorganic e.g. clay and sand
(b) Organics e.g. oil globules, vegetable and animal matters

Colloidal impurities:

Clay and finely divided silica colloidal particles of 10^{-4} – 10^{-6} mm size

Micro-organisms:

Bacteria, Fungi, algae and other forms of animal and vegetable life

Effects of Impurities in natural water

- ➤ **Colour**
- ➤ **Taste and odour**
- ➤ **Turbidity and sediments**
- ➤ **Micro-organisms**
- ➤ **Dissolved mineral matter**

  (a) hardness
  (b) Alkalinity
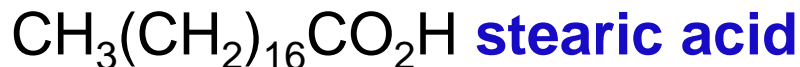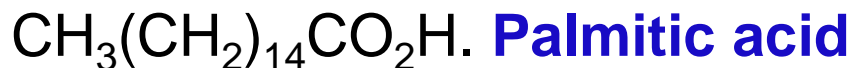 *(c) Total solids*
  (d) corrosion

- ➤ **Dissolved gas**
- ➤ **Silica contents**

Hardness of water

Hardness of water is originally defined as the soap consuming capacity of a water sample. The soap consuming capacity of water is mainly due to the certain salt of calcium, magnesium and other heavy metals dissolved in it.
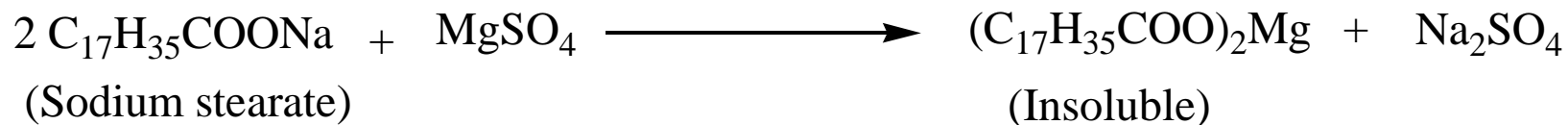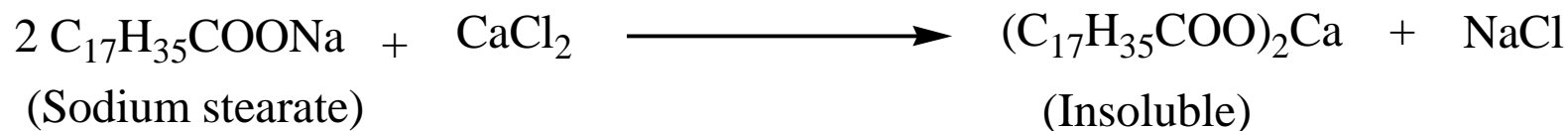
The soap is generally consisting of sodium salts of fatty acids such as Oleic acid, Palmitic acid and stearic acid. Calcium and magnesium react with the sodium salts of long chain fatty acid present in the soap to form insoluble scums of calcium and magnesium soaps.

$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$ **Oleic acid**

$CH_3(CH_2)_{14}CO_2H$. **Palmitic acid**

$CH_3(CH_2)_{16}CO_2H$ **stearic acid**

HARDNESS OF WATER

Hard water:

- **Does not produce good lather or foam with soap.**
- **Consume more soap.**
- **Contains bicarbonates, chlorides and sulphates of calcium & magnesium.**

$$2\ C_{17}H_{35}COONa\ +\ CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca\ +\ NaCl$$
(Sodium stearate)   (Insoluble)

$$2\ C_{17}H_{35}COONa\ +\ MgSO_4 \longrightarrow (C_{17}H_{35}COO)_2Mg\ +\ Na_2SO_4$$
(Sodium stearate)   (Insoluble)

Other metal ions such as Fe^{2+}, Mn^{2+}, Al^{3+} also contribute to hardness, but they are present in water only in small traces

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HARDNESS OF WATER

The hard water when treated with soap i.e. sodium stearate, then no lather will be formed because sodium stearate of soap reacts with salts of calcium and magnesium giving insoluble Ca & Mg stearate.
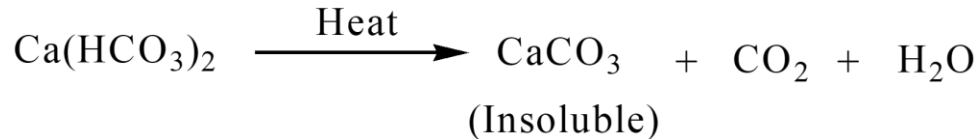
SOFT WATER :

The soft water when treated with soap produces more lather and consume less soap and this is due to the absence of dissolved salts of Ca & Mg in water.
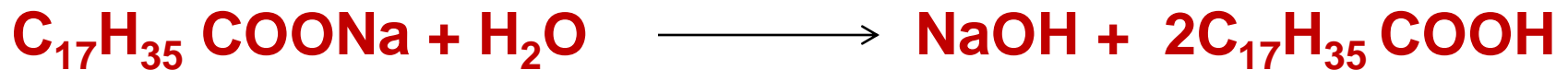
$$C_{17}H_{35}\ COONa + H_2O \longrightarrow NaOH +\ 2C_{17}H_{35}\ COOH$$

Temporary hardness (carbonate hardness)

Temporary hardness is caused by the presence of dissolved "bicarbonate of calcium and magnesium" and other heavy metal ions

Temporary hardness is mostly **destroyed by boiling of water**. During boiling bicarbonate are decomposed in the insoluble carbonate and hydroxide, which are deposited at the bottom of the vessel.

$$Ca(HCO_3)_2 \xrightarrow{\text{Heat}} CaCO_3 + CO_2 + H_2O$$
$$\text{(Insoluble)}$$

$$Mg(HCO_3)_2 \xrightarrow{90\ ^oC} xMgCO_3 \cdot yMg(OH)_2 \cdot zH_2O + aMgO + bH_2O + cCO_2$$

Here, x,y,z, and a,b,c vary as per the decomposition conditions

Permanent hardness (non-carbonate hardness)

This is due the presence of "chlorides and sulphates" of calcium, magnesium, iron and other heavy metal ions.

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Temporary hardness (carbonate hardness)

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Permanent hardness (non-carbonate hardness)

- This is due the presences of chlorides and sulphates of calcium, magnesium, iron and other heavy metal ions.

Salts producing hardness of water
(1) Temporary Hardness :

Calcium bicarbonate $Ca(HCO_3)_2$
Magnesium bicarbonate $Mg(HCO_3)_2$

(2) Permanent Hardness :

Calcium chloride $CaCl_2$
Magnesium chloride $MgCl_2$
Calcium sulphate $CaSO_4$
Magnesium sulphate $MgSO_4$

Hardness is expressed in terms of *equivalent of calcium carbonate* because it is an **insoluble salt** that can most easily be precipitated in water treatment

$$\text{Equivalent of CaCO}_3 \quad = \quad \frac{\text{Mass of hardness producing substances} \times 50}{\text{Chemical equivalent of hardness producing substances}}$$

Measurement

Dissolved salt	Molar Mass	Chemical equivalent	Multiplication factor for converting into equivalent of $CaCO_3$
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$CaCl_2$	111	55.5	100/111
$MgSO_4$	120	60	100/120
$MgCl_2$	95	47.5	100/95
$MgCO_3$	84	42	100/84

Example – 1:
A water sample contains following dissolved salt
$Ca(HCO_3)_2$ = 8.1mg/lit. ; $Mg(HCO_3)_2$ = 29.2mg/lit
$CaCl_2$ = 11.1mg/ lit.; $MgSO_4$ = 6.0mg/ lit.

Find out temporary hardness, permanent hardness & total hardness.

Hardness of soluble salt equivalent to $CaCO_3$

$$= \frac{W \times 100}{Mol. \ Wt. of \ soluble \ salt}$$

Hardness due to $Ca(HCO_3)_2$ $= \frac{8.1 \times 100}{162}$ = 5mg/lit

Hardness due to $Mg(HCO_3)_2$ $= \frac{29.2 \times 100}{146}$ = 20mg/lit

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Hardness due to $CaCl_2$ = $\dfrac{11.1 \times 100}{111}$ =10mg/lit.

Hardness due to $MgSO_4$ = $\dfrac{6.0 \times 100}{120}$ =5mg/lit

Temporary Hardness = Hardness due to $Ca(HCO_3)_2$ + Hardness due to $Mg(HCO_3)_2$

= 5 + 20 = 25 mg / lit.

Permanent Hardness = Hardness due to $CaCl_2$ + Hardness due to $MgSO_4$

= 10 + 5, = 15 mg / lit.

Total hardness = Temporary hardness + Permanent hardness

= 25 + 15, = 40 mg / lit.

Units of Hardness

- **ppm**

- **mg/l**

- **Degree Clarke (°Cl)**

- **Degree French (°Fr)**

mg/L

a)	parts per million	ppm	parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.
b)	Milligrams per litre	Mg/l	no. of milligrams of $CaCO_3$ equivalent hardness per litre of water.
c)	Degree Clark	°Cl	parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.
d)	Degree French	°Fr	parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

Relation between various units of hardness

$1 ppm = 1 mg/l = 0.1°Fr = 0.07 °Cl$

Problems

1)A water sample contains 200 mg of $CaSO_4$ per liter. Calculate the hardness in terms of $CaCO_3$ equivalent in mg/L, ppm, ^oCl and ^oFr.

Answer:

$$= Weight\ of\ CaSO_4\ in\ \frac{mg}{L} \times \frac{Eq.weight\ of\ CaCO_3}{Eq.weight\ of\ CaSO_4}$$

$$= 200\frac{mg}{L} \times \frac{100/2}{136/2} = \mathbf{147.06}\frac{mg}{L}\ or\ ppm$$

$$\mathbf{1\,°Cl\ =\ 14.254\ ppm \Rightarrow 1\frac{mg}{L} = 0.07°Cl}$$

$$\mathbf{1\,°Fr\ =\ 10\ ppm \Rightarrow 1\frac{mg}{L} = 0.1°Fr}$$

$$147.06\ mg/L\ = \mathbf{10.29\ {}^oCl}\ or\ \mathbf{14.71\ {}^oFr}$$

Practice Question

2)Calculate the temporary hardness and permanent hardness of a sample of water containing: $Mg(HCO_3)_2$ = 7.3 mg/L; $Ca(HCO_3)_2$ = 16.2 mg/L; $MgCl_2$ = 9.5 mg/L; $CaSO_4$ = 13.6 mg/L

Molecular weights:

$Ca(HCO_3)_2$ = 162; $Mg(HCO_3)_2$=146; $CaSO_4$= 136; $MgSO_4$ = 120;

$MgCl_2$ = 95; $Al_2(SO_4)_3$ = 114; $Ca(NO_3)_2$=164

Practice Question

3)Three samples A, B and C were analyzed for their salts contents:
Sample A was found to contain **168 mg of magnesium carbonate** per L
Sample B was found to contain **820 mg of calcium nitrate** per L
Sample C was found to contain **2 g calcium carbonate** per 500 ml

// these are just the weight of salts in 1L water and not the hardness

Determine the hardness in all above three sample in ppm

Molecular weights:
$Ca(NO_3)_2 = 164$; $MgCO_3 = 84$; $CaCO_3 = 100$

Water Technology:

➢ Determination of hardness by EDTA method
➢ Numerical problems

Estimation of hardness:

Hardness is usually determined by : **EDTA Method**

Determination of hardness By:
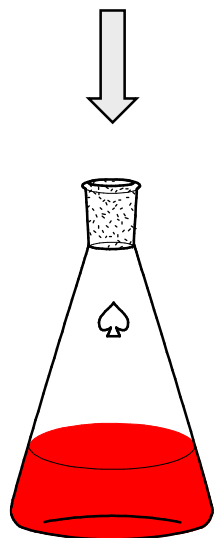# Complexometric Method / EDTA Method

Principle: The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA)

- using Eriochrome Black-T as an indicator
- keeping the pH of the water at 9.0 - 10.0
- The end point is the change in color from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.
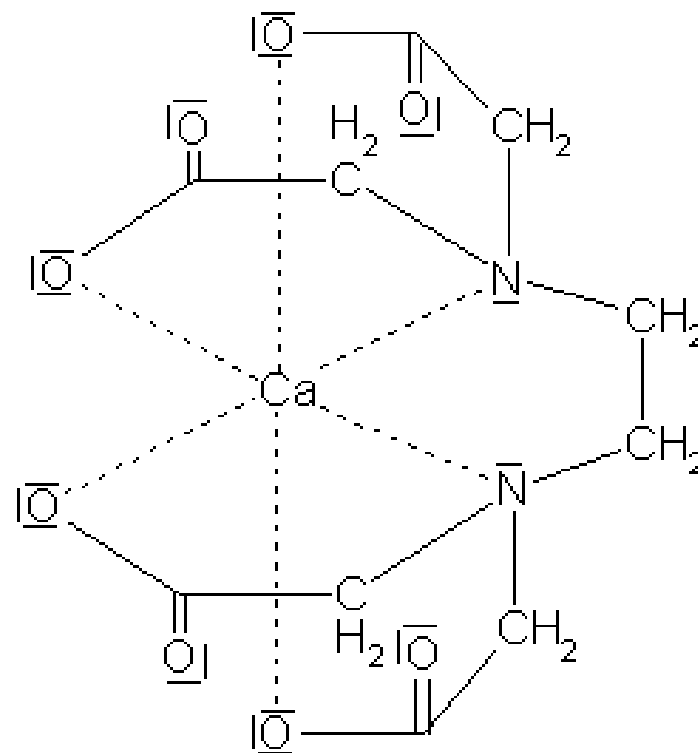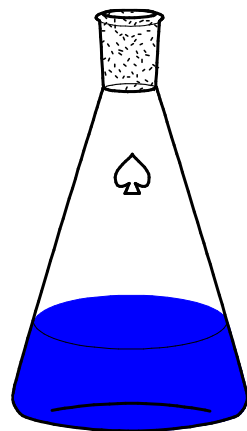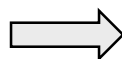
$$(Ca^{2+} \text{ or } Mg^{2+}) \quad + \quad EBT \quad \rightarrow \quad [Ca-EBT] \text{ (or) } [Mg-EBT]$$

Hardness-salts   indicator   unstable complex (wine red)

$$[Ca-EBT] \text{ (or) } [Mg-EBT] + EDTA \quad \rightarrow \quad [Ca-EDTA] \text{ (or) } [Mg-EDTA] \quad + \quad EBT$$

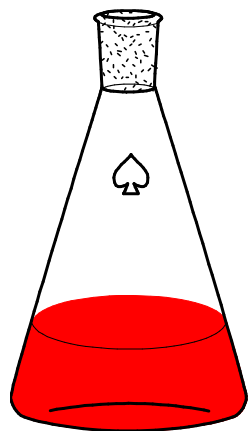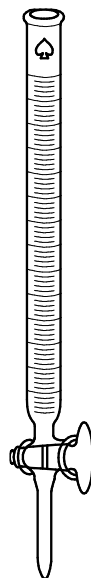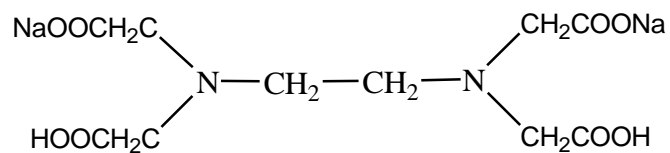Unstable complex (wine red)   stable complex (colourless)   blue
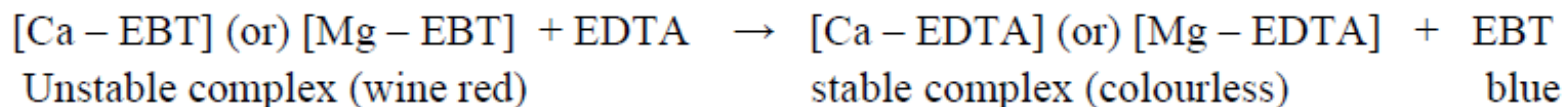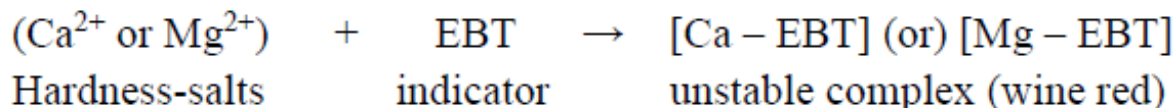
3) EDTA method

Hard water
+
EBT Indicator
+
10 pH buffer
solution
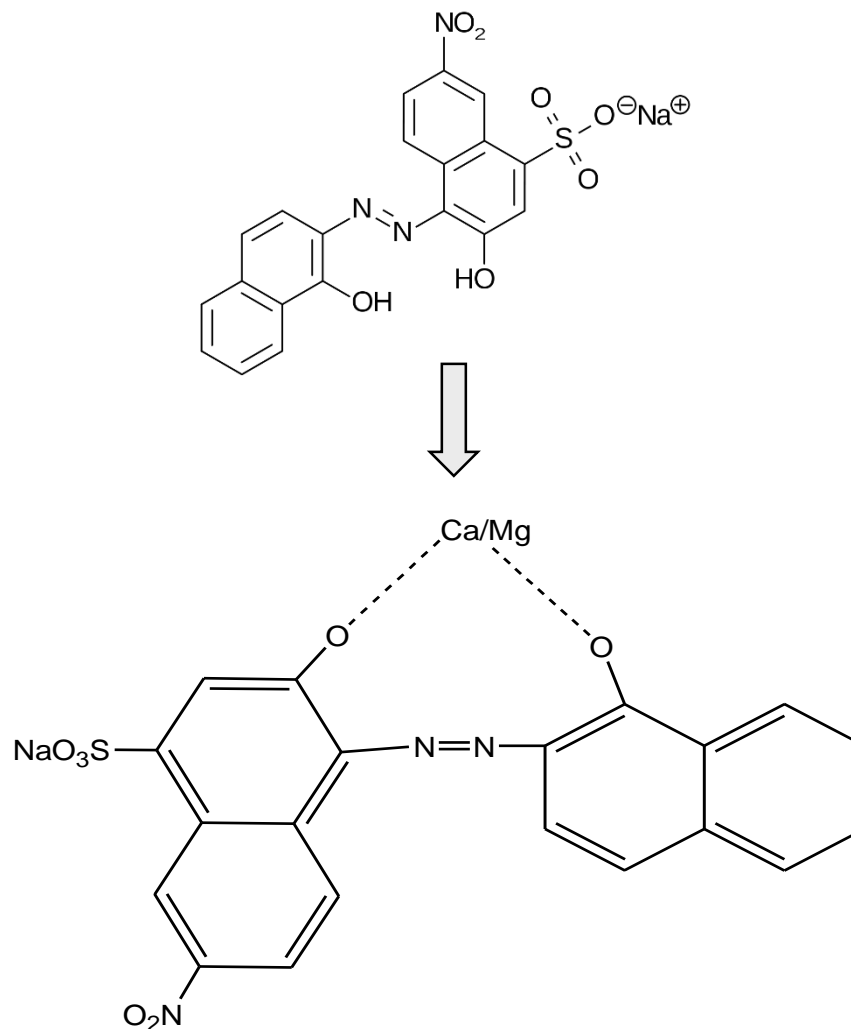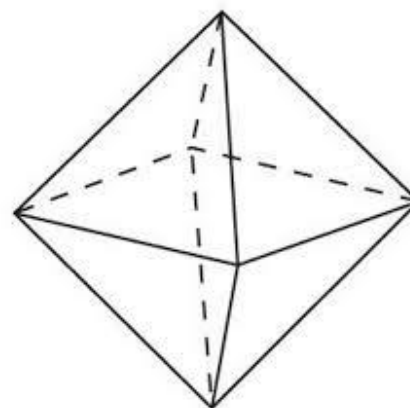
Various steps involved I-n this method

1. Standardization of EDTA solution:

Rinse and fill the burette with EDTA solution. Pipette out V_1 ml of standard hard water (M_1) in a conical flask. Add 4-5 ml of buffer solution and 2 drops of EBT indicator. Titrate with EDTA solution till wine-red color changes to clear blue. Let volume used by 'V_2' ml.

$$M_1.V_1 = M_2.V_2 \quad » \quad M_2 = (M_1.V_1)/V_2$$

Where, M_1 = Molarity of Standard Hard water,
V_1 = Volume of Standard Hard water,
M_2 = Molarity of EDTA,
V_2 = Volume of EDTA

2. Determination of Total Hardness:

Rinse and fill the burette with EDTA solution. Pipette out sample water (V_3) in a conical flask. Add 4-5 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red color changes to clear blue. Let volume used by 'V_4' ml.

$$M_3.V_3 = M_4.V_4 \quad >> \quad M_3 = (M_2.V_4)/V_3$$

Where, M_3 = Molarity of Sample Hard water,
V_3 = Volume of Sample Hard water,
M_4 = Molarity of EDTA = M_2,
V_4 = Volume of EDTA

Total Hardness = $M_3 \times$ Molecular weight of $CaCO_3$ (100) $\times$ One Litre (1000ml)

$$= M_3 \times 10^5 \text{ ppm}$$

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3. Determination of Permanent Hardness:

Take 100 ml of sample water in 250 ml beaker. Boil it to remove temporary hardness to about half of its volume and cool to room temperature, filter through filter paper to remove insoluble salts.

Make up the volume to the original 100ml by adding distilled water. Now Pipette out this solution (V_3 ml) in a conical flask. Add 4-5 ml of buffer solution and 2 drops indicator. Titrate with EDTA solution till wine-red color changes to clear blue. Let volume used by 'V_4' ml.

$$M_3.V_3 = M_4.V_4 \quad » \quad M_3 = (M_2.V_4)/V_3$$

Where, M_3 = Molarity of Permanent Hard water,
V_3 = Volume of Permanent Hard water,
M_4 = Molarity of EDTA = M_2,
V_4 = Volume of EDTA

Permanent Hardness = M_3 × Molecular weight of $CaCO_3$ (100) × One Litre (1000ml)

$$= M_3 \times 10^5 \text{ ppm}$$

4. Determination of Temporary Hardness:

Temporary Hardness = Total Hardness - Permanent Hardness

Problem:

4)50 ml of standard hard water containing 1 gram of pure $CaCO_3$ per liter consumed 20 ml of EDTA. 50 ml of hard water consumed 25 ml of same EDTA solution and EBT indicator. Calculate the total hardness of water sample in ppm.

Solution:

Strength of standard hard water sample ($CaCO_3$ solution) M_1 =

$$= \frac{\text{Weight of } CaCO_3}{\text{Mol. wt of } CaCO_3} \times \frac{1000}{1000}$$

$$= \frac{1 \text{ gm}}{100} \times \frac{1000}{1000} = 0.01 \text{ M}$$

Strength of EDTA solution M_2 $= \dfrac{V_1 M_1}{V_2} = \dfrac{50 \times 0.01}{20} = 0.025$ M

V_1 = Volume of standard hard water (50 ml), M_1 = Strength of standard hard water (0.01M)
V_2 = Volume of EDTA solution (20 ml), M_2 = Strength of EDTA solution =?

Calculation of Total hardness M_3 $= \dfrac{V_2 M_2}{V_3} = \dfrac{25 \times 0.025}{50} = 0.0125$ M

V_2 = Volume of EDTA solution (25 ml), M_2 = Strength of EDTA solution = 0.025M
V_3 = Volume of sample hard water (50 ml), M_3 = Strength of sample hard water =?

Total Hardness $= 0.0125 \times 10^5$ ppm

$= 0.0125 \times 100$ (Mol. Wt of $CaCO_3$) $\times$ 1000 (ml)ppm

$= 1250$ ppm.

Problem:

0.28 grams of CaCO$_3$ were dissolved in HCl and the solution was made up to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample consumed 33 ml of same EDTA solution EBT indicator. 100 ml of this water after boiling cooling and filtering required 10 ml of EDTA solution in titration. Calculate the permanent and temporary hardness of water sample in ppm.

Strength of standard hard water sample ($CaCO_3$ solution) $M = \dfrac{\text{Weight of } CaCO_3}{\text{Mol. wt of } CaCO_3} \times \dfrac{1000}{1000}$

$$= \dfrac{0.28\,gm}{100} \times \dfrac{1000}{1000} = 0.0028\ M$$

Strength of EDTA solution $M_2 = \dfrac{V_1 M_1}{V_2} = \dfrac{100 \times 0.0028}{28} = 0.01\ M$

V_1 = Volume of standard hard water (100 ml), M_1 = Strength of standard hard water (0.0028M)
V_2 = Volume of EDTA solution (28 ml), M_2 = Strength of EDTA solution=?

Calculation of Total hardness $M_3 = \dfrac{V_2 M_2}{V_3} = \dfrac{33 \times 0.01}{100} = 0.0033\ M$

V_2 = Volume of EDTA solution (33 ml), M_2 = Strength of EDTA solution (0.01M)
V_3 = Volume of sample hard water (100 ml), M_3 = Strength of sample hard water =?

Total Hardness $= 0.0033 \times 10^5$ ppm $= 0.0033 \times 100$ (Mol. Wt of $CaCO_3$) $\times 1000$ (ml)ppm
$$= 330\ ppm$$

Calculation of Permanent hardness $M_4 = \dfrac{V_2 M_2}{V_4} = \dfrac{10 \times 0.01}{100} = 0.001\ M$

V_2 = Volume of EDTA solution (10 ml), M_2 = Strength of EDTA solution (0.01M)
V_4 = Volume of sample hard water after boiling cooling and filtering (100 ml)
M_4 = Strength of sample hard water after boiling cooling and filtering =?
Permanent Hardness $= 0.001 \times 10^5$ ppm
$$= 0.001 \times 100 \text{ (Mol. Wt of } CaCO_3) \times 1000 \text{ (ml)ppm}$$
$$= 100\ ppm$$
Calculation of Temporary hardness = Total hardness - Permanent hardness
$$= 330 - 100 = 230\ ppm$$

Water Technology:

- Softening of hard water: Internal treatment by PHOSPHATE and CALGON condition.
- Softening of hard water: External treatment by LIME SODA PROCESS.

WATER SOFTENING

- Removal of hardness
  - » Hardness is?...

    primarily Ca, Mg, plus Fe, Mn, St, Al

- How is Softening done?...

    Precipitation of Ca and Mg, or
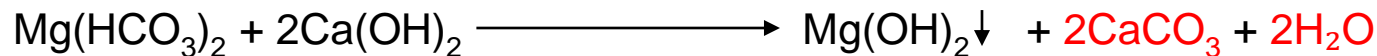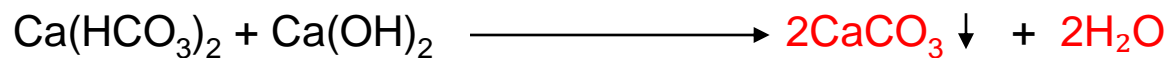   Ion exchange of Ca / Mg with ion such as Na

- Hardness in 300-500 mg/L as $CaCO_3$ range is considered excessive and leads to:

  - High soap consumption
  - Scaling in heating vessels and pipes

- Even > 150 mg/L may result in consumer objection

- 60-120 mg/L as $CaCO_3$ is considered a moderate amount
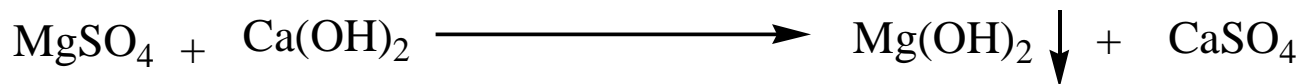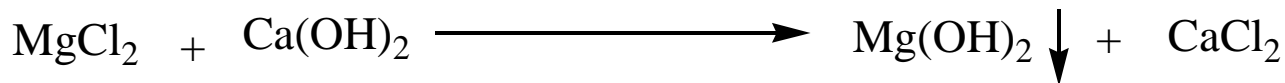
Lime-Soda process

In this process, all the soluble hardness-causing impurities are converted into insoluble precipitates which may be removed by setting and filtration.

In the lime soda process, calculated amount of <u>lime $Ca(OH)_2$</u> and <u>soda Na_2CO_3</u> is added in the hard water. The soluble calcium and magnesium salts in water are converted into insoluble compound such as calcium carbonate and magnesium hydroxide which may removed by setting and filtration.
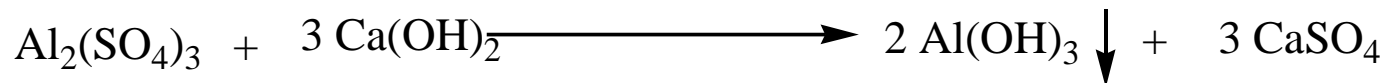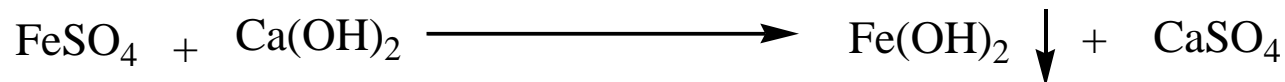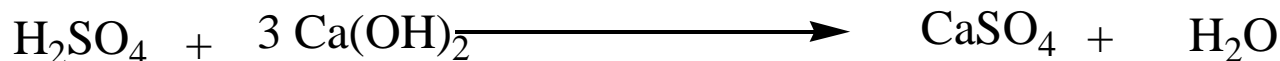
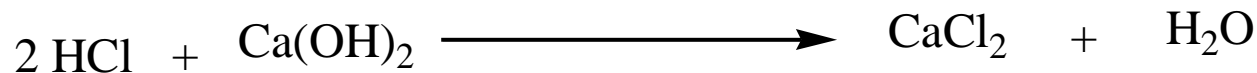**(i) Lime removes the temporary hardness:**

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CaCO_3 + 2H_2O$$

(ii) Lime removes the permanent magnesium hardness:

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaSO_4$$

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(iii) Lime removes the dissolved iron and aluminum salts:

$$FeSO_4 \ + \ Ca(OH)_2 \longrightarrow Fe(OH)_2 \downarrow \ + \ CaSO_4$$

$$Al_2(SO_4)_3 \ + \ 3\,Ca(OH)_2 \longrightarrow 2\,Al(OH)_3 \downarrow \ + \ 3\,CaSO_4$$

(iv) Lime removes free mineral acids:

$$2\,HCl \ + \ Ca(OH)_2 \longrightarrow CaCl_2 \ + \ H_2O$$

$$H_2SO_4 \ + \ 3\,Ca(OH)_2 \longrightarrow CaSO_4 \ + \ H_2O$$

(v) Lime removes dissolved CO$_2$ and H$_2$S:

$$CO_2 \ + \ Ca(OH)_2 \longrightarrow CaCO_3 \downarrow \ + \ H_2O$$

$$H_2S \ + \ 3\,Ca(OH)_2 \longrightarrow CaS \downarrow \ + \ 2\,H_2O$$
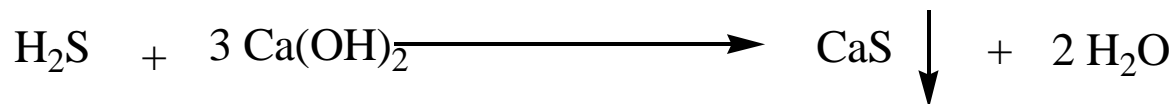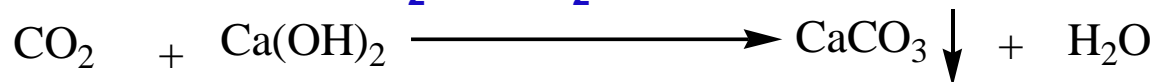
(vi) Soda removes all calcium permanent hardness:

$$CaCl_2 \ + \ Na_2CO_3 \longrightarrow CaCO_3 \downarrow \ + \ NaCl$$

$$CaSO_4 \ + \ Na_2CO_3 \longrightarrow CaCO_3 \downarrow \ + \ Na_2SO_4$$
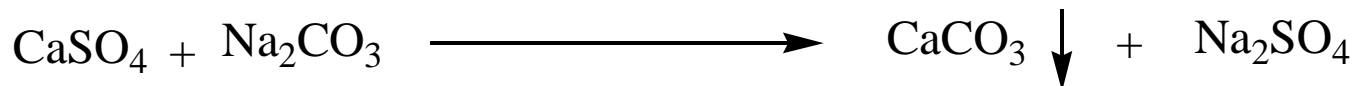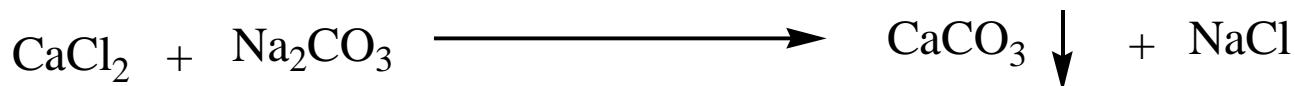
Now the 100 parts by mass of $CaCO_3$ are equivalent to :
(i)   74 part of $Ca(OH)_2$ and
(ii) 106 parts of Na_2CO_3

Lime required for softening:

$$= \frac{74}{100} [\text{Temp. } Ca^{2+} + 2\times\text{Temp. } Mg^{2+} + \text{Perm. } (Mg^{2+} + Fe^{2+} + Al^{3+}) + CO_2 + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^-]$$

Soda required for softening:

$$= \frac{106}{100} [\text{Perm. } (Ca^{2+} + Mg^{2+} + Fe^{2+} + Al^{3+}) + H^+ (HCl \text{ or } H_2SO_4) - HCO_3^-]$$

Problem: Calculate the amount of lime (84% pure) required for treatment of 20000 litres of water whose analysis is as follows:

$Ca(HCO_3)_2$	40.5 ppm	$CaSO_4$	34.0 ppm
$Mg\ (HCO_3)_2$	36.5 ppm	$CaCl_2$	27.75 ppm
$MgSO_4$	30.0 ppm	$NaCl$	10.0 ppm

Also calculate the temporary and permanent hardness of the water sample.

Solution:

Salt	$CaCO_3$ equivalent
$Ca(HCO_3)_2$ $Mg(HCO_3)_2$	40.5 x (100/162) = 25 ppm 36.5 x (100/146) = 25 ppm
$MgSO_4$	30.0 x (100/120) = 25ppm
$CaSO_4$	34.0 x (100/136) = 25 ppm
$CaCl_2$	27.75 x (100/111) = 25 ppm
NaCl	Ignored as it does not contribute to hardness

Temporary hardness = 25 + 25 = 50 ppm
Permanent hardness = 25 + 25 + 25 = 75 ppm

Lime required for softening:

$$= \frac{74}{100} \left[\text{Temp. } Ca^{2+} + 2 \times \text{Temp. } Mg^{2+} + \text{Perm. } (Mg^{2+} + Fe^{2+} + Al^{3+}) \right.$$
$$\left. + CO_2 + H^+ (HCl \text{ or } H_2SO_4) + HCO_3^- \right]$$

$$= \frac{74}{100} \left[25 + 2 \times 25 + 25 \right] \times \frac{100}{84} \times 20000$$

$$= 1761.90 \times 10^3 \text{ mg} = 1.76 \text{ Kg}$$

Answer:

Lime = 532.8 gm, Soda = 381.6 gm

Lime =

$74/100 \times$ (temp + perm Mg) $\times$ Vol of water

= 532.8 gm

Soda =

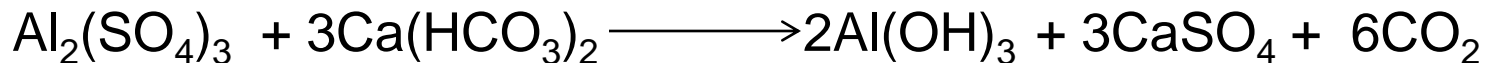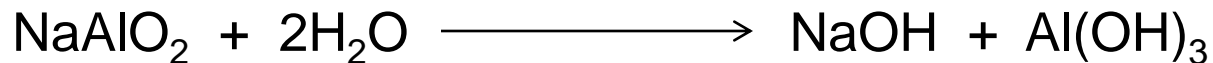$106/100 \times$ permanent $\times$ vol of water

381.6 gm

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Problem

Q. Calculate the amount of lime and soda required for 18000 lit of a water sample which on analysis gave the following data:

Temporary hardness = 25 ppm, Permanent hardness = 20 ppm, Permanent Mg hardness = 15 ppm
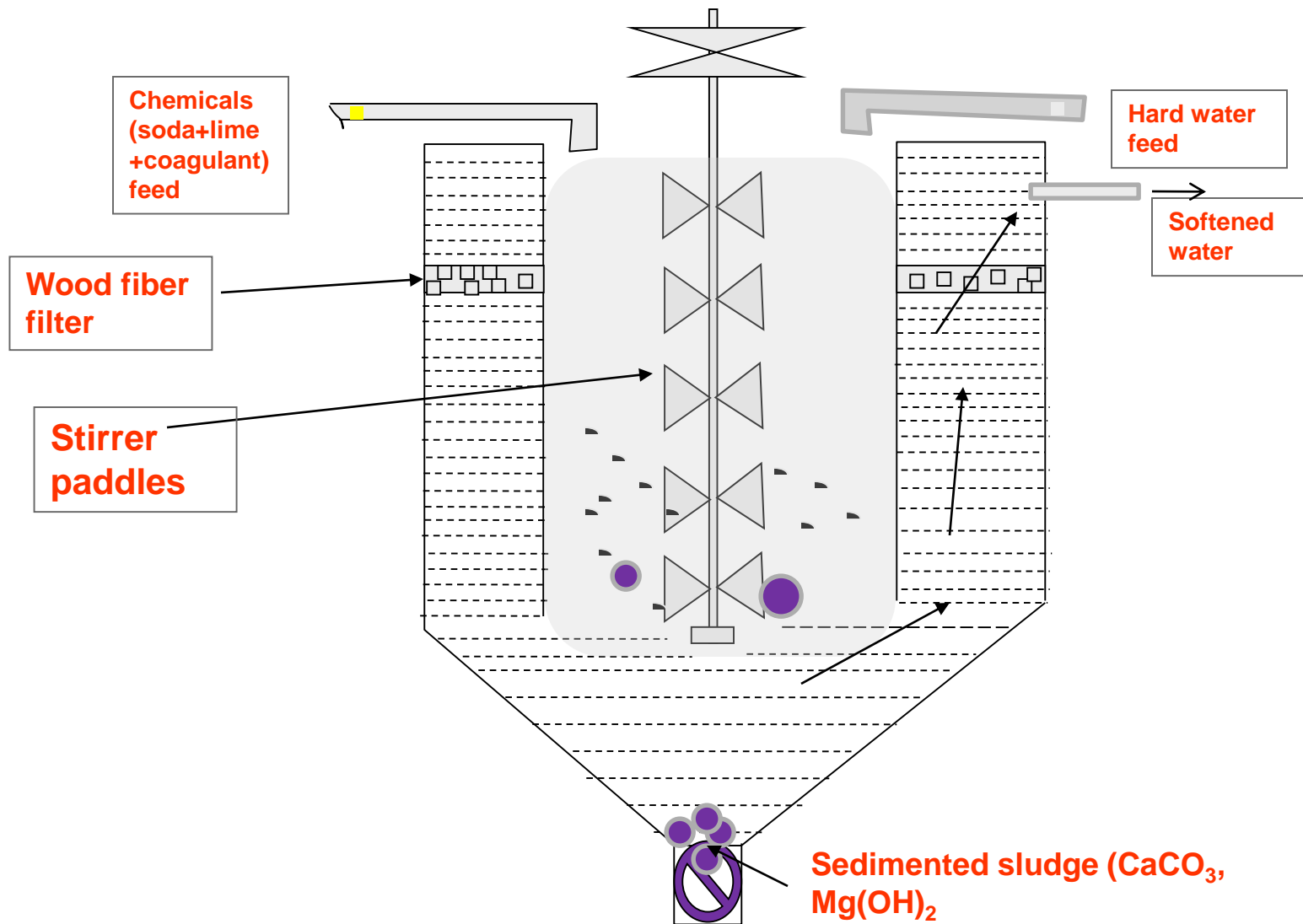
Cold lime soda process:

Calculated quantity of lime and soda are mixed with water at room temperature, the precipitates formed are finely divided, so they do not settle down easily. Therefore, It is essential to add small amounts of coagulants (like alum, aluminum sulphate, sodium aluminates *etc*).

Use of sodium aluminate as coagulant also helps the removal of silica as well as oil if present in water..

$$NaAlO_2 \ + \ 2H_2O \ \longrightarrow \ NaOH \ + \ Al(OH)_3$$

$$Al_2(SO_4)_3 \ + 3Ca(HCO_3)_2 \longrightarrow 2Al(OH)_3 \ + 3CaSO_4 + \ 6CO_2$$

Continuous cold lime soda softener

Chemicals (soda+lime +coagulant) feed

Wood fiber filter

Stirrer paddles

Hard water feed

Softened water

**Sedimented sludge ($CaCO_3$, $Mg(OH)_2$)**

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Hot lime soda process:

Calculated quantity of lime and soda are mixed with water at 80^{0}C.

Advantages of high temperature:

➢ The reaction proceeds faster.
➢ Softening capacity is increased.
➢ No coagulant needed as the precipitate and sludge formed settle down rapidly.
➢ Much of the dissolved gases are driven out of water.
➢ Viscosity of soften water is lower, so filtration of water becomes easier.
➢ This process produces water of comparatively low residual hardness 15 to 30 ppm.

Continuous Hot Lime Soda Process
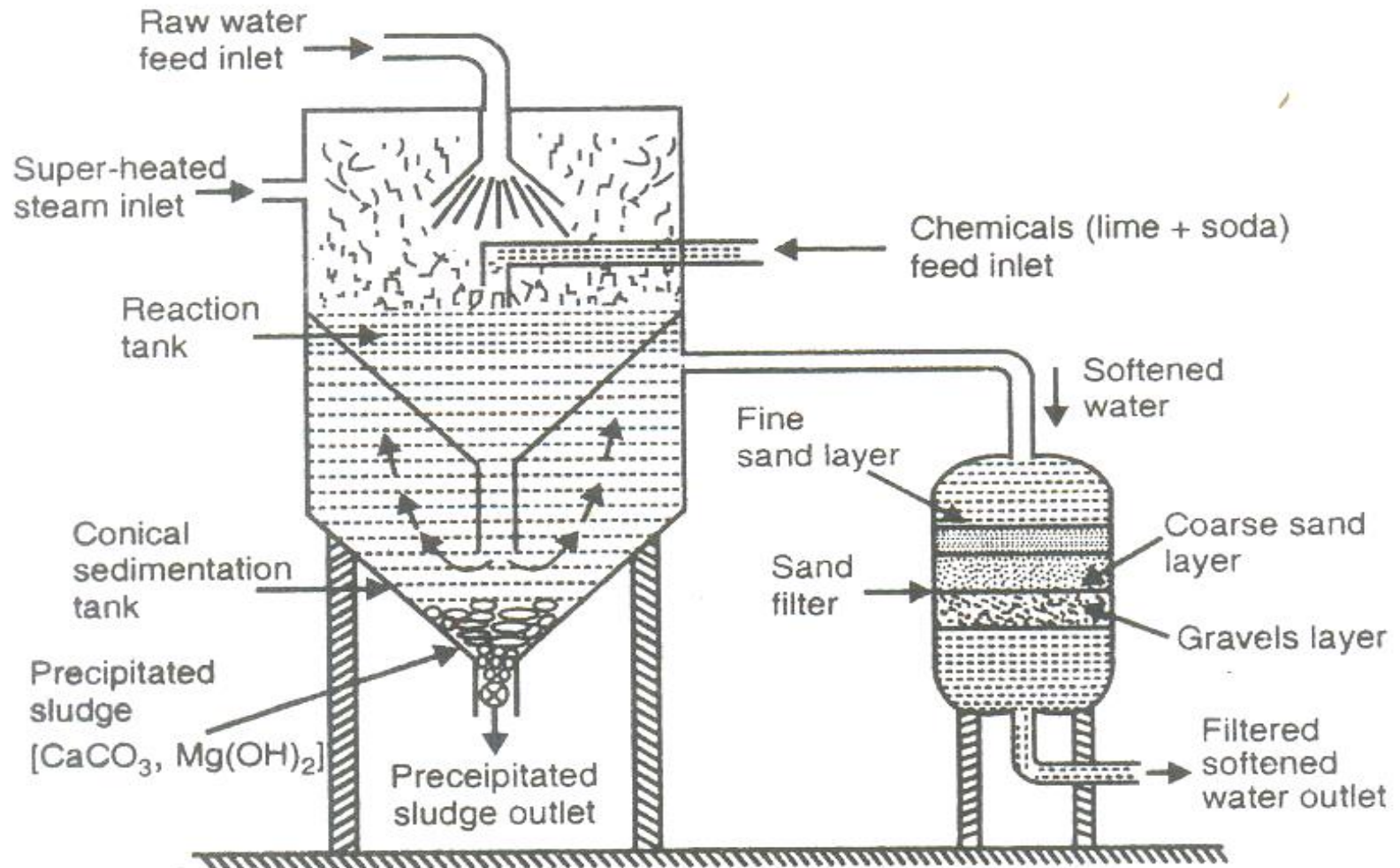
Advantages of lime soda process:

➢ It is very economical.

➢ If the process is combined with sedimentation/coagulation lesser amounts of coagulants shall be needed.

➢ The process increases the pH of the treated water.

➢ In addition to the removal of hardness, the quantities of minerals in the water are reduced.

➢ Due to alkaline nature of treated water amount of pathogenic bacteria in water is considerably reduced.

Disadvantages of lime soda process:

➢ For efficient and economical softening, careful operation and skilled supervision is required.

➢ Disposal of large amount of sludge poses a problem.

➢ This can remove hardness up to 15 ppm which is not good for boilers.

Practice Problems

Problem: Calculate the amount of lime required for softening 50,000 litre of hard water containing $CaCO_3$=25ppm; $MgCO_3$=144ppm; $CaCl_2$=111ppm; $MgCl_2$=95 ppm; Na_2SO_4= 15 ppm; Fe_2O_3 = 25 ppm.

Molecular weights:

$Ca(HCO_3)_2$ = 162; $Mg(HCO_3)_2$=146; $CaSO_4$= 136; $MgSO_4$ = 120; ;

$MgCl_2$ = 95; $MgCO_3$ = 84; $CaCl_2$ = 111

Problem: Calculate the amount of lime and soda required for softening 50,000 litre of hard water containing $Ca(HCO_3)_2 = 8.1$ mg; $Mg(HCO_3)_2 = 7.5$ mg; $CaSO_4 = 13.6$ mg; $MgSO_4 = 12.0$ mg; $MgCl_2 = 2.0$ mg; $NaCl = 4.7$ mg.

Molecular weights:
$Ca(HCO_3)_2 = 162$; $Mg(HCO_3)_2 = 146$; $CaSO_4 = 136$; $MgSO_4 = 120$; ; $MgCl_2 = 95$

Problem: Explain with chemical equation and calculate the amount of lime and soda needed for softening 1,00,000 litrs of water containing Following:
HCL = 7.3 mg/L; $Al_2(SO_4)_3$ = 34.2 mg/L; $MgCl_2$ = 9.5 mg/L; NaCl = 29.25 mg/L
Purity of lime is 90% and that of the soda is 98%.

Molecular weights:
Ca(HCO3)2 = 162; Mg(HCO3)2=146; CaSO4= 136; MgSO4 = 120; ; MgCl2 = 95; Al2(SO4)3 = 114

Problem: A water sample on analysis gave the following data: Ca^{2+} = 30 mg/L; Mg^{2+} = 24 mg/L; CO_2 = 24mg/L; K^+ = 10 mg/L Calculate the quantities of lime (90%) and soda (94%) required to soften one million litres of water sample.

Problem: A water sample have the following impurities:
Ca^{2+} = 20ppm; Mg^{2+} = 18 ppm; HCO_3^- = 183 ppm; SO_4^{2-} = 24 ppm.
Calculate the amount of lime and soda needed for softening.

Water Technology:

➢ Softening of hard water: Ion exchange method; Zeolite methods

WATER SOFTENING

Ion exchange or deionization or demineralization process: Ion-exchange resins are widely used in different separation, purification, and decontamination processes. The most common examples are water softening and water purification.

Ion-exchange resins are insoluble, cross linked, long chain organic polymer with micro porous structure and the functional groups attached to the chains are responsible for the ion exchange properties.
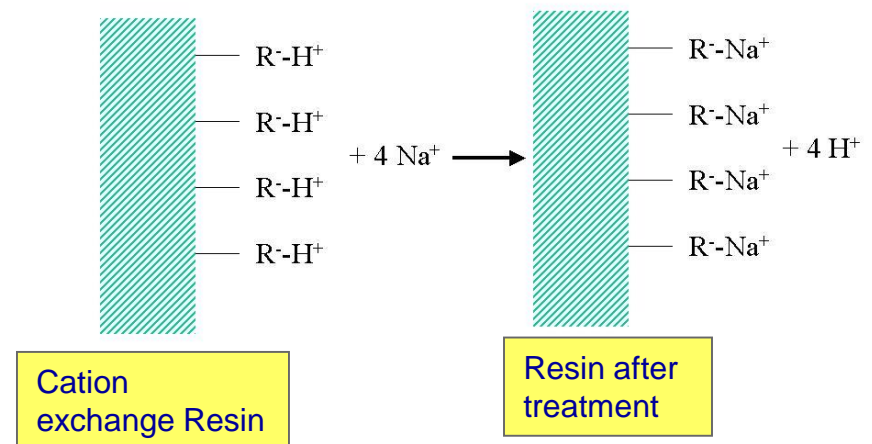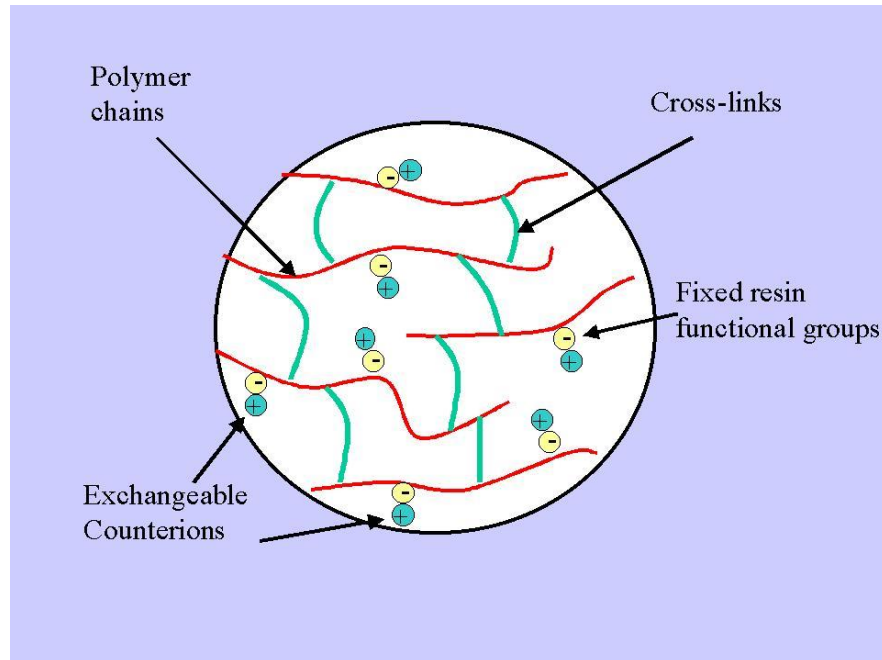
Resins containing **basic functional groups** ($-NR_3^+OH^-$) are capable of exchanging their anions with other anions which comes in their contacts, known as a **Anion exchange resins** (**ROH$^-$**).

They are styrene divinyl benzene or amine-formaldehyde copolymerization which contains **quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups** as an integral part of the resin matrix. These after treated with dil NaOH becomes capable of exchanging their OH$^-$ ions with anions of water.
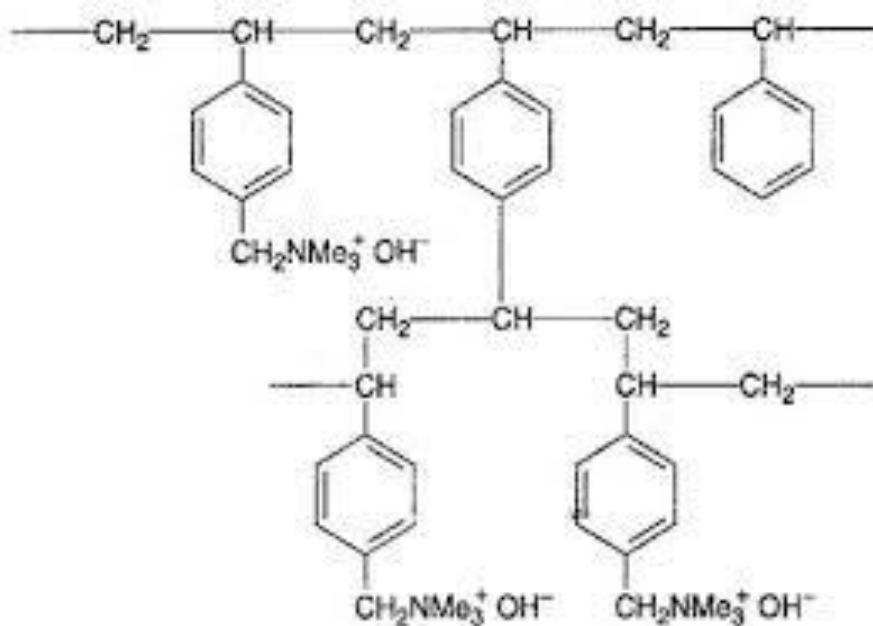
Resins containing **acidic functional groups** (-COOH, -SO$_3$H) are capable of exchanging their H$^+$ ions with other cations which comes in their contacts, known as a **cation exchange resins (RH$^+$)**.

e.g. *styrene-divinyl benzene copolymer*, which on sulphonation and carboxylation, become capable to exchange their hydrogen ions with the **cations (Metal ions)** in the water.
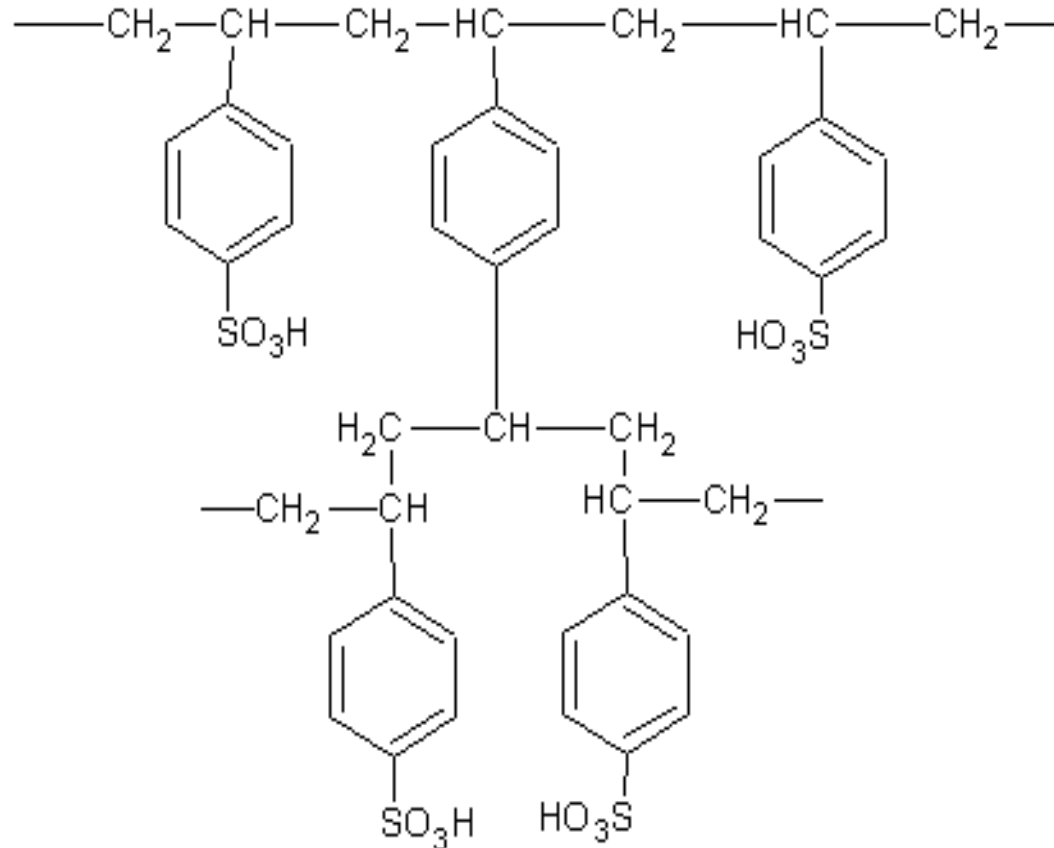
Process:- The hard water is passed first through cation exchange column, which remove all the cations from it and **equivalent amount of hydrogen** ions are released from this column to water:

$$2RH^+ + Ca^{2+} \longrightarrow R_2Ca^{2+} + 2H^+$$
$$2RH^+ + Mg^{2+} \longrightarrow R_2Mg^{2+} + 2H^+$$
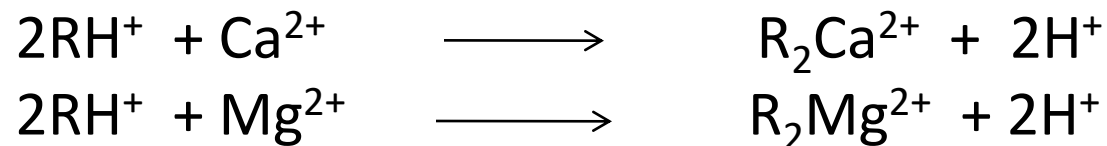
After cation exchange column the hard water is passed through anion exchange resin column, which remove all the anions from it and **equivalent amount of hydroxide** ions are released from this column to water :

$$ROH^- + Cl^- \longrightarrow RCl^- + OH^-$$
$$2ROH^- + SO_4^{2-} \longrightarrow R_2SO_4^{2-} + 2OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$
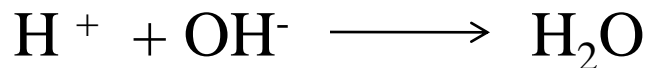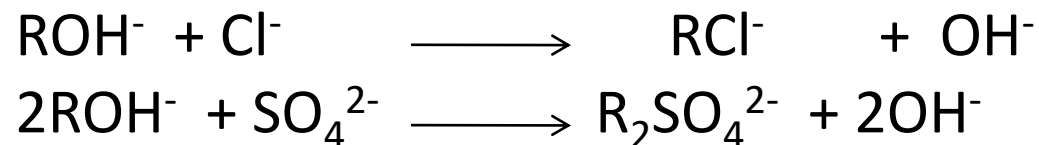
Thus water coming out from the exchange is free from cations as well as anions.
        Ion free water is known as deionized or demineralised water.

Ion exchange purifier or softener

Hard water

Injector

Cation exchange Resin

Gravel bed

Anion exchange Resin

Injector

Acid solution for regeneration of resin

Wastages to sink

pump

Wastages to sink

Alkaline solution for regeneration of resin

Soft water
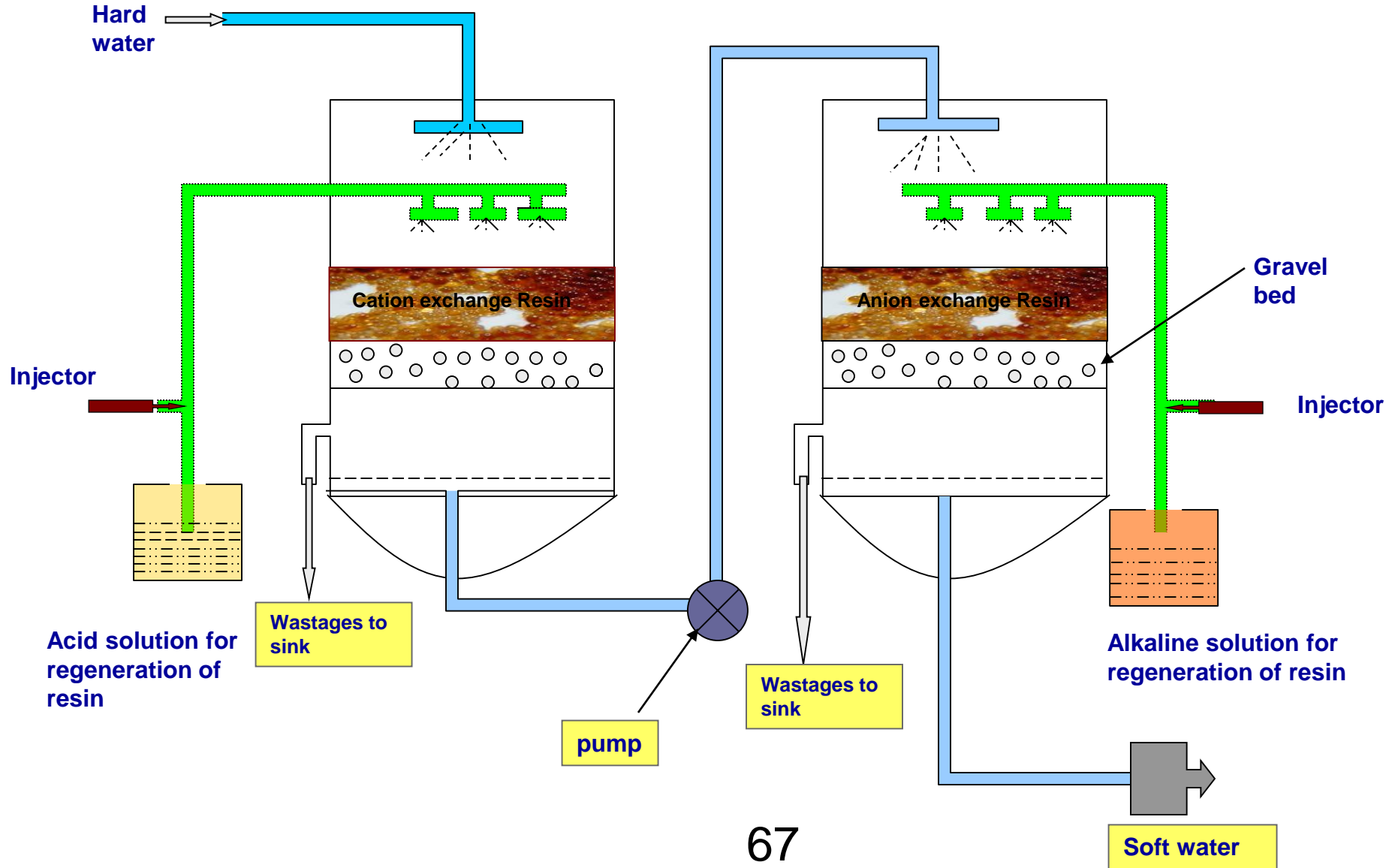
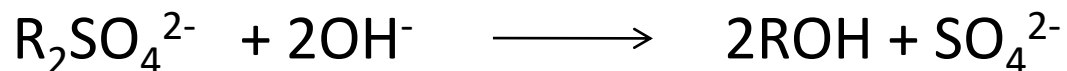# Regeneration:

Cation exchange column is regenerated by passing a solution of dil HCl or dil H_2SO_4. The regeneration can be represented as

$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH + Ca^{2+}$$
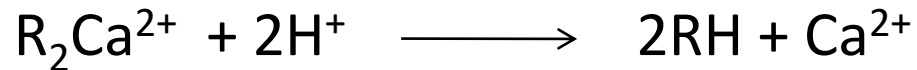
Exhausted anion exchange column is regenerated by passing a solution of dil. NaOH. The regeneration can be represented as

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

Advantages:

➢Can be used to soften highly acidic or alkaline waters.

➢It produces water of very low hardness.

Disadvantages:

➢The equipment is costly

➢Expensive chemicals are needed

➢Output of the process is reduced if water contains turbidity.(turbidity must be below10 ppm)

Zeolite (Permutit) method of Softening of water

Zeolite is a Hydrated Sodium Alumino Silicate (HSAS), capable of exchanging reversibly its sodium ions for hardness producing ions in water.

The general chemical structure of zeolite is given below $Na_2O.Al_2O_3.xSiO_2.yH_2O$ (x = 2-10 and y = 2-6)
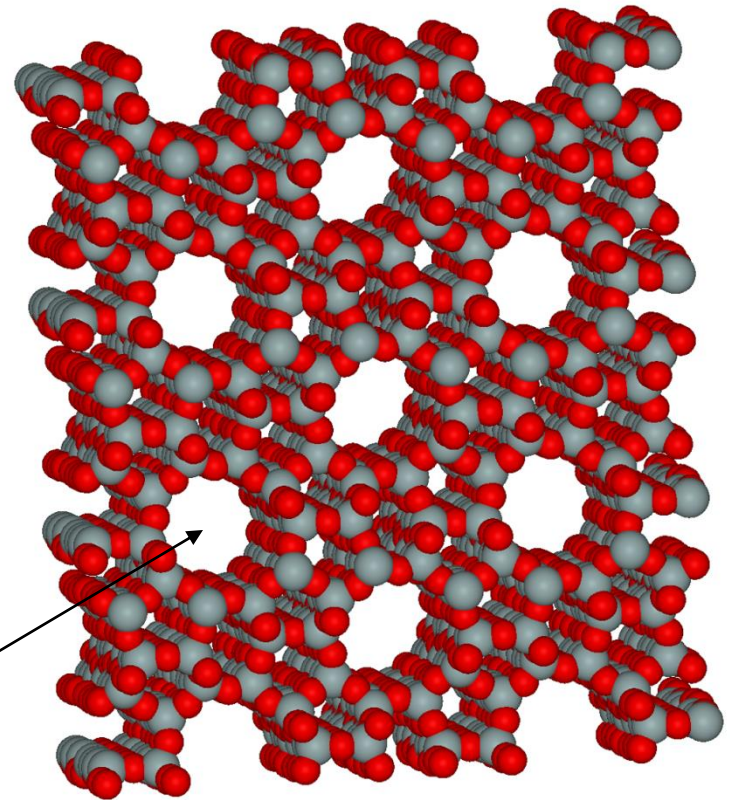
Micro pores of Zeolite

Porous Structure of zeolite

❖ **Porosity or cavity size of synthetic zeolite structures can be controlled by varying the Si/Al ratio**
❖ **Ion-exchange process of zeolite structure is associated with sodium ions**

Zeolite softener

Hard water in

Hard water spray

Zeolite bed

Gravel

Injector

NaCl storage

To sink

Softened water
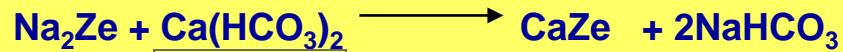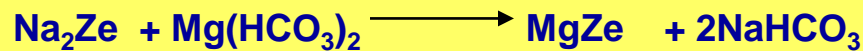
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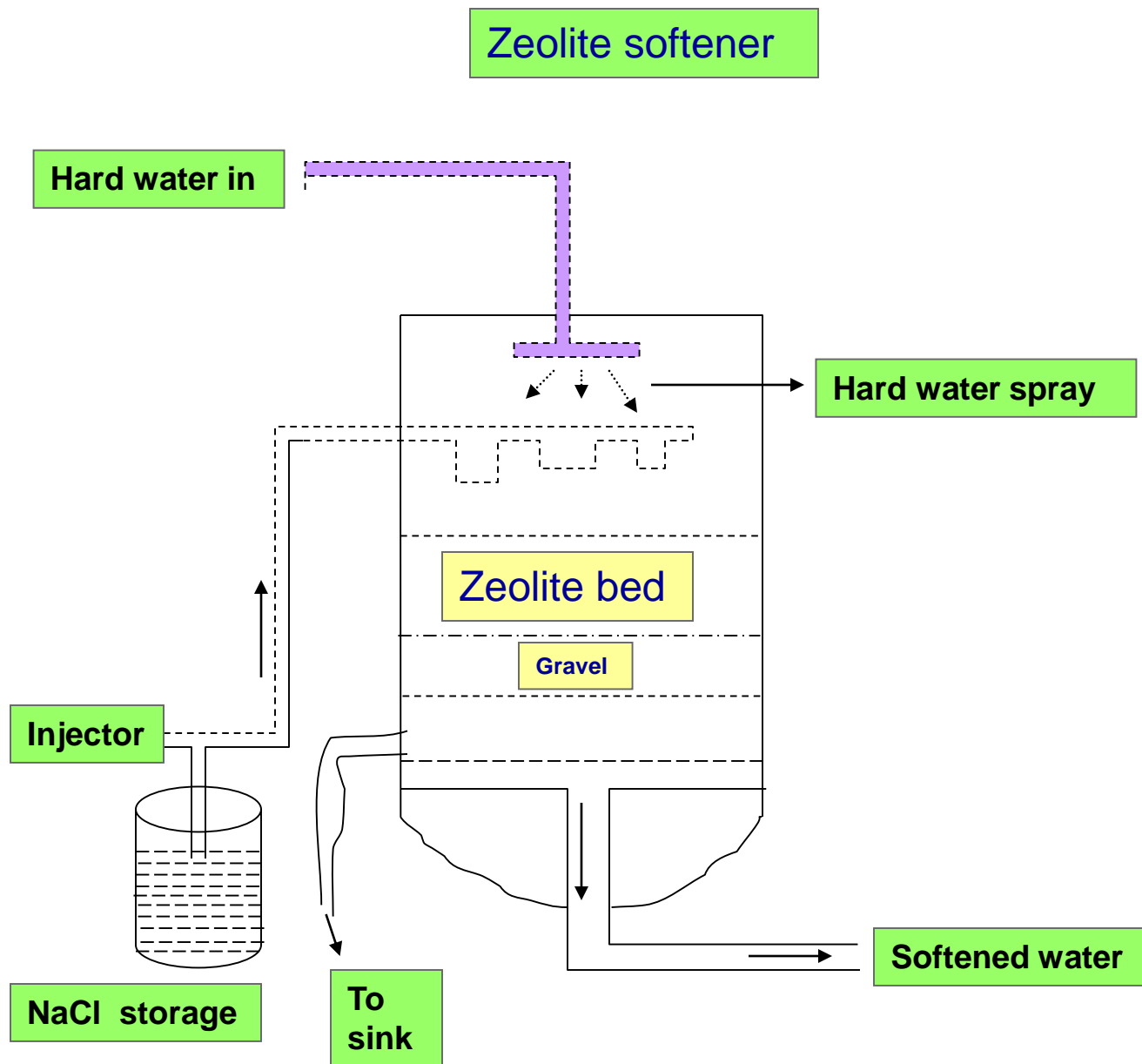
Process of softening by Zeolite method

For the purification of water by the zeolite softener, hard water is passed through the zeolite bed at a specified rate. The hardness causing ions such as Ca^{2+}, Mg^{2+} are retained by the zeolite bed as CaZe and MgZe respectively; while the outgoing water contains sodium salts. The following reactions takes place during softening process

To remove temporary hardness

$$Na_2Ze + \underset{\text{Hardness}}{Ca(HCO_3)_2} \longrightarrow CaZe + 2NaHCO_3$$

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

To remove permanent hardness

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

$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$
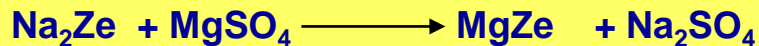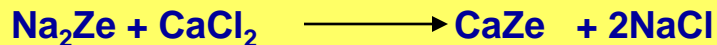
Regeneration of Zeolite Bed

$$CaZe \ (or) \ MgZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \ (MgSO_4)$$
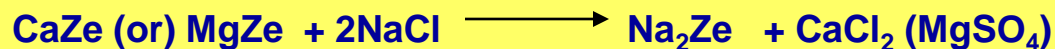
| Used Zeolite | 10% brine solution | Regenerated Zeolite | Washings drained |

Limitations of Zeolite process

1. If the water is **turbid**: then the turbidity causing particles clogs the pores of the Zeolite and making it inactive

2. The ions such as **Mn^{2+} and Fe^{2+} forms stable complex Zeolite which can not be regenerated** that easily as both metal ions bind strongly and irreversibly to the zeolite structure.

3. Any acid present in water **(acidic water) should be neutralized** with soda before admitting the water to the plant.

Advantages of Zeolite process

1. Soft water of 10-15 ppm can be produced by this method

2. The equipment occupies less space

3. No impurities are precipitated, hence no danger of sludge formation in the treated water

4. It does not require more time and more skill

Disadvantages of Zeolite process

1. Soft water contains more sodium salts than in lime soda process

2. It replaces only Ca^{2+} and Mg^{2+} with Na^+ but leaves all the other ions like HCO_3^- and CO_3^{2-} in the softened water (then it may form $NaHCO_3$ and Na_2CO_3 which releases CO_2 when the water is boiled and causes corrosion)

3. It also causes caustic embrittlement when sodium carbonate hydrolyses to give NaOH

Water Technology:

➢ Softening of hard water: internal treatment by phosphate, calgon condition and colloid conditioning

Internal treatment:

In this process, an ion is prohibited to exhibit its original character by complexing or converted into other more soluble salt by adding appropriate reagent.

An internal treatment is accomplished by adding a proper chemical to water either:

(a) To precipitate the scale forming impurities in the form of sludge, which can be removed.

(b) To convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.

Important Internal Treatments are:

Phosphate conditioning:
Scale formation can be avoided by adding sodium phosphate which reacts with hardness of water forming non-adherent and easily removable soft sludge of calcium and magnesium phosphate.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3 (PO_4)_2 + 6NaCl$$
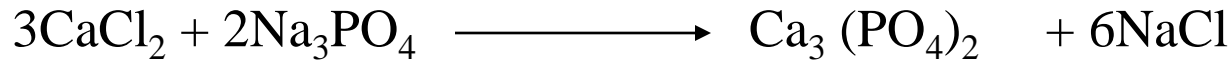
➢ Trisodium phosphate is most suitable for treatment when alkalinity is low
➢ Disodium phosphate is used when the water alkalinity is sufficient.
➢ Monosodium phosphate is used when the alkalinity of boiler water is too high.

Calgon conditioning:

Its involve in adding <u>calgon (Sodium hexa-meta phosphate (NaPO$_3$)$_6$</u> to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

$$[Na_6(PO_3)_6] \longrightarrow 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{2-} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$
$$\text{soluble complex ion}$$

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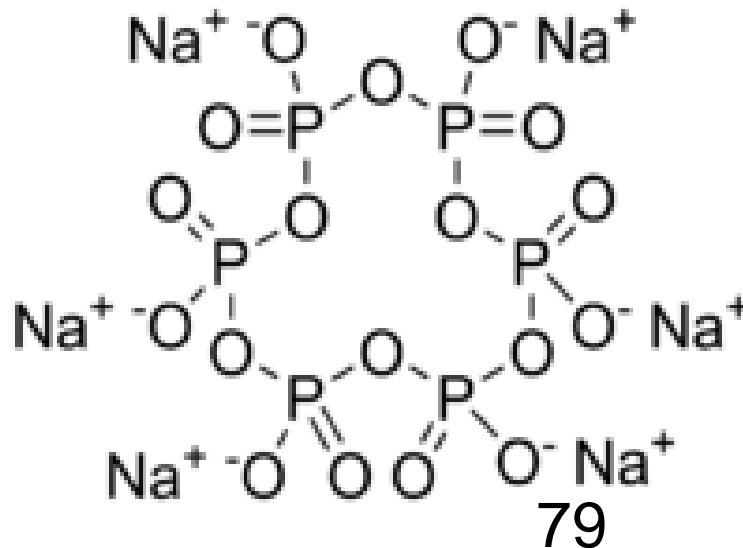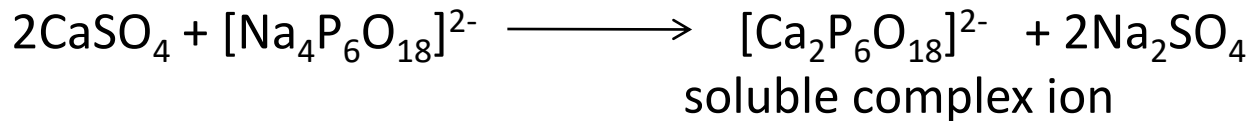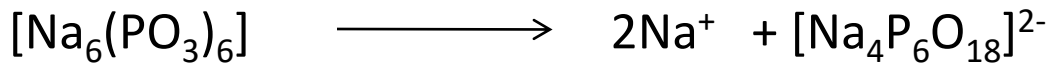
Colloidal conditioning:

Scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar (a gel) etc., which get coated on over the scale forming precipitate, thereby, **yielding non-sticky and loose deposits**.

(i) A zeolite softener was exhausted and regenerated by passing 100 litres of NaCl solution of strength 585 g/l. Calculate the total hardness of the water sample in ppm, if the zeolite softener can soften 1000 litres of water before regeneration.

Sol: 50,000 ppm in terms of $CaCO_3$ equivalent (formula 1.5 marks, correct answer 1 mark)

(ii) Compare the advantages and disadvantages of permutit process with those of lime-soda process.

Sol: Advantages over lime-soda process (1.5 marks)

(i) Soft water of 10-15 ppm can be produced by this method whereas lime-soda provides softness of 15-30 ppm only.

(i) No impurities are precipitated, hence no danger of sludge formation in the treated water while in lime soda a lot of sludge formation takes place. Disposal of large amount of sludge poses a problem in the lime soda process.

(ii) It does not require more time and more skill while in lime soda, for efficient and economical softening, careful operation and skilled supervision is required.

Dis-advantages over lime-soda process (1.5 marks)

(i) If the water is turbid: then the turbidity causing particles clogs the pores of the Zeolite and making it inactive but this is not in the case of lime-soda process.

(ii) The ions such as Mn^{2+} and Fe^{2+} forms stable complex with zeolite which can not be regenerated that easily as both metal ions bind strongly and irreversibly to the zeolite structure.

(iii) Any acid present in water (acidic water) should be neutralized with soda before admitting the water to the plant otherwise it will change the original nature and property of zeolite bed.

(iv) Soft water contains more sodium salts than in lime soda process.

(v) It replaces only Ca^{2+} and Mg^{2+} with Na^+ but leaves all the other ions like HCO_3^- and CO_3^{2-} in the softened water (then it may form $NaHCO_3$ and Na_2CO_3 which releases CO_2 when the water is boiled and causes corrosion)

(a) Treatment of hard water with a solid insoluble material produced soft water with increased amount of sodium ion (Na^+). Identify the process and write the reactions involved in the process.

Sol: Zeolite process

Reactions:

To remove hardness:

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$
$$Na_2Ze + CaSO_4 \longrightarrow CaZe + 2NaHCO_3$$

To regenerate zeolite bed

$$CaZe \text{ (or) } MgZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \text{ (MgSO}_4)$$

(b) Write a short note on ion-exchange process for softening of hard water.

Sol: Ion exchange resin structure (0.5 mark) reactions for water hardness remove (1 marks) regeneration reactions (1 marks)

Calculate the quantities of lime and soda required for treatment of 125,000 litres of water with the following composition:

Ca^{2+} = 95 ppm, Mg^{2+} = 36 ppm, CO_2 = 66 ppm, HCO_3^- = 244 ppm and H^+ = 2 ppm. What would be the quantities required for treatment of same water if purity of lime is 60% and soda is 90%?

Answer:

Lime required = $[Mg^{2+} + CO_2 + HCO_3^- + H^+]$ x 74/100
Soda required = $[Mg^{2+} + Ca^{2+} + CO_2 - HCO_3^- + H^+]$ x 106/100
Hardness in terms of $CaCO_3$ equivalent:
Ca^{2+} = 95x 100/40 = 237.5 ppm
Mg^{2+} = 36 x 100/24 = 150 ppm
CO_2 = 66 x 100/44 = 150 ppm
HCO_3^- = 244x 100/61x2 = 200 ppm
H^+ = 2 x 100/1x2 = 100 ppm
Total lime required=92.5 kg
Total soda required= 43.32 kg

A sample of hard water was only passed through a column of cation exchange resin. What will be the pH of water sample after the above treatment? Justify your answer and write the chemical reaction involved.

Answer:

Sol: **The pH of only cation exchange resin treated water will be less than 7 (acidic). Cation exchange resin removes all metal cations and exchanges with equivalent amount of H^+ ions. Due to increase in of H^+ ion concentration the treated water will be acidic.**

$$2RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$$
$$2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+} + 2H^+$$

(R= resin with $-SO_3^-$ or $-COO^-$ functional group)

A standard hardwater was prepared by mixing 410 mg $Ca(NO_3)_2$ and equimolar (having the same amount of moles) amount of $CaCl_2$. The total volume of the solution is 500 mL. Calculate the hardness of the solution in ppm unit. (Molecular weights of $Ca(NO_3)_2$= 164; $CaCl_2$=111 and $CaCO_3$= 100)

Answer:

$Ca(NO_3)_2$= 410 mg/164 = 2.5×10^{-3} mol;

$CaCl_2$=2.5×10^{-3} mol

Total = 5×10^{-3} mol

$CaCO_3$= 5×10^{-3} mol $\times 100$ g= 0.5 g in 500 mL or 1000mg in 1000 mL

1000 ppm

50,000-liter neutral hard water was passed through column containing organic insoluble material. The analysis of treated water showed pH 3. Calculate the hardness of the water.

Answer:

$pH = 3$, 1×10^{-3} molar H^+ solution.

1 mole H^+ ion = 50 g $CaCO_3$

1×10^{-3} mole H^+ ion = 50 mg $CaCO_3$

Hardness = 50 ppm

A zeolite softener was exhausted and regenerated by passing 100 litres of NaCl solution of strength 585 g/l. Calculate the total hardness of the water sample in ppm, if the zeolite softener can soften 1000 litres of water before regeneration.

Answer:

585 g NaCl = 585 x 10^3 mg NaCl in 1L water

100 L NaCl solution contains = 585 x 10^5 mg NaCl

$CaCO_3$ equivalent = [(585 x 10^5) x 50]/58.5 = 50 x 10^6 mg

50 x 10^6 mg CaCO3 in 1000 L of water = 50000 mg/L or ppm