WATER AND ITS TREATMENT

Hardness and alkalinity of water: Units and determination, External and internal method of Softening of water: Lime-soda Process, Ion exchange process, Desalination of brackish water

Source of Water

A) Surface Waters

- **Rain Water**

- **River Water**

- **Lake Water**

- **Sea Water**

B) Underground Waters

- **Spring Water**

- **Well Water**

Surface water

River water – dissolved minerals Cl^-, SO_4^{2-}, HCO^{3-} of Na^+, Mg^{2+}, Ca^{2+} and Fe^{2+}

       suspended impurities- Organic matter, sand, rock

composition is NOT constant – depend on the contact with soil.

Lake water: High in organic and less in minerals.

                composition is constant.

Rain water – pure form dissolved organic and inorganic particles and dissolved industrial gases CO_2, NO_2, SO_2 etc

Underground water- free from organic impurities due to filtering action of the soil

Sea water – very impure; too saline for industrial use except cooling

Impurities in water

- Suspended impurities like inorganic (clay, sand) organic (oil, plant, and animal matter)

- Colloidal impurities- finely divided silica and clay

- Dissolved impurities – salts and gases

- Microorganisms – bacteria, fungi and algae

Major Impurities of Water

- **Turbidity, silt, mud, dirt**

- **Magnesium Carbonate, Calcium Bicarbonate , Sodium Hydroxide**

- **Potassium Sulfate, Ammonium Chloride, Iron Nitrate**

- **Manganese**

- **Phosphate**

- **Hydrogen sulfide and Carbon dioxide , Ammonia ,Methane , Oxygen , Chlorine**

- **other suspended matter**

- **Colloidal silica, Silica Oil**

- **Bacteria phage, Microorganisms, plankton**

- **Organic Matter* ,Corrosion products (condensate)**

Important Properties in water chemistry

Natural water may contain

1) Conductivity

2) Turbidity

3) Color

4) pH

5) Alkalinity

6) Solids

7) Hardness

ALKALINITY

- Alkalinity of water is refers to the total amount of those substance present in water which tend to increase the concentration of hydroxide ions on account of dissociation and hydrolysis in water.

- It is a measure of ability of water to neutralize acids.

Total Alkalinity =Methyl Orange Alkalinity + Phenolphthalein Alkalinity

CAUSE OF ALKALINITY:

Presence of HCO_3^-, $HSiO_3^-$, SiO_3^-

Presence of salts of weak acids

Presence of buffer forming salts

CLASSIFICATION OF ALKALINITY : It is of three types:

1) OH^- (hydroxyl) *ALKALINITY*

2) *CO_3^{2-} (carbonate) ALKALINITY*

3) *HCO_3^- (bicarbonate) ALKALINITY*

Determination of Alkalinity

PRINCIPLE: The type and extent of alkalinity of water sample is determined by TITRIMETRIC METHOD.

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

$$CO_3^{2-} \ + \ H^+ \longrightarrow HCO_3^-$$

$$HCO_3^- + \ H^+ \longrightarrow H_2CO_3$$

Hardness of water

It is defined as a characteristic property of water that prevents the lathering of soap.

Hardness of water may also be defined as the soap-consuming capacity of water, or the capacity of precipitation of soap.
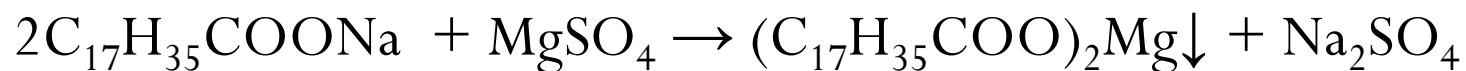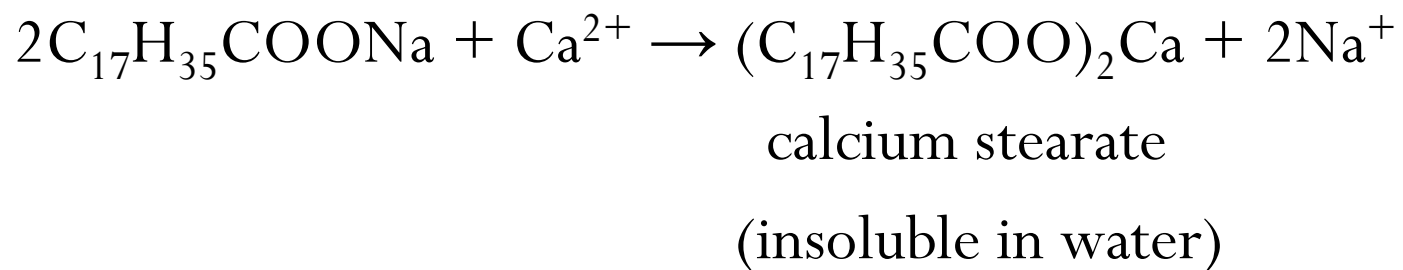
Hardness prevents the lathering of soap, due to the presence of salts of Ca, Mg, Al, Fe and Mn dissolved in it.

Soap – Na or K salts of long chain fatty acids $C_{17}H_{35}COOH$

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow (C_{17}H_{35}COO)_2Ca\downarrow + 2NaCl$$
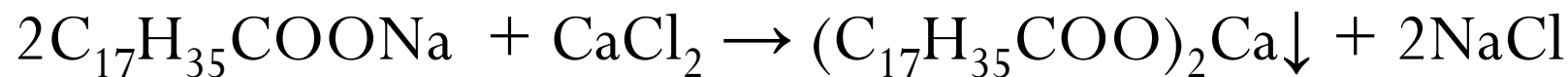
CAUSE OF HARDNESS

Hard water does not produce lather with soap solutions, but produces white precipitate (scum). For example, sodium stearate reacts with calcium:

$$2C_{17}H_{35}COONa + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca + 2Na^+$$

calcium stearate

(insoluble in water)

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$$

Hard Water	Soft Water
Does not produce lather with soap	Produces lather easily with soap
Contains Ca and Mg salts	Does not contain dissolved Ca and Mg salts
Soap is wasted and cleaning quality is depressed	Cleaning quality of soap not depressed.
Boiling point elevated, more time and fuel for cooking	Less fuel and time required for cooking

TYPES OF HARDNESS

a) TEMPORARY HARDNESS /Carbonate/Alkaline

This hardness refers to the amount of carbonate and bicarbonates of Ca & Mg in solution

It can be removed or precipitated by boiling.

This type of hardness is responsible for the deposition of scale in hot water pipes and kettles.

b) Permanent/ Non-carbonate hardness/non-alkaline

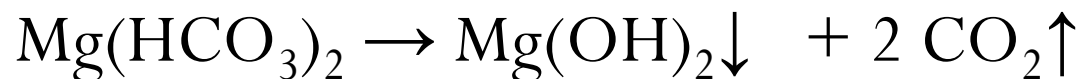This hardness is caused by sulfate, chloride or nitrate of Ca & Mg

.

This type of hardness cannot be removed by boiling.

Temporary Hardness

caused by dissolved bicarbonates of Ca and Mg
   Temporary hardness can be removed by boiling of water

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow \ + H_2O \ + CO_2\uparrow$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2\downarrow \ + 2\ CO_2\uparrow$$

Also known as 'alkaline or carbonate hardness'

Determined by titration with HCl using methyl orange as
   indicator

Permanent Hardness

$CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$

Cannot be destroyed on boiling the water

Also known as *non-carbonate* or *non alkaline* hardness

non alkaline hardness $=$ Total hardness $-$ alkaline hardness

Hard Water

Advantages

Ca in water helps produce strong teeth and bones

Hard water coats lead pipes with layer of insoluble $CaCO_3$, preventing any poisonous lead dissolving in drinking water

Disadvantages

Boiler feed water should be free from hardness or even explosions can occur

UNITS OF HARDNESS

There are several different scales used to describe the hardness of water in different contexts.

1) ppm   2) Mg/l   3) Clark's Degree   4) Degree french

- Parts per million (ppm)
  Usually defined as one milligram of calcium carbonate ($CaCO_3$) per litre of water.

- Clark degrees (°Clark)/English degrees (°e or e)
  One degree Clark is defined as equivalent of $CaCO_3$

  per 70,000 parts of water.

- French degrees (°F or f)
  One degree French is defined as 10 milligrams of calcium carbonate per litre of water, equivalent to 10 ppm.

RELATIONSHIP: 1ppm= 1 mg/l = 0.07 °Clark =0.1 °F

EXPRESSION OF HARDNESS

- The equivalent of $CaCO_3$ for a hardness causing salt is given by:

- Equivalent mass of $CaCo_3$ = W X 50

  W = Mass of hardness producing substance

  E = Equivalent mass of $CaCO_3$

Draw backs (or) Disadvantages of Hard Water

Domestic Use

1. Washing
2. Bathing
3. Drinking
4. Cooking

> The sticky precipitate adheres on the fabric/cloth and gives spots and streaks. Fe salts stain the cloths.

> Produces sticky scum on the bath tub and the body

> Bad to the digestive system and calcium oxalate formation is possible in urinary tracts

> Requires more fuel and time. Certains food don't cook soft and also gives unpleasant taste

Industrial Use

1. Textile Industry
2. Sugar Industry
3. Dyeing Industry
4. Paper Industry
5. Pharmaceutical Industry
6. In Steam generation in Boilers

SLUDGE FORMATION IN BOILERS:

- In boilers, because of continuous evaporation of water, the concentration of salts increase progressively and after the saturation point is reached, precipitate form on the inner walls of boiler.

- SLUDGE: Sludge is a soft, loose and slimy precipitate formed within the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.
  These are formed by substances which have greater solubilities in hot water than in cold-water.
  E.g.. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$.

Boiler troubles due to Hard Water

1. Scale and Sludge

2. Caustic embitterment

3. Priming and Foaming

4. Boiler corrosion

1. Sludge
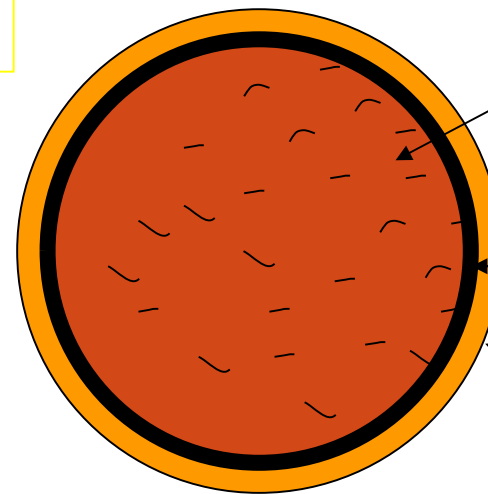
Slimy loose precipitate called sludge suspended in water

water

Boiler wall

Sludge is a soft, loose and slimy precipitate formed within the boiler. It can be easily scrapped off with a wire brush.

It is formed at comparatively colder portions of the boiler and collects in areas of the system, where the flow rate is slow or at bends.

It is formed by substances which have greater solubility's in hot water than in cold water, e.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.,

Remedy: Sludges can be removed using wire brush or mild acid

1. Scale

Hard adherent coating on inner walls of boiler

water
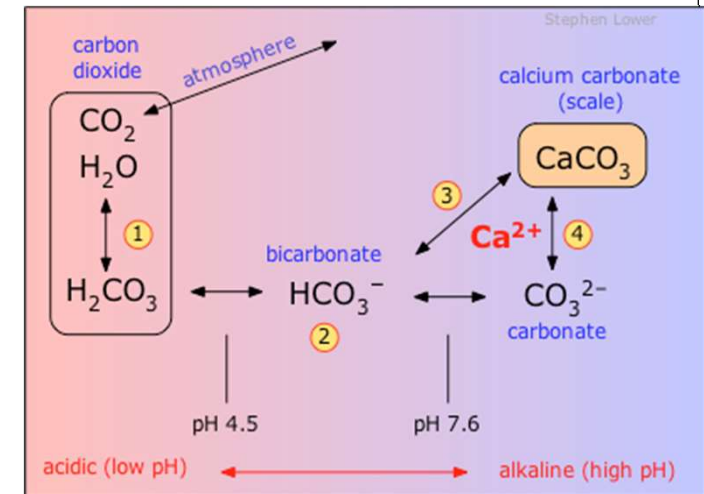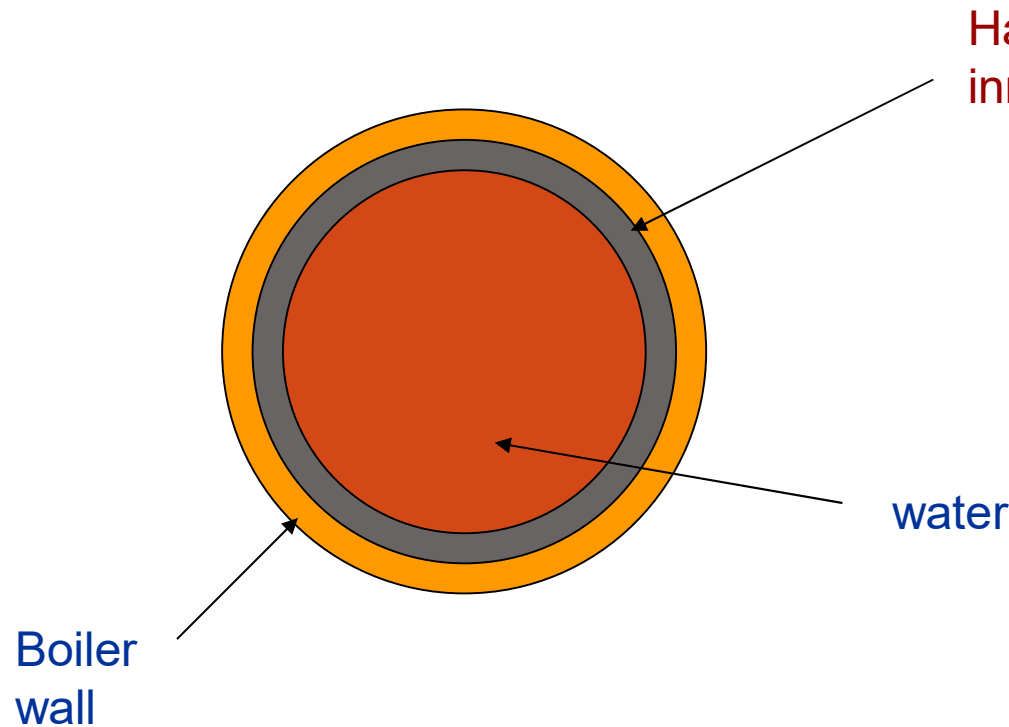
Boiler wall

Scales are hard substances which sticks very firmly to the inner surfaces of the boiler wall.

Scales are difficult to remove even with the help of a hammer and chisel.

Examples: $CaSO_4$, $CaCO_3$, $Mg(OH)_2$

Reasons for formation of scale

1. Presence of $Ca(HCO_3)_2$ in low pressure boilers

$$Ca(HCO_3)_2 \longrightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

Calcium bicarbonate   Calcium Carbonate (scale)

Low pressure boilers but in high pressure boilers it is soluble by forming $Ca(OH)_2$

2. Presence of $CaSO_4$ in high pressure boilers

T°C	Solubility of $CaSO_4$
15	3200 ppm
230	15 ppm
320	27 ppm
Cold water	soluble
Super heated water	Insoluble (scale)

4. Presence of SiO_2

It forms insoluble hard adherent $CaSiO_3$ and $MgSiO_3$ as scales

3. Presence of $MgCl_2$ in high temperature boilers

$$MgCl_2 + 2\,H_2O \longrightarrow Mg\,(OH)_2\downarrow + 2HCl\uparrow$$

Magnesium chloride   scale
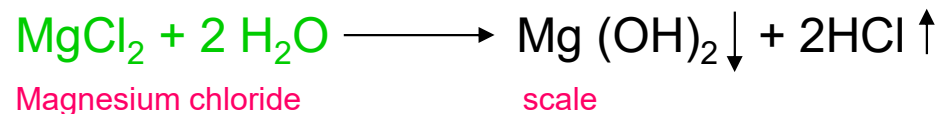
$Mg(OH)_2$ can also be generated by thermally decomposing $Mg(HCO_3)_2$

Disadvantages of scale formation

1. Fuel wastage – scales have low thermal conductivity

2. Degradation of boiler material and increases of risk of accident

3. Reduces the efficiency of the boiler and- deposit on the valves and condensers

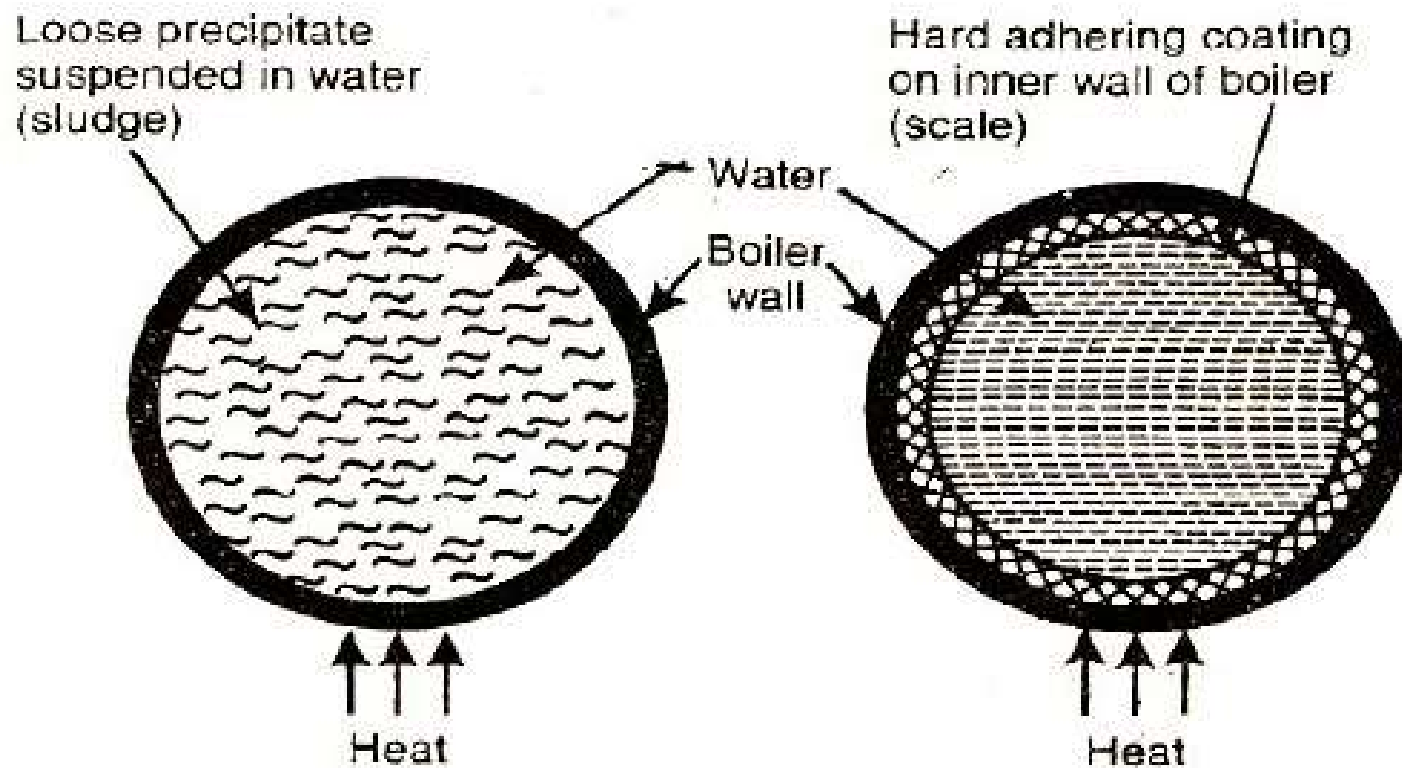4. The boiler may explode – if crack occurs in scale

Remedies: Removal of scale

1. Using scrapper, wire brush often

2. By thermal shock- heating and cooling suddenly with cold water

3. Using chemicals – 5-10% HCl and by adding EDTA

PREVENTION:

- a. <u>External treatment:</u> Efficient softening of water is to be carried out.

- b.<u>Internal treatment:</u> Suitable chemicals are added to the boiler water either to precipitate or to convert scale in to compounds.

Diagrams of scale and sludge:

Loose precipitate suspended in water (sludge)

Hard adhering coating on inner wall of boiler (scale)

Water

Boiler wall

Heat

Heat

Prevention of scale formation

Scale formation can be prevented by two methods

1. Internal conditioning or Internal Treatment

2. External conditioning or External treatment- will be discussed later

1. Internal conditioning methods - of boiler water to prevent scale formation

1. Phosphate conditioning – addition of phosphate compound

2. Carbonate conditioning – addition of carbonate compound

3. Calgon conditioning – addition of sodium hexa meta phosphate

4. Colloidal conditioning – spreading of organic compounds like tannin, agar gel

5. Sodium Aluminate – removes oil and silica

6. Complexometric method – using EDTA (refer expt. 1 chemistry lab manual)

1. Phosphate conditioning

Scale formation can be prevented by adding sodium phosphate to the boiler water which reacts with the hardness producing ions and forms easily removable phosphate salts of respective ions

$$3CaCl_2 \text{ (Boiler water)} + 2\ Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6\ NaCl$$

Calcium chloride

Sodium phosphate

calcium phosphate

(non adherent and can be removed by blow down method)

Selection of Phosphate compound

Calcium can not be precipitated below a pH = 9.5, hence the selection of phosphate has to be based on the pH of the boiler feed water.

NaH_2PO_4 (acidic in nature) ,

Na_2HPO_4 (weakly alkaline in nature),

Na_3PO_4 (Alkaline in nature)

2. Carbonate conditioning

$$CaSO_4 \text{ (Boiler water)} + Na_2CO_3 = CaCO_3 + Na_2SO_4$$

Calcium sulfate

Sodium carbonate

calcium carbonate

(non adherent loose sludge and can be removed by blow down method)

Caution: Excess Na_2CO_3 can result in caustic embrittlement

3. Calgon conditioning

$$Na_2[Na_4(PO_3)_6] \rightleftharpoons 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

Calgon – sodium hexa meta phosphate

$$2CaSO_4 \text{ (Boiler water)} + [Na_4P_6O_{18}]^{2-} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$
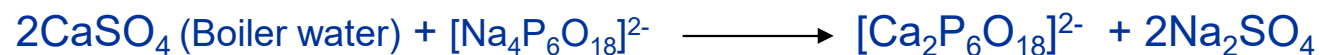
Calcium sulfate

Soluble complex ion of calcium - can be removed easily

Calgon tablets are used in the cleaning of washing machine drums

❖ Excess sodium carbonate used up for removing hardness can also result in the formation of NaOH in high pressure boilers.

❖NaOH has better mobility and can percolate into fine cracks present in boiler walls.

$$Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2$$

❖ NaOH gets concentrated in the fine cracks present in the boiler walls.

❖ A concentration cell corrosion is established between the conc. NaOH and dilute NaOH solution in contact with boiler walls.

❖ Concentrated NaOH region behaves as anode thus resulting in corrosion of boiler leading to the formation of sodium ferroate.

Remedies: (i) Use phosphate salts instead of sodium carbonate
(ii) use Na_2SO_4 or agar-agar gel compounds to fill the fine cracks.

Softening of hard water – External treatment

II External treatment of water – External Conditioning of water

Softening of hard water can be done by the following methods

1. Lime soda process

2. Zeolite methods

3. Ion exchange resin method

4. Mixed bed deionizer method

1. Lime soda process

It is a process in which Lime ($Ca(OH)_2$) and soda (Na_2CO_3) are added to the hard water to convert the soluble calcium and magnesium salts to insoluble compounds by a chemical reaction. The $CaCO_3$ and $Mg(OH)_2$ so precipitated are filtered off and removed easily.

It is further divided in to two types

1. Cold lime soda process

2. Hot lime soda process

Step 1

In this process a calculated quantity of $Ca(OH)_2$ (lime) and Na_2CO_3 (soda) are mixed with water at room temperature and added to the hard water. The following reactions takes place depending on the nature of hardness

Chemical reactions

If it is permanent hardness and due to calcium salt
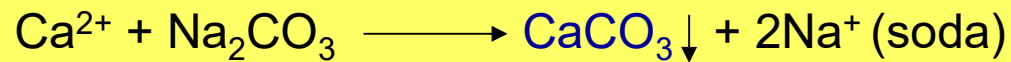
$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2Na^+ \text{ (soda)}$$

slimy suspended precipitate

If it is due to Magnesium salt

$$Mg^{2+} + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + Ca^{2+} \text{ (lime)}$$

slimy suspended precipitate

$$Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2Na^+ \text{ (soda)}$$
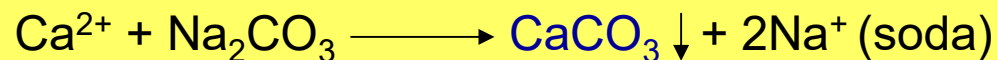
slimy suspended precipitate

Chemical reactions contd..

<u>If it is Temporary hardness and due to calcium salt</u>

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

slimy suspended precipitate

<u>If it is due to Magnesium salt</u>

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

slimy suspended precipitates
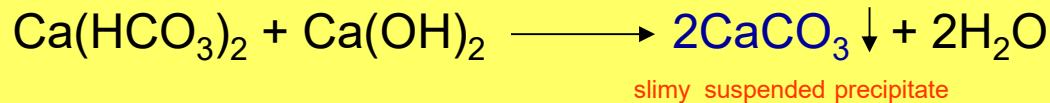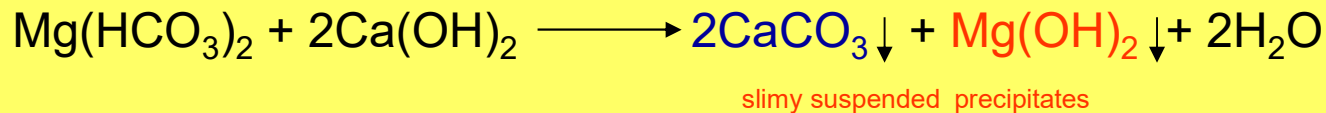
Step 2

The precipitates $CaCO_3$ and $Mg(OH)_2$ are very fine and forms sludge like precipitates in the boiler water and are difficult to remove because it does not settle easily making it difficult to filter and the removal process. Finally reduces the efficiency of the boiler.

Therefore, it is essential to add small amount of coagulant (such as Alum, Aluminium sulfate, sodium aluminate etc) which hydrolyses to flocculent precipitate of $Al(OH)_3$ which entraps the fine precipitates.

NOTE: Particles finer than 0.1 μm (10^{-7}m) in water remain continuously in motion due to electrostatic charge (often negative) which causes them to repel each other. Once their electrostatic charge is neutralized by the use of coagulant chemical, the finer particles start to collide and agglomerate (combine together) under the influence of Van der Waals's forces. These larger and heavier particles are called flocs.

When coagulants are added flocculation takes place followed by the formation of flocculants.

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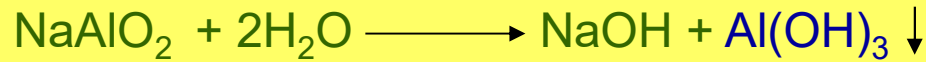
Coagulant

Flocculent- Gelatinous precipitate which entraps the fine precipitates of $CaCO_3$ and $Mg(OH)_2$

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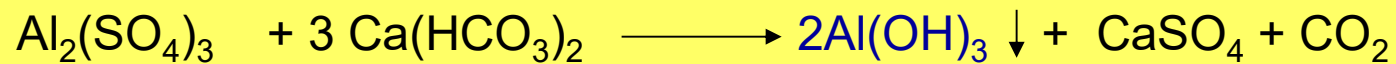
Aluminium sulfate

Hard water sample

Flocculent- Gelatinous precipitate which entraps the fine precipitates of $CaCO_3$ and $Mg(OH)_2$

The $Al(OH)_3$ formed by the addition of coagulants initiates the process of flocculation and entraps the fine precipitates and becomes heavy. The heavier flocs then settles at the bottom and filtered off easily.

CONTINUOUS COLD LIME SODA SOFTENER
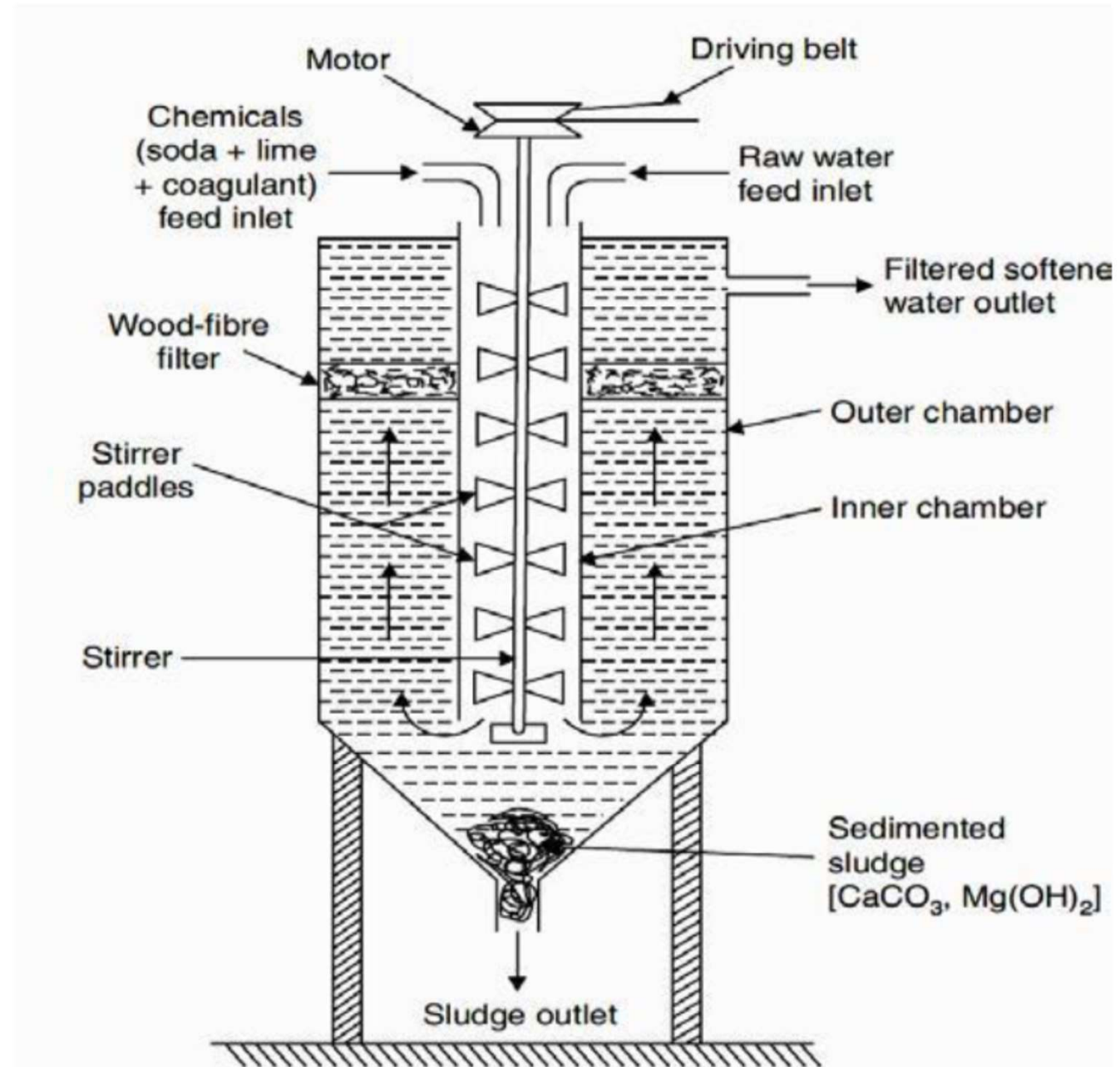
Continuous Lime Soda

2. Hot lime soda Process

In this process a calculated quantity of $Ca(OH)_2$ (lime) and Na_2CO_3 (soda) are mixed with hot water at a temperature range of 80 to 150°C and added to the hard water. The following reactions takes place depending on the nature of hardness

Advantages of Hot Lime Soda Process

1. The reaction between hardness producing substance and lime soda proceeds at a faster rate

2. The precipitates and sludges formed are settled at the bottom easily and hence No coagulants are required

3. The dissolved gases such as CO_2 escapes and the water becomes free from dissolved gases

4. It produces soft water with the residual hardness of 15-30ppm in contrast to the cold lime soda process which produces soft water with 50-60ppm of residual hardness

Hot lime soda Plant consists of three parts

1. Reaction tank: water, chemicals and steam are mixed

2. Conical sedimentation tank : sludge settles down

3. Sand filter : complete removal of sludge from the soft water is ensured

CONTINUOUS HOT LIME SODA PROCESS
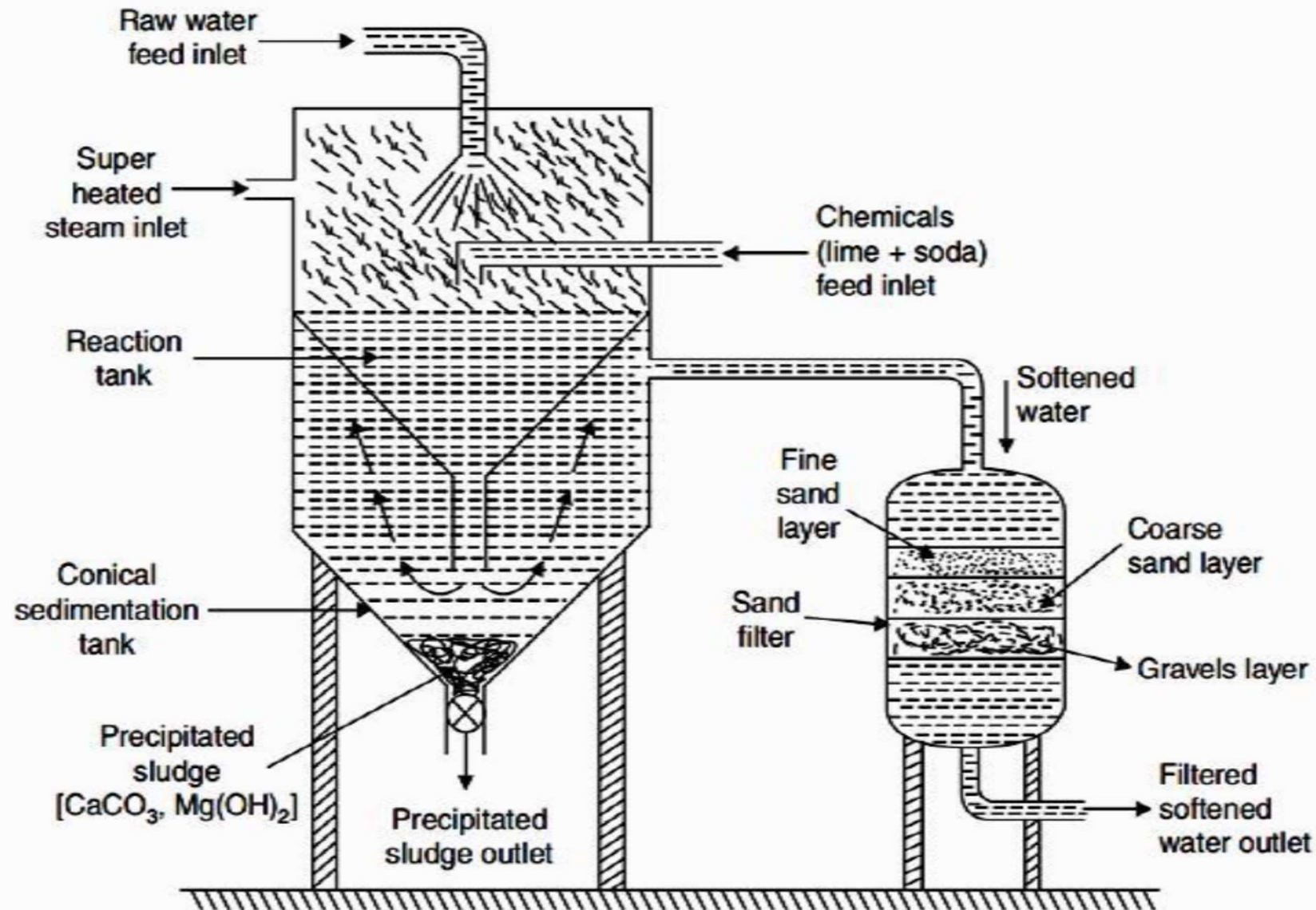
Hot lime soda softener

1. It is very economical compared to other methods

2. Iron and manganese salts are also removed by this process

3. It increases the pH of the softened water hence corrosion is minimized also pathogenic bacteria

1. Disposal of large amount of sludge (insoluble precipitates) poses a problem

2. This can remove hardness to the extent of 15ppm which is not good for boilers

Calculation of lime and soda required for the softening of hard water by the lime soda process

Hardness producing substance	Chemical reaction with lime and soda	Need
Permanent Hardness **Ca Salts**	$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$	S
Mg salts	$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2 \downarrow + CaSO_4$ $CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$	L + S
Temp. Hardness $Ca(HCO_3)_2$ $Mg(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + 2H_2O$ $Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow 2CaCO_3 \downarrow + Mg(OH)_2 \downarrow + 2H_2O$	L 2L
Acids **HCl** H_2SO_4	$2H^+ + Ca(OH)_2 \longrightarrow Ca^{2+} + 2H_2O$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2Na^+$	L+S
HCO_3^-	$HCO_3^- + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O + CO_3^{2-}$	L - S
$FeSO_4$	$Fe^{2+} + Ca(OH)_2 \longrightarrow Fe(OH)_2 \downarrow + Ca^{2+}$ $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2Na^+$	L+S
$NaAlO_2$	$NaAlO_2 + H_2O \longrightarrow Al(OH)_3 \downarrow + NaOH$	L/2

Rules

1. If $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ are considered as ions $(Ca^{2+} + 2HCO_3^-)$ and $(Mg^{2+} + 2HCO_3^-)$ respectively then the calculation result will be the same based on the ability of the ions to take up bicarbonate ions

2. If treated water found to contain excess of OH^- and CO_3^{2-} ions these are formed from excess equivalent each of $Ca(OH)_2$ and Na_2CO_3 and hence these excess amounts should be added to the calculation (in temp. hardness and perm. hardness)

3. When the impurities are given as $CaCO_3$ and $MgCO_3$ present in water it should be considered as due to bicarbonates of calcium and magnesium respectively

4. Substances like NaCl, KCl, Na_2SO_4, SiO_2, Fe_2O_3 etc do not contribute to hardness and therefore, they do not consume any soda or lime and hence if these present need not be taken in to consideration during calculation.

5. Soda (Na_2CO_3) neutralizes only permanent hardness

Molecular weight of lime = 74

Molecular weight of soda = 106

Molecular weight of $CaCO_3$ = 100

Therefore, 100 parts by mass of $CaCO_3$ are equivalent to

(i) 74 parts by mass of $Ca(OH)_2$

(ii) 106 parts by mass of Na_2CO_3

Therefore, Lime requirement for softenening

$$= \frac{74}{100} \left[\text{T.H of } Ca^{2+} + 2 \times \text{T.H of } Mg^{2+} + \text{P.H of } (Mg^{2+} + Fe^{2+} + Al^{3+}) + CO_2 + H^+ + HCO_3^- - NaAlO_2/2 \right] \times \text{Vol .of water (L)}$$

T.H = temporary hardness

P.H = Permanent Hardness

III^{ly}, Soda requirement for softenening

$$= \frac{106}{100} \left[\text{P.H of } (Ca^{2+} + Mg^{2+} + Fe^{2+} + Al^{3+}) + H^+ - HCO_3^- \right] \times \text{Vol .of water (L)}$$

Problem 1

Calculate the amount of lime required for softening 5,000 litres of hard water containing 72 ppm of $MgSO_4$ (mol wt = 120) Ans = 222g

Solution

Step 1 List out the given data

Given data : Hardness 72 ppm due to $MgSO_4$; water qty = 5000 litres; mol. wt. MgSO4 = 120

Step 2 calculate the $CaCO_3$ equivalent

Hardness producing substance	Quantity (ppm)	Multiplication factor	$CaCO_3$ equivalent hardness (ppm or mg/L)
$MgSO_4$	72	100/120	72 X (100/120) = 60

Step 3 calculation of lime requirement

Lime required = 74/100 (hardness due to MgSO4) x vol. of water

= 74/100 (60 mg/L) x 5000 L

= 222,000 mg

= 222 g

Problem 2

Calculate the amount of lime and soda required for softening 50,000 litres of hard water containing:
$Mg(HCO_3)_2$ = 144 ppm, $CaCO_3$ = 25 ppm, $MgCl_2$ = 95ppm, $CaCl_2$ = 111ppm, Fe_2O_3 = 25ppm and Na_2SO_4 = 15ppm

Solution

Step 1 List out the given data

Given data : $MgCO_3$ = 144 ppm, $CaCO_3$ = 25 ppm, $MgCl_2$ = 95ppm, $CaCl_2$ = 111ppm, Fe_2O_3 = 25ppm and Na_2SO_4 = 15ppm

Step 2 calculate the $CaCO_3$ equivalent

Hardness producing substance	Quantity (ppm)	Multiplication factor	$CaCO_3$ equivalent hardness (ppm or mg/L)
$Mg(HCO_3)_2$	144	100/84	144 x(100/84) = 171.4
$CaCO_3$	025	100/100	25 x (100/100) = 25.0
$MgCl_2$	095	100/95	95 x (100/95) = 100.0
$CaCl_2$	111	100/111	111 x (100/111) = 100.0
Fe_2O_3	025 (does not cause hardness)		
Na_2SO_4	015 (does not cause hardness)		

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

$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2 + CaCl_2$; $CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$

What happens when lime is treated with $CaCl_2$?

Step 3 calculation of lime requirement

Lime required = 74/100 ({2 x $MgHCO_3$} + $CaCO_3$ + $MgCl_2$ in terms of $CaCO_3$ eq) x vol. of water

= 74/100 (2 x 171.4 + 25.0 +100.0) mg/L x 50,000 L

= 74/100 (467.8) mg x 50,000

= 17, 309,000 mg

Answer = 17. 31 kg

Step 4 calculation of soda requirement

soda required = 106/100 ($MgCl_2$ + $CaCl_2$ in terms of $CaCO_3$ eq) x vol. of water

= 106/100 (100 +100.0) mg/L x 50,000 L

= 106/100 (200) mg x 50,000

= 10, 6,00,000 mg

Answer = 10. 6 kg

II. 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)

Why synthetic zeolite is better than natural zeolite for the softening of water? Ans: Natural zeolites are non-porous

Micro pores of Zeolite
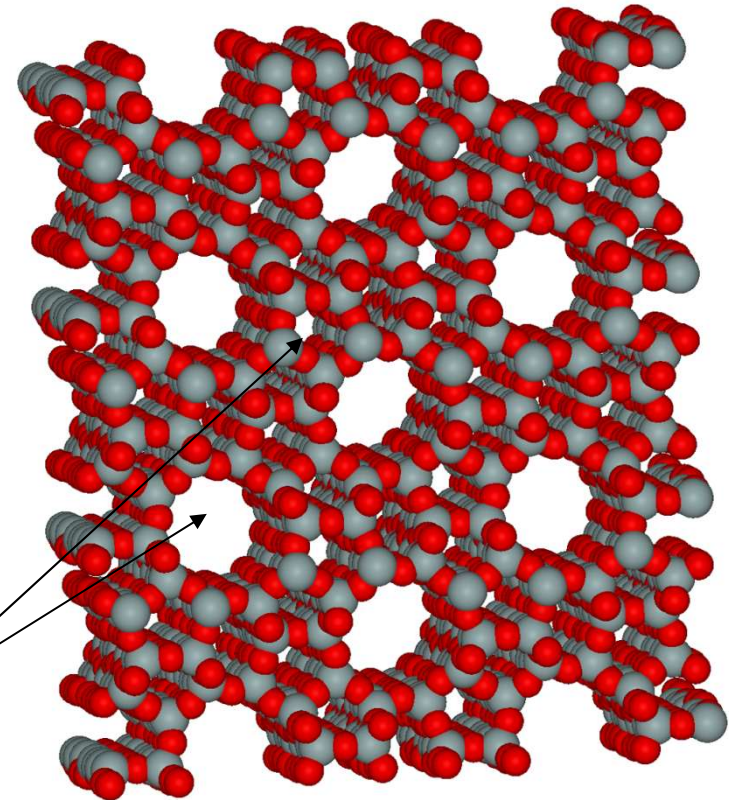
Porous Structure of zeolite

❖ 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

Hard water inlet

Zeolite bed

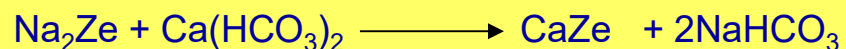Gravel

Injector

To sink

Brine stock

Soft water outlet
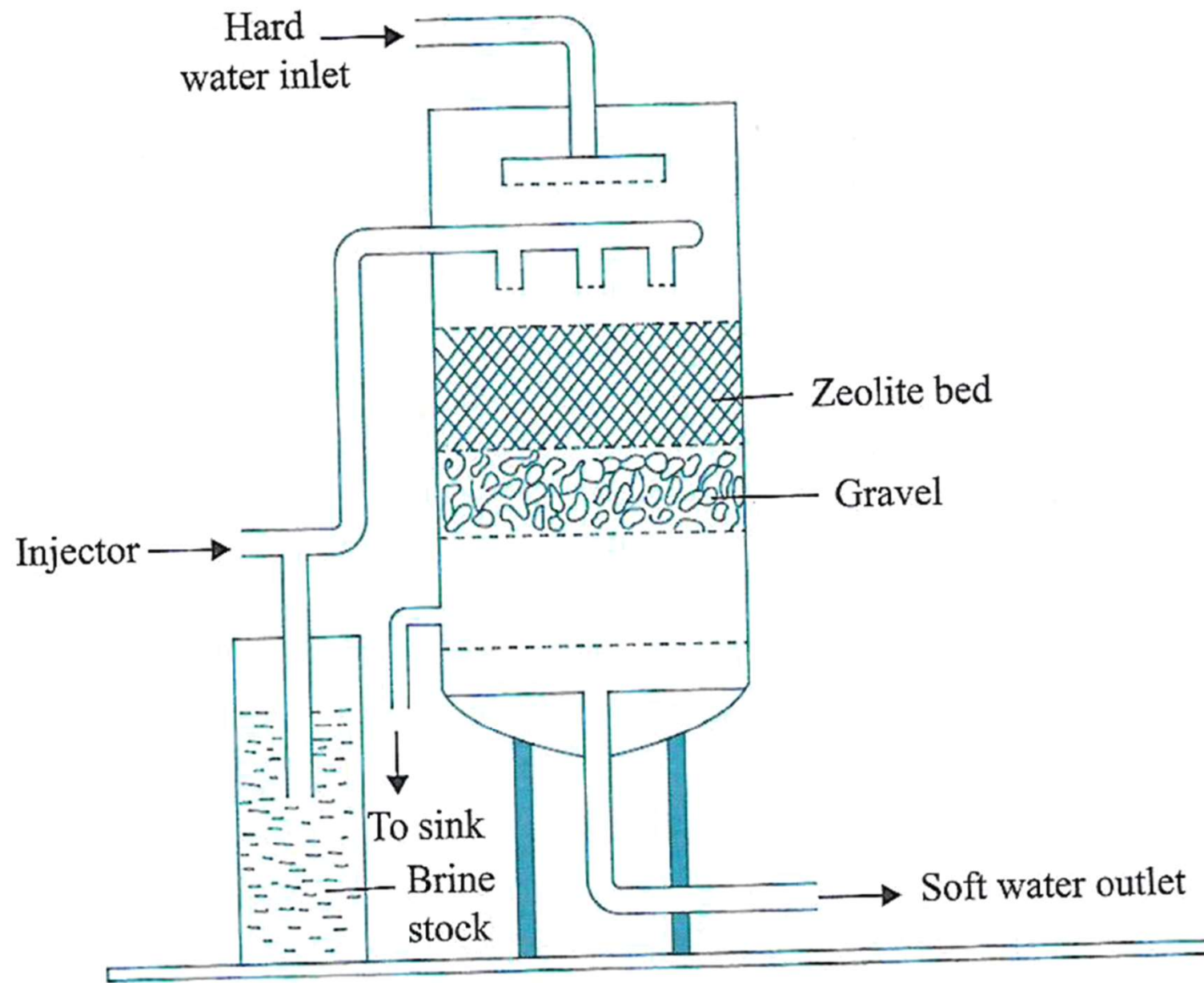
Zeolite softener
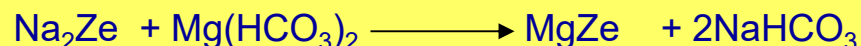
Process of softening by Zeolite method

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

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

Hardness

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

To remove permanent hardness

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

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

Regeneration of Zeolite Bed

$$CaZe \ (or) \ MgZe + 2NaCl \longrightarrow Na_2Ze + CaCl_2 \ (MgSO_4)$$
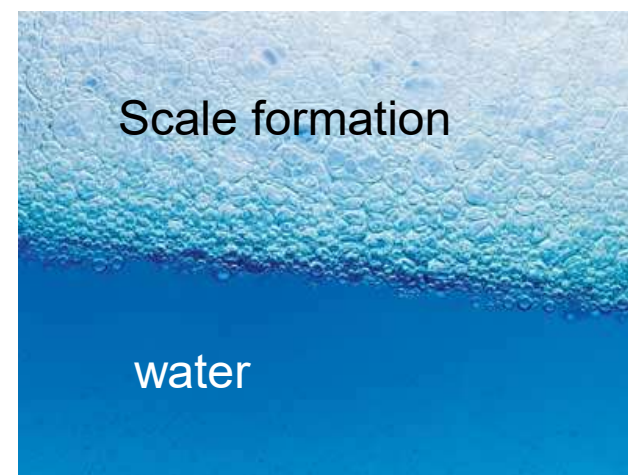
Used Zeolite

10% brine solution

Regenerated Zeolite

Washings drained

Scale formation

water

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, since acid will hydrolyze SiO_2 forming silicic acid

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
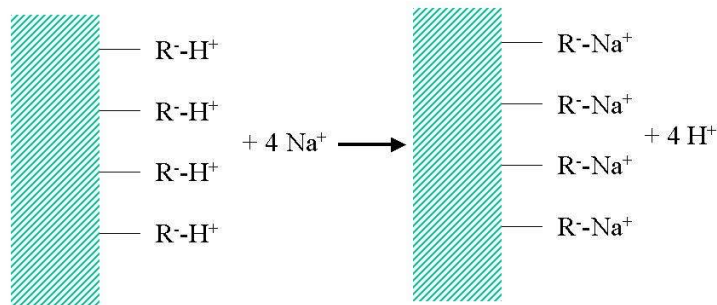
4. It does not require more time and more skill

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 embitterment when sodium carbonate hydrolyses to give NaOH

III. Ion-Exchange resin (or) deionization (or) demineralization process

Polymer chains

Cross-links

Fixed resin functional groups

Exchangeable Counterions

Ion exchange resin

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.

$R^- - H^+$

$R^- - H^+$

$R^- - H^+$

$R^- - H^+$

$+ \ 4 \ Na^+ \longrightarrow$

$R^- - Na^+$

$R^- - Na^+$

$R^- - Na^+$

$R^- - Na^+$

$+ \ 4 \ H^+$
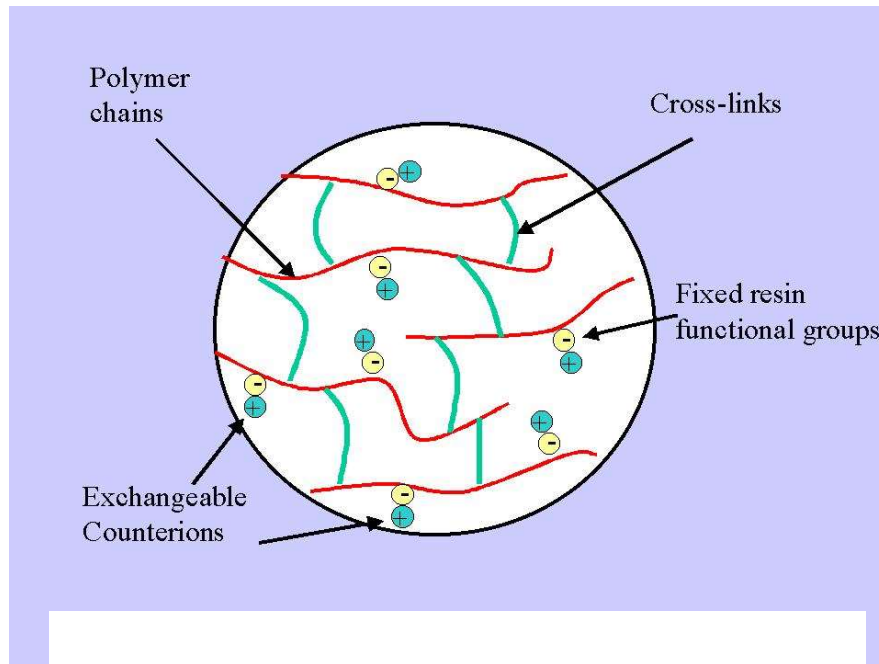
Cation exchange Resin

Resin after treatment

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.

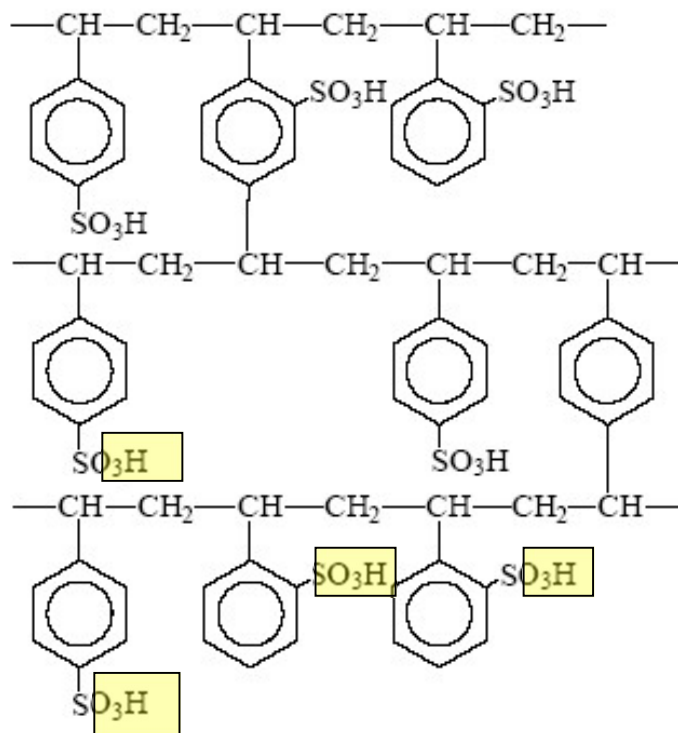Based on the above fact the resins are classified into two types

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
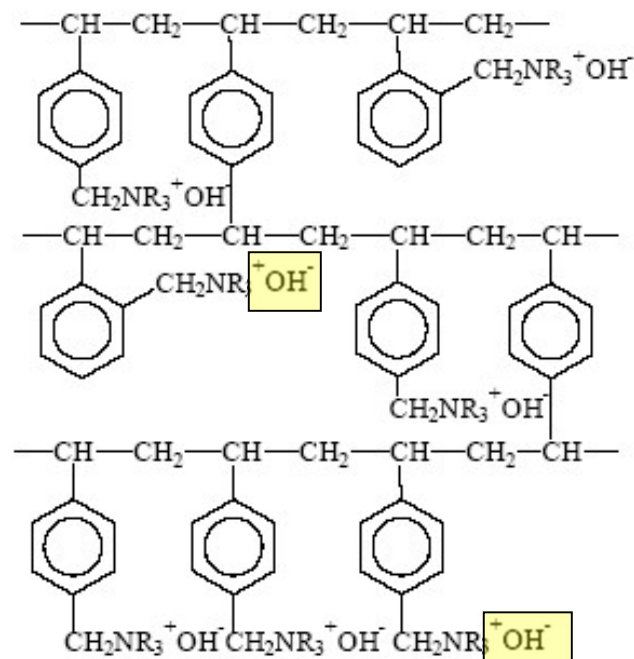
Continued… next slide

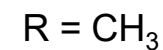Structure of Cation and Anoin exchange resins

Cation exchange resin

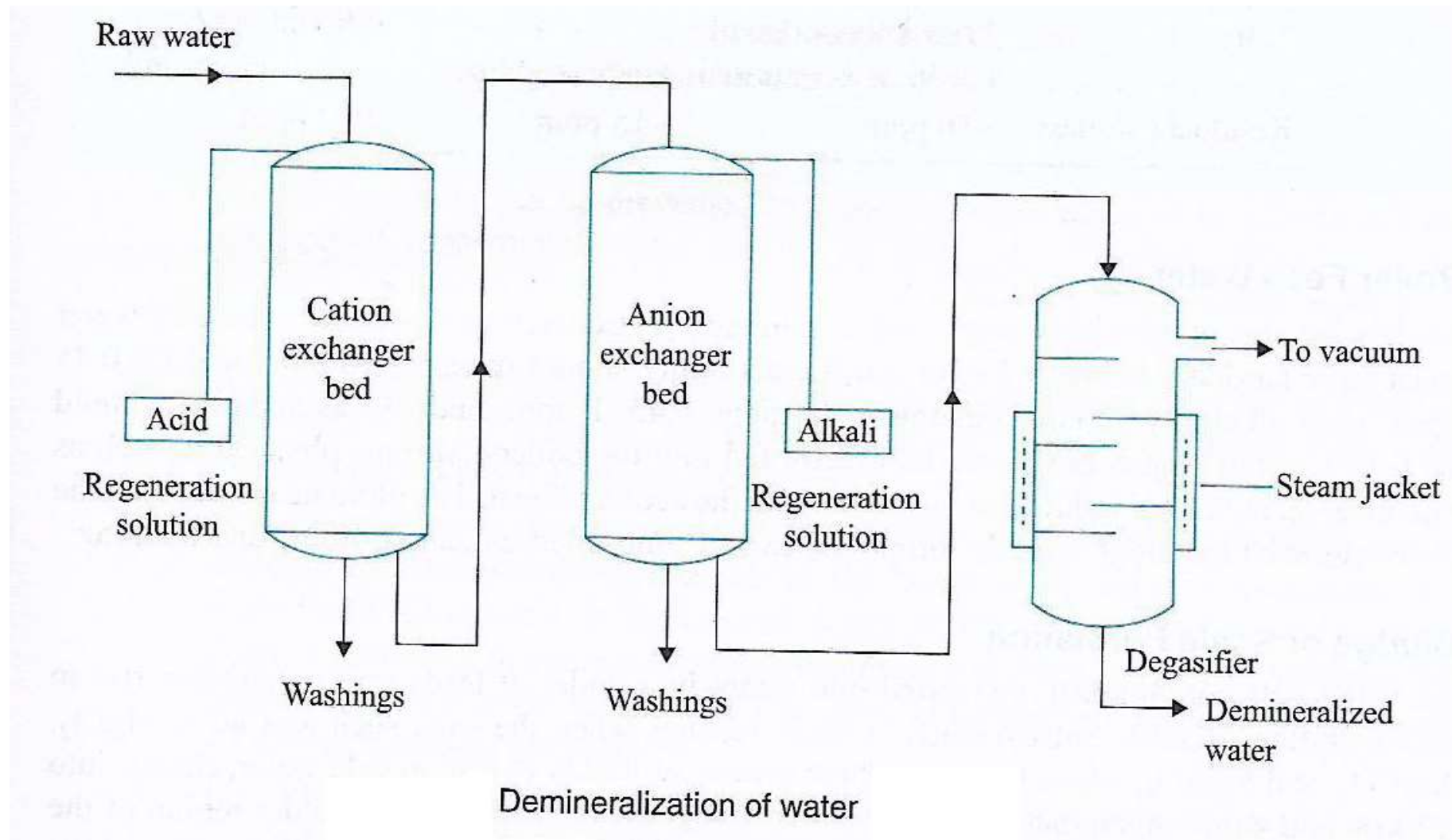A strongly acidic sulphonated polystyrene cation exchange resin

Anion exchange resin
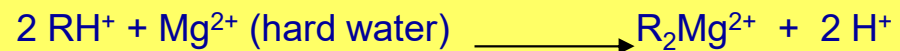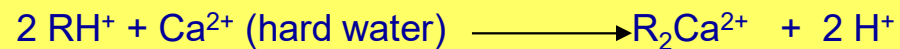
A strongly basic quaternary ammonion anion exchange resin

R = CH_3

ION EXCHANGE PURIFIER OR SOFTENER

Demineralization of water

Process or Ion-exchange mechanism involved in water softening

Reactions occurring at Cation exchange resin

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

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

Reactions occurring at Anion exchange resin

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

$2 ROH^- + Cl^-$ (hard water) $\longrightarrow R_2Cl^- + 2 OH^-$
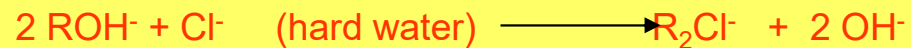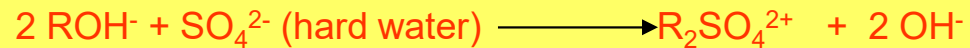
At the end of the process

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

Regeneration of ion exchange resins

Regeneration of Cation exchange resin

$R_2Ca^{2+} + 2H^+$ (dil. HCl (or) H_2SO_4) $\longrightarrow$ $2 RH^+ + Ca^{2+}$ ($CaCl_2$, washings)
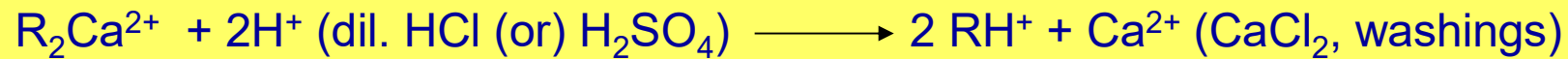
Regeneration of Anion exchange resin

$R_2SO_4^{2-} + 2OH^-$ (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

IV. Softening of water by Mixed Bed deioniser

Description and process of mixed bed deionizer

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
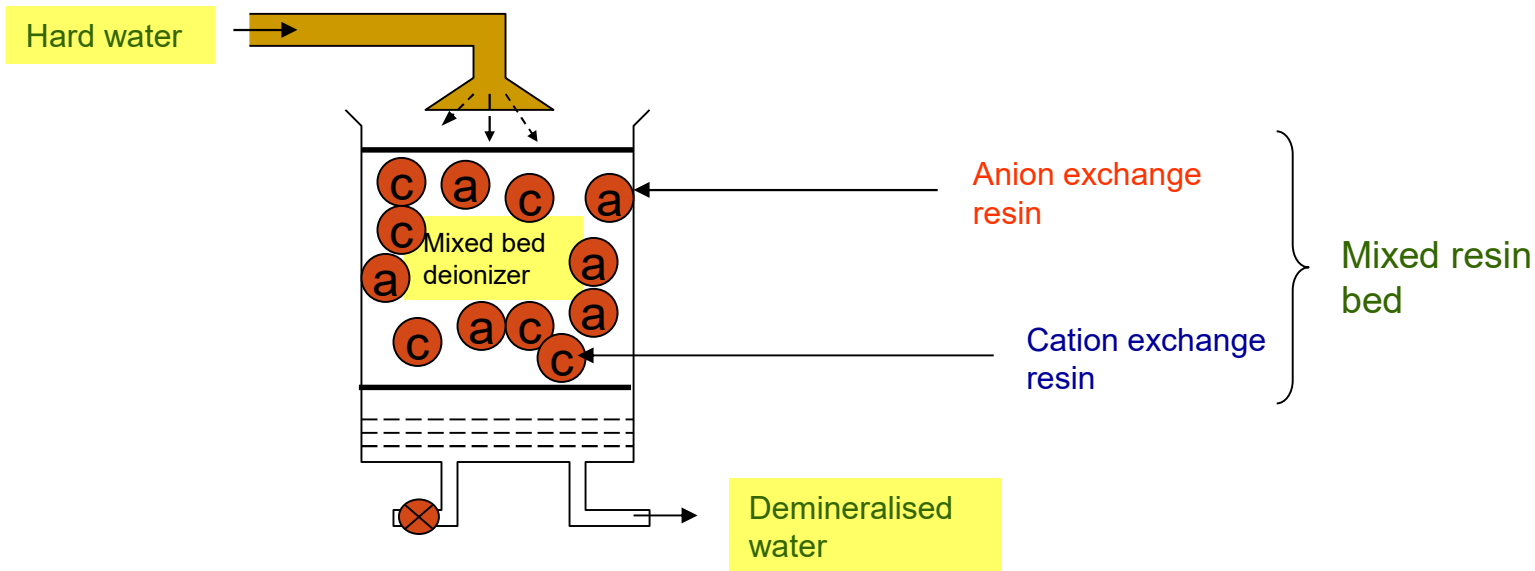
Regeneration of mixed bed deionizer

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