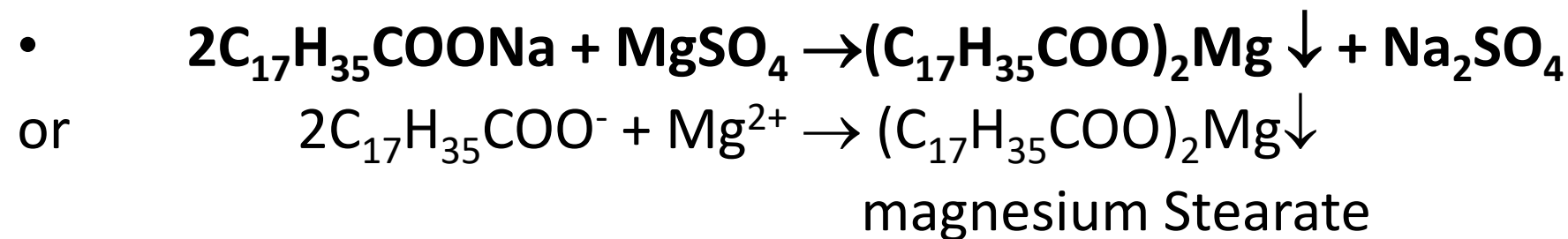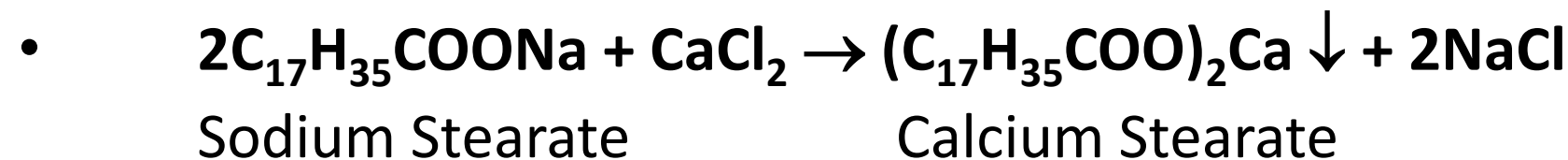# Hardness of Water

- That characteristic which **prevents the lathering of soap.**

- This is due to the presence of certain salts of calcium, magnesium and other heavy metals.

- Hard water forms a white scum or precipitate with soap, due to formation of insoluble soaps of calcium and magnesium.

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

  Sodium Stearate   Calcium Stearate

  or $2C_{17}H_{35}COO^- + Ca^{2+} \rightarrow (C_{17}H_{35}COO)_2Ca \downarrow$

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

  or $2C_{17}H_{35}COO^- + Mg^{2+} \rightarrow (C_{17}H_{35}COO)_2Mg \downarrow$

                     magnesium Stearate

Classification of Hardness

Temporary Hardness (or Carbonate Hardness)

- It is caused by the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals and the carbonate of iron.

- It is mostly destroyed by mere boiling of water, when bicarbonates are decomposed, form insoluble carbonates or hydroxides.

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

$$\text{Mg(HCO}_3)_2 \xrightarrow{\text{Heat}} \text{Mg(OH)}_2 \downarrow + 2\text{CO}_2 \uparrow$$

- The Ca/Mg carbonates or hydroxides thus formed, being almost insoluble, are deposited as a crust at the bottom of vessel; while carbon dioxide escapes.
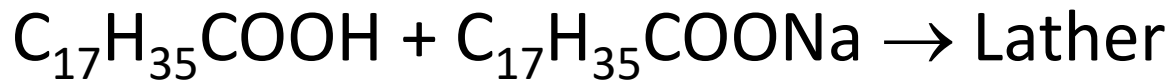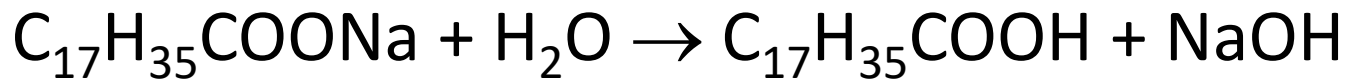
Permanent Hardness (or Non-Carbonate Hardness)

- **It** is due to the presence of chlorides and sulfates of calcium, magnesium, iron and other heavy metals. i.e. $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$ etc.

- Boiling cannot destroy permanent hardness.

Disadvantages of Hard Water

In Domestic Use

Washing: The formation of insoluble sticky precipitates happens till all calcium and magnesium salts present in water are precipitated. After that, the soap gives lather with water.

$$C_{17}H_{35}COONa + H_2O \rightarrow C_{17}H_{35}COOH + NaOH$$

$$C_{17}H_{35}COOH + C_{17}H_{35}COONa \rightarrow Lather$$

- wastage of soap.

- sticky precipitate adheres on the cloth giving spots.

Bathing: produces a sticky scum on the bathroom tiles, bath tub and body. Thus, the cleansing quality of soap is depressed.

Cooking: Due to salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking.

- tea and coffee, prepared in hard water, have an unpleasant taste and muddy-looking extract.

- deposition on the inner walls of the water heating utensils, leading to over-heating of utensils, thereby their life is also shortened.

Drinking: bad effects on our digestive system. calcium oxalate crystals can get accumulated either in kidney or bladder leading to the formation of stones.

In Industrial Use

Textile Industry: wastage of soap

• precipitation of calcium and magnesium soaps to the fabrics. These fabrics, when dyed later on, do not produce exact shade of color.

Dyeing industry: The dissolved salts may react with costly dyes, forming undesirable precipitates, which exhibit impure shades and give spots on the fabrics being dyed.

Laundry: Hard water containing dissolved calcium, magnesium, iron, manganese and aluminum salts, if used in laundry, causes much of the soap used in the washing to go as waste.

- <u>Sugar Industry</u>: Hard water causes difficulties in the crystallization of sugar.

- <u>Paper Industry</u>: Salts destroy smooth and glossy finish of paper.

- <u>Bakeries</u>

- <u>Concrete making</u>: affects the hydration of cement and the final strength of the hardened concrete.

- <u>Pharmaceutical industry</u>: produce certain undesirable products in drugs, injections, ointments etc., which harm the human beings.

- <u>Boilers</u>:

Priming & Foaming

- <u>Foaming</u> is the production of persistent foam or bubbles in boilers, which do not break easily.

- When a boiler produces steam rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation is called <u>Priming</u>.

<u>Causes of Priming</u>

- Presence of a large amount of dissolved solids

- High steam velocities

- Sudden boiling or sudden increase in steam-production rate

- Improper boiler design

<u>Priming and Foaming, usually, occur together</u>

Problems Due to Priming & Foaming

- Dissolved salts in boiler water are carried by the wet steam to super-heater and turbine blades, where they get deposited as water evaporates. This deposit reduces their efficiency.

- Dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery.

- Actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.

Priming can be avoided by:

- fitting mechanical steam purifiers;
- avoiding rapid changing steaming rate;
- maintaining low water levels in boilers, and
- efficient softening and filtration of the boiler-feed water.

Foaming can be avoided by:

- adding anti-foaming chemicals like castor oil

Scale & Sludge Formation in Boilers

- In boilers, water evaporates continuously and the concentration of the dissolved salts increase progressively.

- When their concentration reaches saturation point, they are thrown out of the water in the form of precipitates on the inner walls of the boiler.

- If the precipitation takes place in the form of loose and slimy precipitates, it is called **Sludge**.

- On the other hand, if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called **Scale**.

Sludge Formation in Boilers

- Sludge is a soft, loose and slimy precipitate formed within the 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 in hot water than in cold water, e.g., $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$, etc.

Disadvantages of Sludge:

- They are poor conductor of heat, so they tend to waste a portion of heat generated.

If sludge is formed along with scales, then they gets entrapped in the scale and both get deposited as scales.

Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, etc, thereby causing even choking of the pipes.

PREVENTION :

- By using well softened water
- By frequently 'blow-down operation', i.e., drawing off a portion of the concentrated water.

Scale Formation in Boilers

Scales are hard deposits, which stick very firmly to the inner surfaces of the boiler. Scales are difficult to remove, even with the help of hammer and chisel.

Formation of Scales :

(1) Decomposition of calcium bicarbonate

In Low Pressure Boilers

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

This is the main cause of scale formation in low pressure boilers.

But in High Pressure Boilers

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 (soluble) + CO_2 \uparrow$$
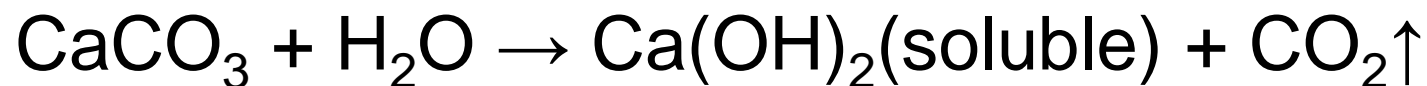
(2) Deposition of calcium sulphate: $CaSO_4$ is soluble in cold water, which decreases with rise of temperature. Thus, it precipitates as hard scale on the heated portions of the boiler.

(3) Hydrolysis of magnesium salts: Forms a soft type of scale

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

(4) Presence of silica (SiO_2): Deposits as calcium silicate ($CaSiO_3$) and/ or magnesium silicate ($MgSiO_3$).

Disadvantages of Scale Formation

- Wastage of fuels: Scales have a low thermal conductivity, so they act as partial heat insulators and the rate of heat transfer from boiler to inside water is greatly decreased. In order to get a steady supply of water, excessive or over-heating is done and this causes increase in fuel consumption, which is very costly affair due to high fuel prices. The wastage of fuel depends upon the thickness and the nature of the scale.

- Decrease in efficiency: Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially.

- <u>Lowering of boiler safety</u>: Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. This makes boiler material softer and weaker. It causes distortion of boiler tube and makes it unsafe to bear the pressure of steam.

- <u>Danger of explosion</u>: When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. Thus a large amount of steam comes out suddenly. So, sudden high-pressure is developed, which may even cause explosion of the boiler.

Removal of Scales

(i) With the help of scraper or wire brush, if they are loosely adhering.

(ii) By giving thermal shocks, if they are brittle.

(iii) By dissolving in chemicals, if they are adherent and hard. e.g. calcium carbonate scales can be dissolved by using 5-10% HCl.

(iv) By frequent blow-down operation, if the scales are loosely adhering.

Prevention of Scales Formation

- The above methods of scale removal are tedious, expensive, time-consuming and less effective. Consequently, it is still better to prevent the boiler scale formation.

- Use soft water or treating hard water by <u>external treatments</u>, like lime-soda process, zeolite process or ion-exchange process.

- Treating water in the boiler, during evaporation process itself, is commonly known as <u>internal conditioning or sequestration</u>.

Sequestration

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

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

- A) to precipitate the scale forming impurities in the form of sludge, which can be removed by blow-down operation, or

- B) to convert them into compounds, which will stay in dissolved form in water thus do not cause any harm.

Internal Treatments/ Sequestration

(i) Colloidal Conditioning

In low-pressure boilers, scale formation can be avoided by adding organic substances like **kerosene, tannin, agar-agar**, etc.

These substances get coated over the scale forming precipitates,

thereby yielding non-sticky and loose deposits,

which can easily be removed by frequent blow-down operations.

(ii) Phosphate Conditioning

In high-pressure boilers, scale formation can be avoided by adding <u>sodium phosphate</u>.

The phosphate reacts with calcium and magnesium salts, in the boiler water, forming non-adherent and easily removable, soft sludge of calcium and magnesium phosphates, which can be removed by blow-down operation, e.g.,

$$3CaCl_2 \;+\; 2Na_3PO_4 \;\;\rightarrow\;\; Ca_3(PO_4)_2 \;+\; 6\,NaCl$$
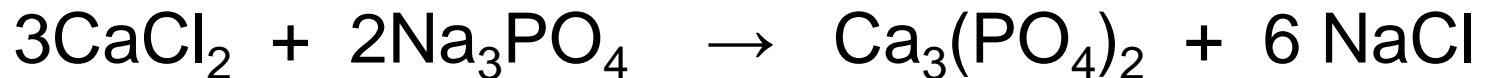
The main phosphates employed are :

(a) NaH_2PO_4, Sodium dihydrogen phosphate (acidic)

(b) Na_2HPO_4, Disodium hydrogen phosphate (weakly alkaline)

(c) Na_3PO_4, Trisodium phosphate (alkaline)

The choice of salt depends upon the economics and alkalinity of the boiler-feed water.

Calcium cannot be precipitated properly below a pH of 9.5. Therefore, it is necessary to select a phosphate that adjusts pH to an optimum value (9.5-10.5).

Trisodium phosphate is most suitable for treatment when the alkalinity of boiler water is low, as it is most alkaline in nature.

If boiler water's alkalinity is sufficient, then disodium phosphate is more preferred.

But if the alkalinity of boiler water is too high and requires to be reduced, then monosodium phosphate, being acidic in nature is preferred.

(iii) Carbonate Conditioning

- For low pressure boilers
- Addition of <u>sodium carbonate</u> to boiler water
- Scale forming salt like $CaSO_4$ is converted into calcium carbonate.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

- Deposition of $CaSO_4$ as scale does not take place and calcium is precipitated as loose sludge of $CaCO_3$
- Removed by blow-down operation.

(iv) Calgon Conditioning

- By adding <u>sodium hexameta phosphate (Calgon).</u>
- It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$

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

- $2CaSO_4 + [Na_4(PO_3)_6]^{2-} \rightarrow$ $[Ca_2(PO_3)_6]^{2-}$ $+\ 2\ Na_2SO_4$

    highly soluble complex ion

- Calgon conditioning is better than phosphate conditioning as it is applicable on every pH.

(v) Treatment with Sodium Aluminate

- Sodium aluminate solution gets hydrolyzed in boiler water to NaOH and gelatinous precipitate of aluminum hydroxide.

$$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3\downarrow$$
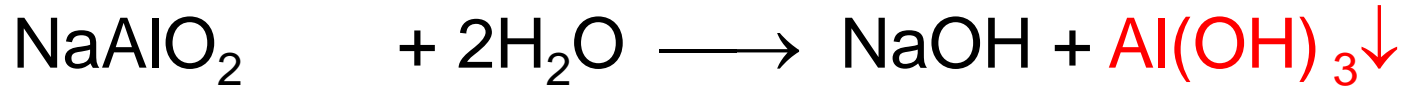
    Sodium Meta-aluminate   Gelatinous ppt.

- The sodium hydroxide precipitates some of the magnesium as $Mg(OH)_2$

$$MgCl_2 + 2NaOH \longrightarrow Mg(OH)_2\downarrow + 2NaCl$$
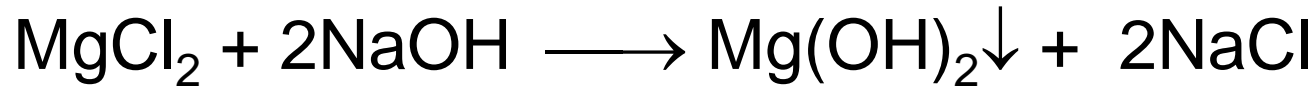
- The flocculent precipitate of $Mg(OH)_2$ plus $Al(OH)_3$ produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica.

- Oil drops and silica are otherwise quite difficult to remove ordinarily.

- The loose precipitate can be removed by blow-down operation.

Boiler Corrosion

- It is decay of boiler material by a chemical or electro-chemical attack by its environment. Corrosion in boilers is due to the following reasons:

- **<u>Dissolved Oxygen</u>** is the main corrosion causing impurity in water.

- Water, usually contains about 8ml of dissolved oxygen per liter at room temperature.

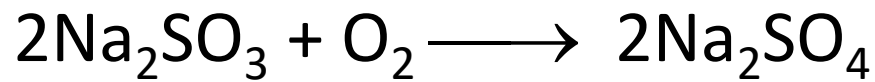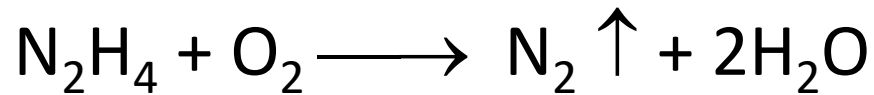- Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2\downarrow$$

$$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3.2H_2O]\downarrow$$
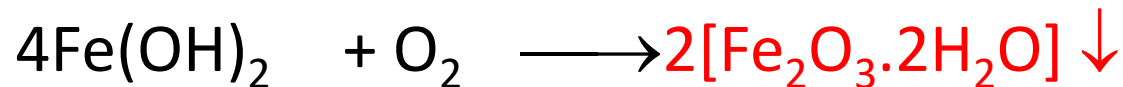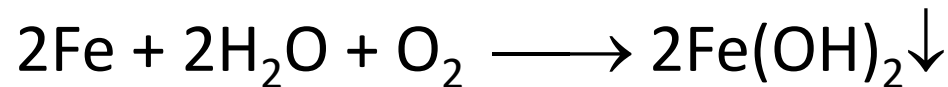
Ferrous hydroxide   Hydrated Iron(III) oxide

(Rust)

Removal of Dissolved Oxygen

- By adding calculated quantity of hydrazine or sodium sulphite or sodium sulphide.

$$N_2H_4 + O_2 \longrightarrow N_2 \uparrow + 2H_2O$$

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$Na_2S + 2O_2 \longrightarrow Na_2SO_4$$
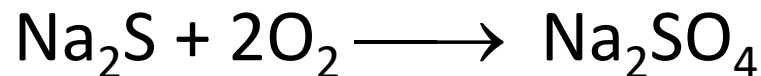
- Hydrazine is an ideal internal treatment chemical for the removal of dissolved oxygen.

- It reacts with oxygen, forming nitrogen with water. Nitrogen is harmless. Consequently, hydrazine removes oxygen without increasing the concentration of dissolved solids/salts.

- if sodium sulphide or sodium sulphite is used, the sodium sulphate so formed is liable to decompose giving SO_2, particularly in high-pressure boilers.

- The SO_2 enters the steam pipes and appears as sulphurous acid (H_2SO_3) in the steam condensate.

- Thus, a very low concentration of 5 to 10 ppm of Na_2SO_3 can be added in the boiler.

- Dissolved oxygen can also be removed by <u>mechanical de-aeration</u>, i.e., spraying water in a perforated plates-fitted tower, heated from sides and connected to vacuum pump.

- High temperature, low pressure and large exposed surface reduce the dissolved oxygen in water.
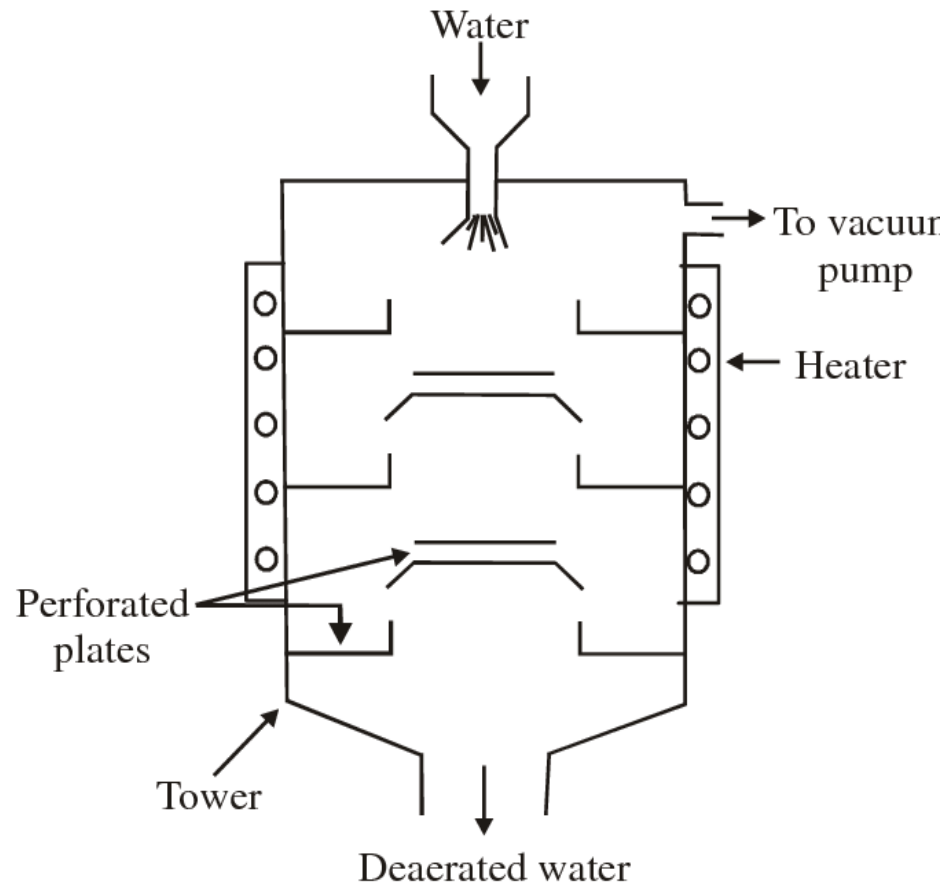
- **Carbon dioxide** is also released inside the boiler, if water used for steam generation contains bicarbonates

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

- Dissolved carbon dioxide forms carbonic acid, which has a slow corrosive effect on the boiler material.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$
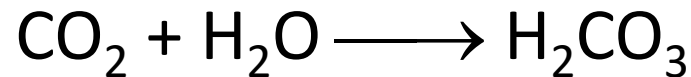
Removal of CO$_2$

- By adding calculated amount of ammonia.

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$
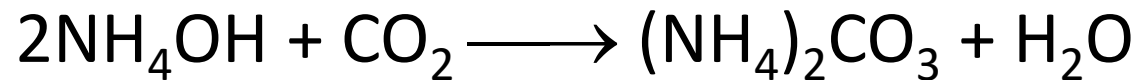
- Carbon dioxide, along with oxygen, in water can also be removed by <u>mechanical de-aeration</u>.

- **<u>Acids from dissolved salts</u>**: If water used for steam-generation contains dissolved magnesium salts, they liberate acids on hydrolysis
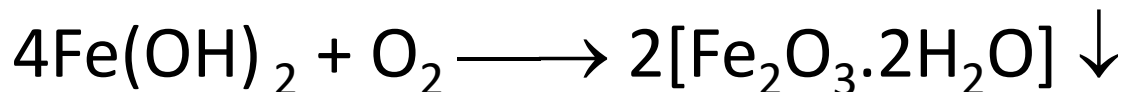
$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$
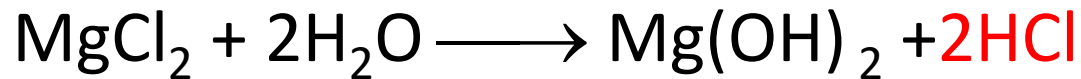
- The liberated acid reacts with iron material of the boiler in a chain-like reaction producing HCl again and again.

$$Fe + 2HCl \longrightarrow FeCl_2 \quad + \quad H_2\uparrow$$

Ferrous chloride

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2\downarrow \quad + 2HCl$$

Ferrous hydroxide

$$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3.2H_2O]\downarrow$$
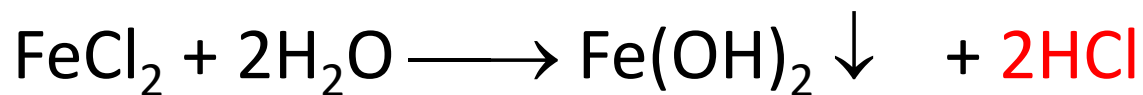
Ferrous hydroxide   Hydrated Iron(III) oxide (Rust)

- Consequently, presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

- Corrosion by acids can be avoided by adding alkalinity from outside to neutralize them.

Caustic Embrittlement

- It is a type of boiler corrosion, caused by using highly alkaline water in the boiler.

- It is most likely to take place in high pressure boilers.

- During softening process by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water.

- In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and carbon dioxide, which makes the boiler water basic /caustic.

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

- The NaOH (caustic soda) containing water flows into the minute hair-cracks by capillary action.

- Inside the cracks, water evaporates continuously and the dissolved caustic soda concentration increases progressively.

- The iron surrounded by the dilute NaOH becomes the cathodic side; while the iron in contact with concentrated NaOH (at high stress) becomes anodic part, which is consequently dissolved or corroded.

- Caustic cracking can be explained by considering the following concentration cell:

Iron at rivets, bends, joints, etc.	+	Concentrated NaOH solution	Dilute NaOH solution	−	Iron at plane surfaces

It dissolves iron of boiler as sodium ferrate, making boiler parts (like bends, joints, rivets, etc.) brittle.

Caustic embrittlement can be avoided:

- by using sodium phosphate as softening reagent instead of sodium carbonate

- by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these

- by adding sodium sulphate to boiler water. Na_2SO_4 also blocks hair cracks, thereby preventing infiltration of caustic soda in these.

Removal of Permanent Hardness

- **Zeolite or Permutit Process**
- **Ion Exchange/Deionization/Demineralization Process**
- **Lime-Soda Method**

Zeolites

- These are naturally occurring minerals, which release their water of hydration in the form of steam. The chemical structure of zeolite may be represented as:
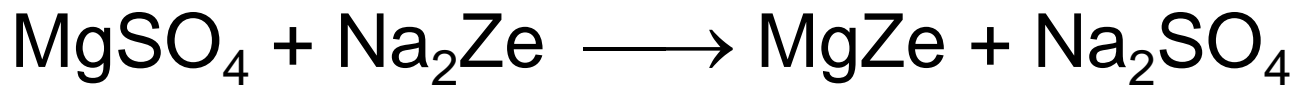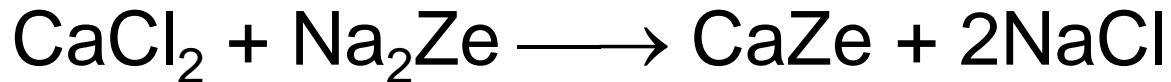
$$Na_2O.Al_2O_3.xSiO_2.yH_2O$$
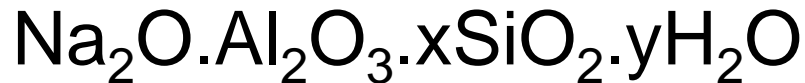
where x = 2 - 10 and y = 2 – 6.

Thus, zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly their sodium ions for hardness-producing ions in water.

Zeolites are of two types:

- **Natural Zeolites** are non-porous. Most important natural sodium zeolite is:

- Natrolite, $Na_2O.Al_2O_3.4SiO_2.2H_2O$. They are more durable.

- **Synthetic Zeolites** are porous and posses gel structure.

- Such zeolites possess higher exchange capacity per unit weight natural zeolites.
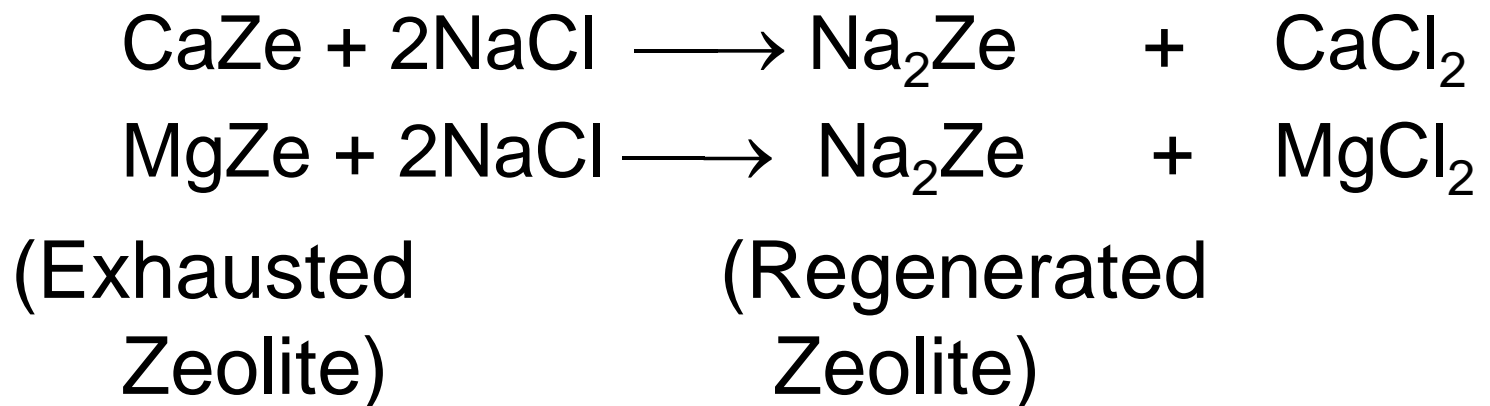
Theory of Zeolites

- These silicates hold sodium ions loosely and can easily exchange their sodium ions with other cations such as Ca^{2+}, Mg^{2+}, etc.

- Thus, if water containing dissolved calcium and magnesium salts is passed over a bed of sodium zeolite, calcium and magnesium are exchanged for sodium:

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

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

$$Ca(HCO_3)_2 + Na_2Ze \longrightarrow CaZe + 2NaHCO_3$$
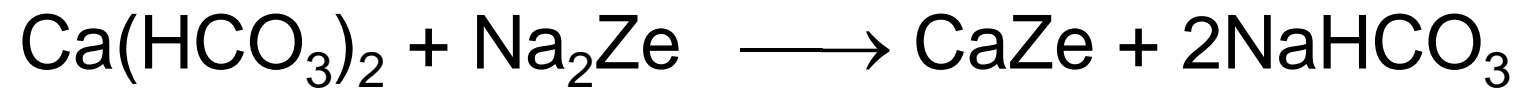
where out of $Na_2 O.Al_2O_3.xSiO_2.yH_2O$

$$Ze = O.Al_2O_3.xSiO_2.yH_2O$$

(Na_2Ze is sodium zeolite)

- Thus, the sodium zeolite is converted into calcium or magnesium zeolites.

- Water becomes free from Ca and Mg, Hence, zeolite is a 'sodium exchanger'.

- When zeolite is exhausted, it can be regenerated by washing the bed with concentrated solution of sodium chloride as:
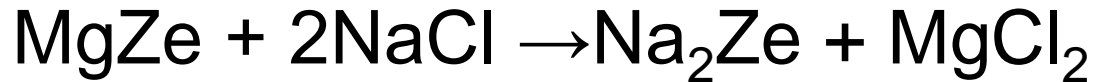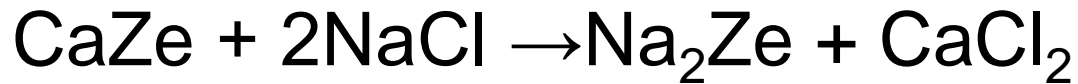
$$CaZe + 2NaCl \longrightarrow Na_2Ze \quad + \quad CaCl_2$$

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

(Exhausted   (Regenerated

Zeolite)   Zeolite)

- In this way the regenerated zeolite can be used again.

Zeolite / Permutit Process
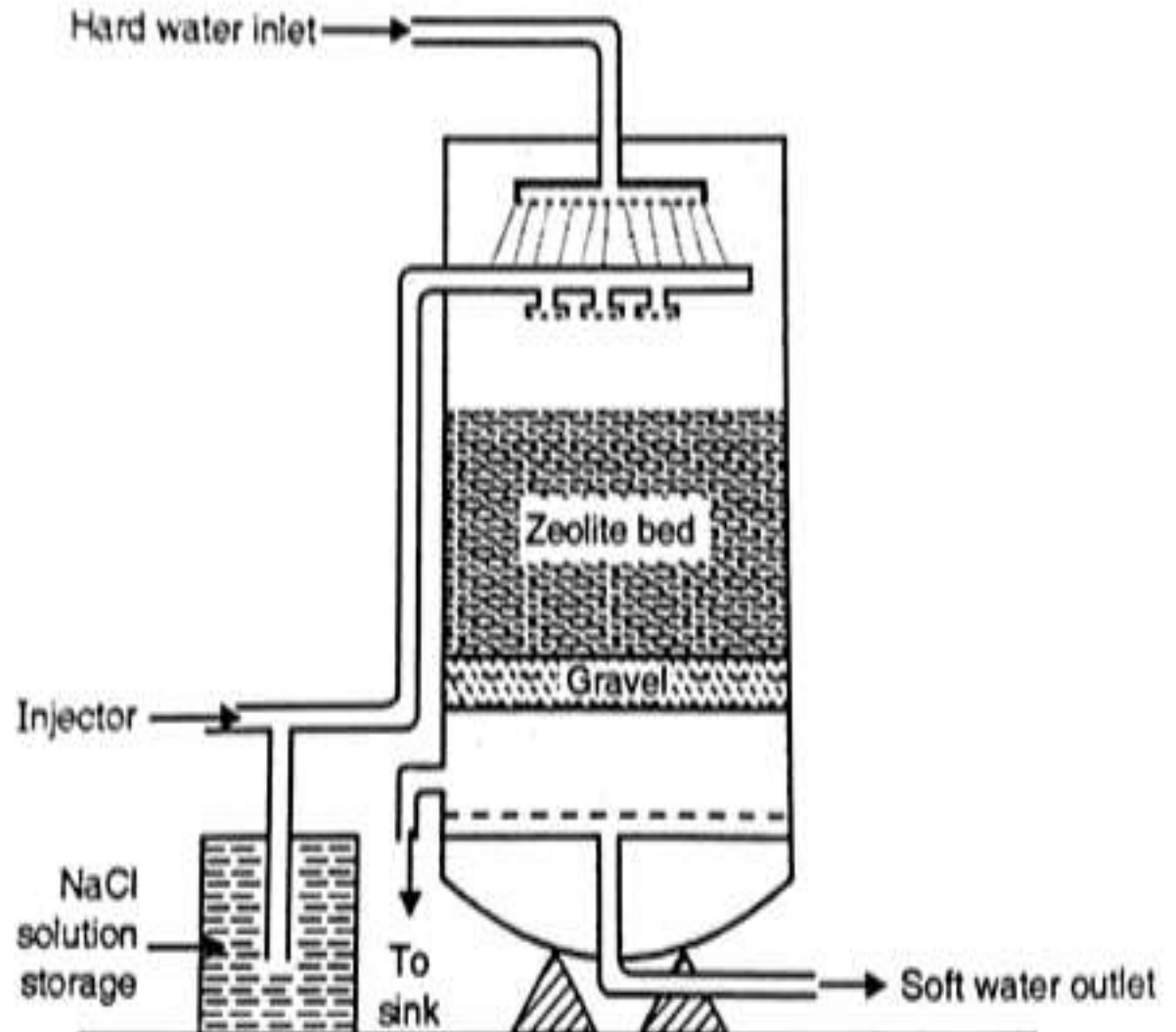
Regeneration:

Treating the bed with 10% brine solution

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

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

Limitations:

- No turbidity should be present in water, else pores will clog.

- Coloured ions, like Mn^{2+} and Fe^{2+}, damages zeolite which cannot be regenerated.

- Mineral acids to be neutralised with soda, else bed gets destroyed.

Advantage of Zeolite Process:

- It removes the hardness almost completely and water of about 10ppm hardness is produced.

- Compact equipment.

- No impurities are precipitated.

- Clean process

- Less time

- Requires less skill for maintenance and operation.

Disadvantage of Zeolite Process:

- The treated water contains more sodium salts than in L-S process.

- The method only replaces Ca^{2+} and Mg^{2+} ions by Na^+ ions, but leaves all the acidic ions (like HCO_3^- & CO_3^{2-}) as such.

- When such softened water is used in boilers for steam generation, sodium bicarbonate decomposes producing CO_2, which causes **corrosion**;

- and sodium carbonate hydrolyses to sodium hydroxide, which causes **caustic embrittlement**.

- High turbidity water cannot be treated efficiently by this method, because fine impurities get deposited on the zeolite bed.

Ion-Exchange (De-ionization/De-mineralization) Process

- De-mineralized water is soft and does not contain any dissolved ions.

- Soft water and de-mineralized water are similar in some respects.

- Soft water does not contain hardness producing Ca^{2+}, Mg^{2+}, ions but may contain other ions like Na^+, Cl^-, K^+, etc.

- De-mineralized water does not contain any type of ions.

- Thus, every soft water is not de-mineralized water; whereas every de-mineralized water is soft water also.

- Ion exchange is a reversible chemical reaction where dissolved ions are removed from solution and replaced with other ions of the same or similar electrical charge.
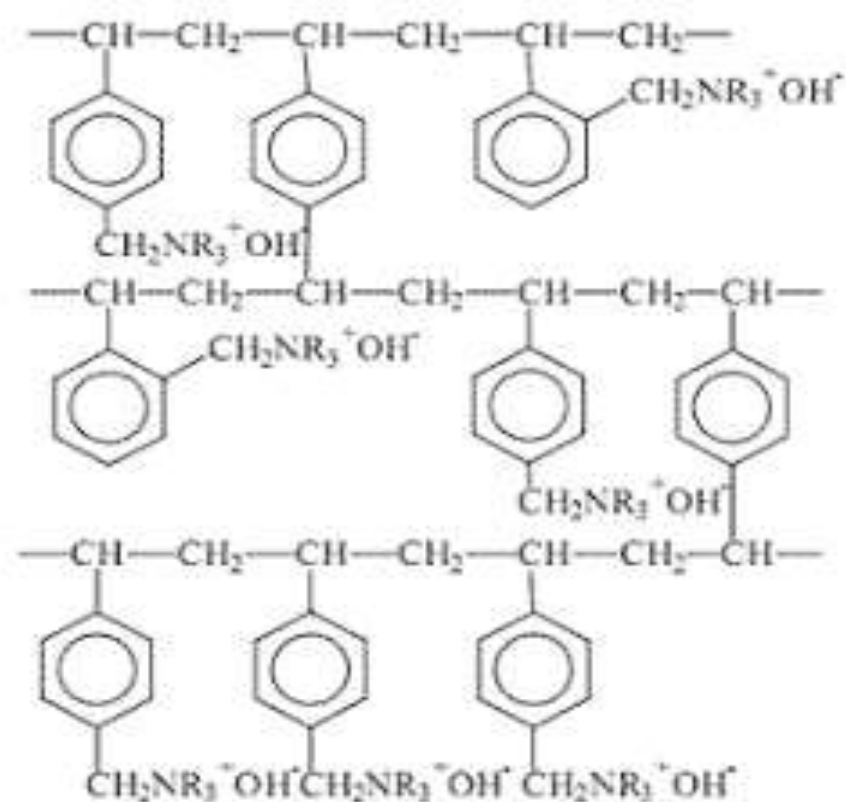
Ion-Exchange Resins

- Insoluble, cross-linked, long-chain organic polymers with a micro porous structure

- The functional groups attached to the chains are responsible for the ion-exchange properties.

- Resins containing acidic functional groups, sulfonic ($-SO_3H$), carboxylic ($-COOH$), or phosphonic ($-PO_3^{2-}$) acids etc. are capable of exchanging their H^+ ions with other cations, which comes in their contact.

- Those containing basic functional group (quaternary ammonium or ammine groups) are capable of exchanging their anions with other anions, which comes in their contact.

- Cation and anion exchange resins are both small, porous, plastic beads (approximately 0.5 mm diameter) that are fixed with a specific charge.

- This "fixed" charge cannot be removed and is part of the resin's cross-linked makeup or structure.

- Each resin bead must also contain a neutralizing counterion that is able to move in and out of the bead, which is replaced with an ion of similar charge during the process of ion exchange.
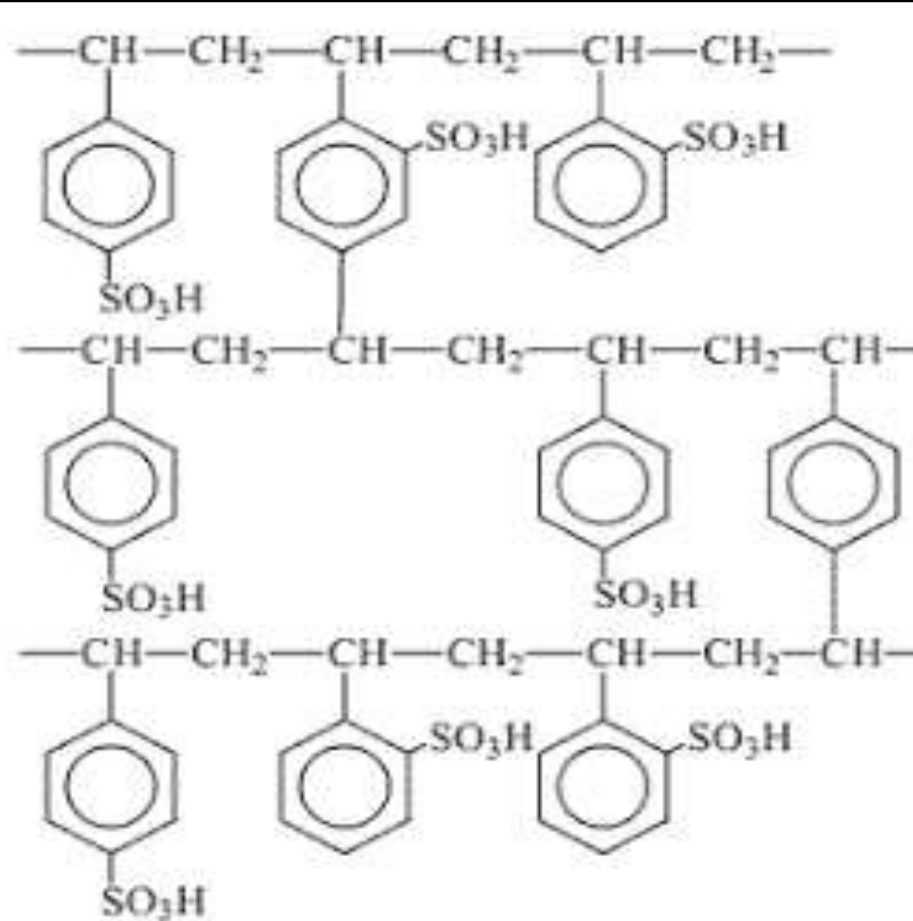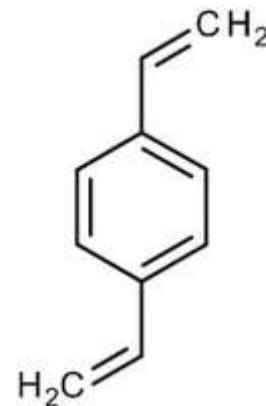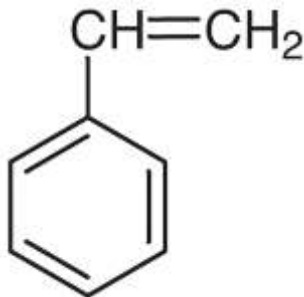
A strongly acidic sulphonated polystyrene cation exchange resin

A strongly basic quaternary ammonion anion exchange resin

Cation Exchange Resins

- mainly styrene-divinyl benzene copolymers, which on sulphonation or carboxylation become capable to exchange their hydrogen ions with the cations in water.
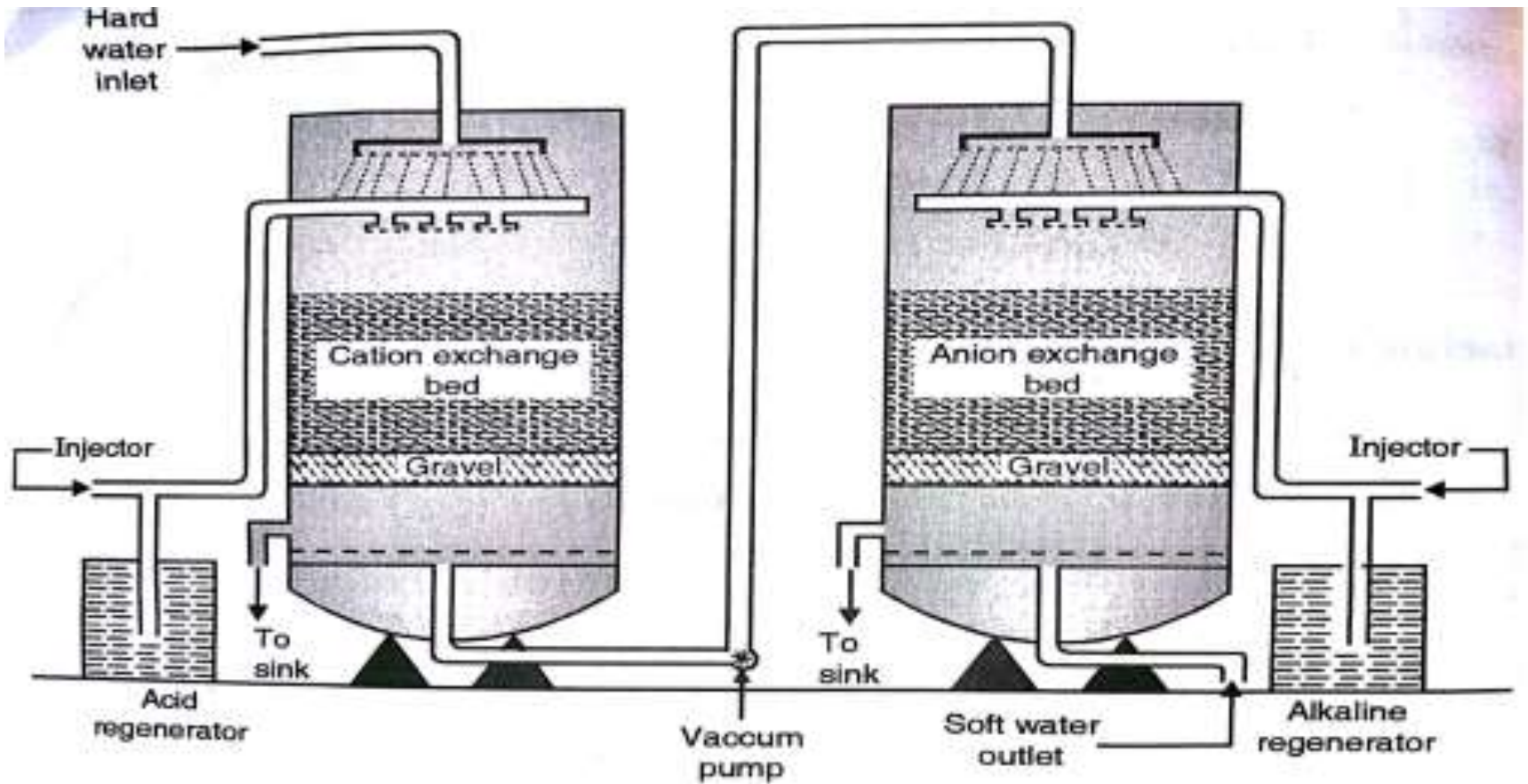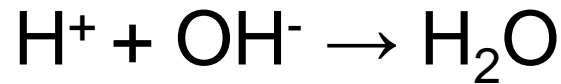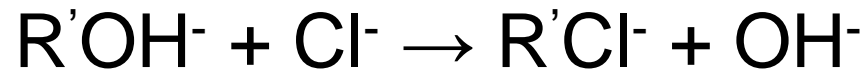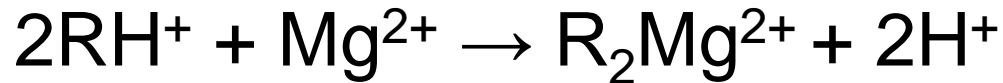
Anion Exchange Resins

- Styrene-divinyl benzene or Amine formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups

- after treatment with dilute NaOH solution, become capable to exchange their OH^- anions with the anions in water.

Resins differ in their functional groups:
- Strongly acidic, featuring sulphonic acid groups, e.g. sodium polystyrene sulphonate,
- Strongly basic, featuring quaternary amino groups, e.g. Trimethylammonium,
- Weakly acidic, featuring carboxylic acid groups,
- Weakly basic, featuring primary, secondary, and/or tertiary amino groups, e.g. polyethylene amine.

Process

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

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

$$R^{'}OH^- + Cl^- \rightarrow R^{'}Cl^- + OH^-$$

$$2R^{'}OH^- + SO_4^{2-} \rightarrow R_2^{'}SO_4^{2-} + 2OH^-$$

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

Regeneration:

Exhausted cation exchange column by dilute HCl or dilute H_2SO_4.

Exhausted anion exchange column by dilute NaOH.

Advantages:

- The process can be used to soften highly acidic or alkaline waters.

- It produces water of very low hardness (2ppm).

Disadvantages:

- The equipment is costly and more expensive chemicals are needed.

- If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10ppm.
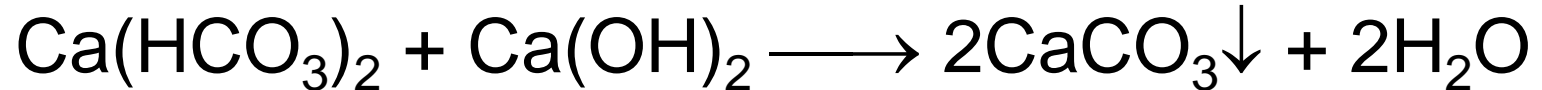
Lime-Soda Process

- Hard water is treated with calculated quantities of slaked lime [$Ca(OH)_2$] and soda [Na_2CO_3].

- The soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, which are removed by filtration.

- The insoluble compounds formed are calcium carbonate [$CaCO_3$] and magnesium hydroxide [$Mg(OH)_2$].

- The chemicals and water are thoroughly mixed.

- Most of the heavy precipitates settle down as sludge at the bottom of the tank and are removed from time to time.

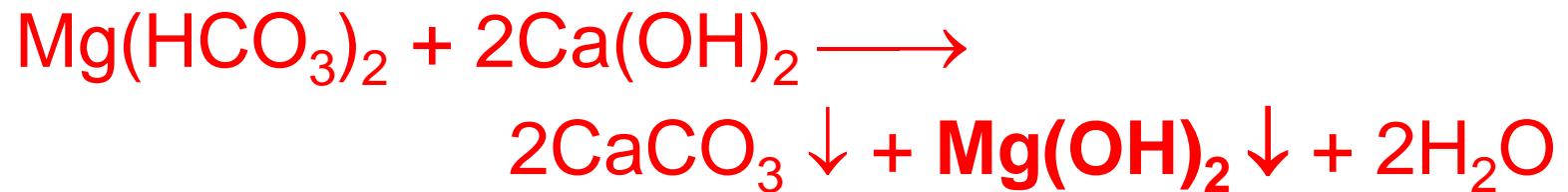- The softened water is then filtered.

Chemical Reactions of Lime Soda Process
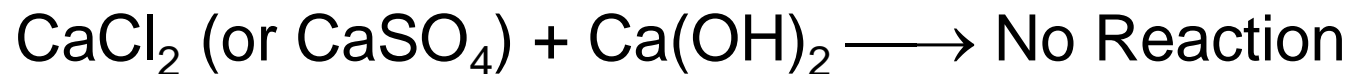
Function of Lime:

- Reaction with Calcium Temporary Hardness

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

- Reaction with Magnesium Temporary Hardness

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

$$2CaCO_3\downarrow + \mathbf{Mg(OH)_2}\downarrow + 2H_2O$$

- Reaction with Calcium Permanent Hardness

$$CaCl_2 \text{ (or } CaSO_4) + Ca(OH)_2 \longrightarrow \text{No Reaction}$$

- Reaction with Magnesium Permanent Hardness

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + \mathbf{CaCl_2}$$
$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + \mathbf{CaSO_4}$$

- Reaction with Carbon Dioxide

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

- Reaction with Free Acid Present

$$2HCl + Ca(OH)_2 \longrightarrow \mathbf{CaCl_2} + 2H_2O$$

$$H_2SO_4 + Ca(OH)_2 \longrightarrow \mathbf{CaSO_4} + 2H_2O$$

- Reaction with Iron and Aluminum salts

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

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

$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3 \downarrow$$

- Reaction with Bicarbonate Ions(like $NaHCO_3$, $KHCO_3$, etc.)

$$2NaHCO_3 + Ca(OH)_2 \longrightarrow$$

$$CaCO_3 \downarrow + 2H_2O + \mathbf{Na_2CO_3}$$
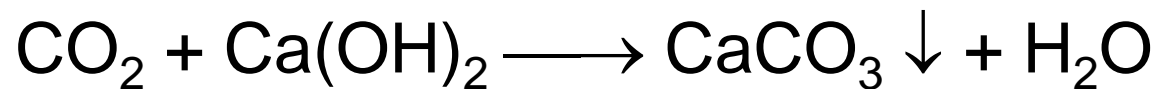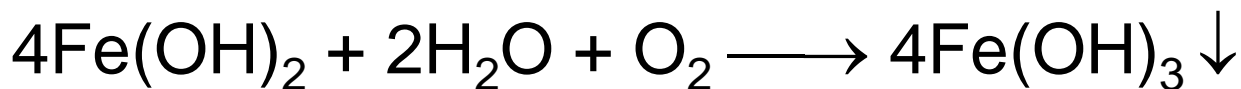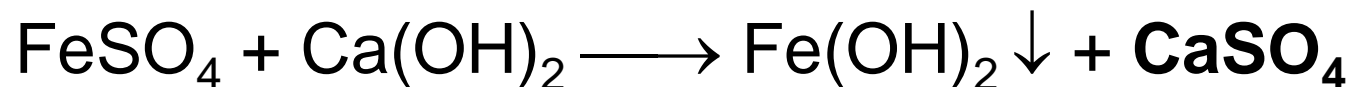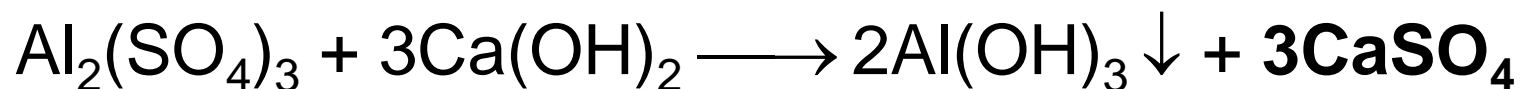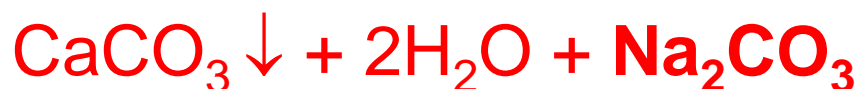
Function of Soda

- The added ingredient soda ash reacts with calcium permanent hardness.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2NaCl$$

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$$
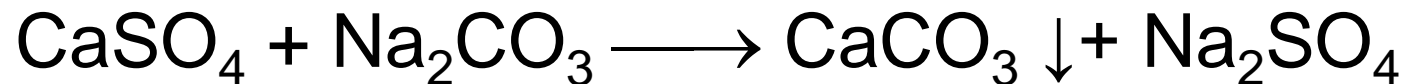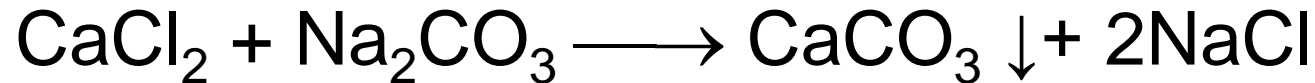
- It may also be noted that bicarbonate ions ($NaHCO_3$/$KHCO_3$), if present produced carbonate ions (as Na_2CO_3 or K_2CO_3) during their reaction with lime and this may be imagined to be equivalent to production of Na_2CO_3.

- Hence, the amount of carbonate ions thus produced form bicarbonate ions are to be subtracted from the total requirement of soda for softening.

Lime-Soda Process

- The precipitates formed, particularly of $CaCO_3$ and $Mg(OH)_2$ are fine particles and they tend to produce a super-saturated solution. This will result in "after deposition", later in the pipes and the boiler tubes, producing sludges.

- These then decrease the effective diameters of pipes, clogs the valves, cause their corrosion, etc.

- To overcome these drawbacks, the following arrangements are made:

1. Thoroughly mixing of the chemicals and water is carried out.

2. Proper time for completion of reactions, to proceed, is given.

3. Alternative means are adopted for accelerating the reactions like

a. hot lime-soda method.

b. Substances that bring down the fine particles of precipitates, called accelerators (like activated charcoal) are added.

c. Substances that help in the formation of coarse precipitates are added. These are called coagulants or flocculants, e.g. alum.

4. Suitable sedimentation chamber is provided before final filtration.

Cold Lime-Soda Process

Batch Process

- Batch Process is carried out in a large tank provided with stirrers for proper mixing.

- A calculated quantity of chemicals (lime and soda) are added to water in the tank and thoroughly mixed by mechanical stirring.

- Then, a suitable amount of coagulant is added and contents of the tank are kept undisturbed for some time (~2hrs) so as to allow the precipitate to settle down completely.

- The sludge formed at the bottom of the tank is removed and tank is washed with water.

- The tank is again ready for treating another batch.

Continuous Process:
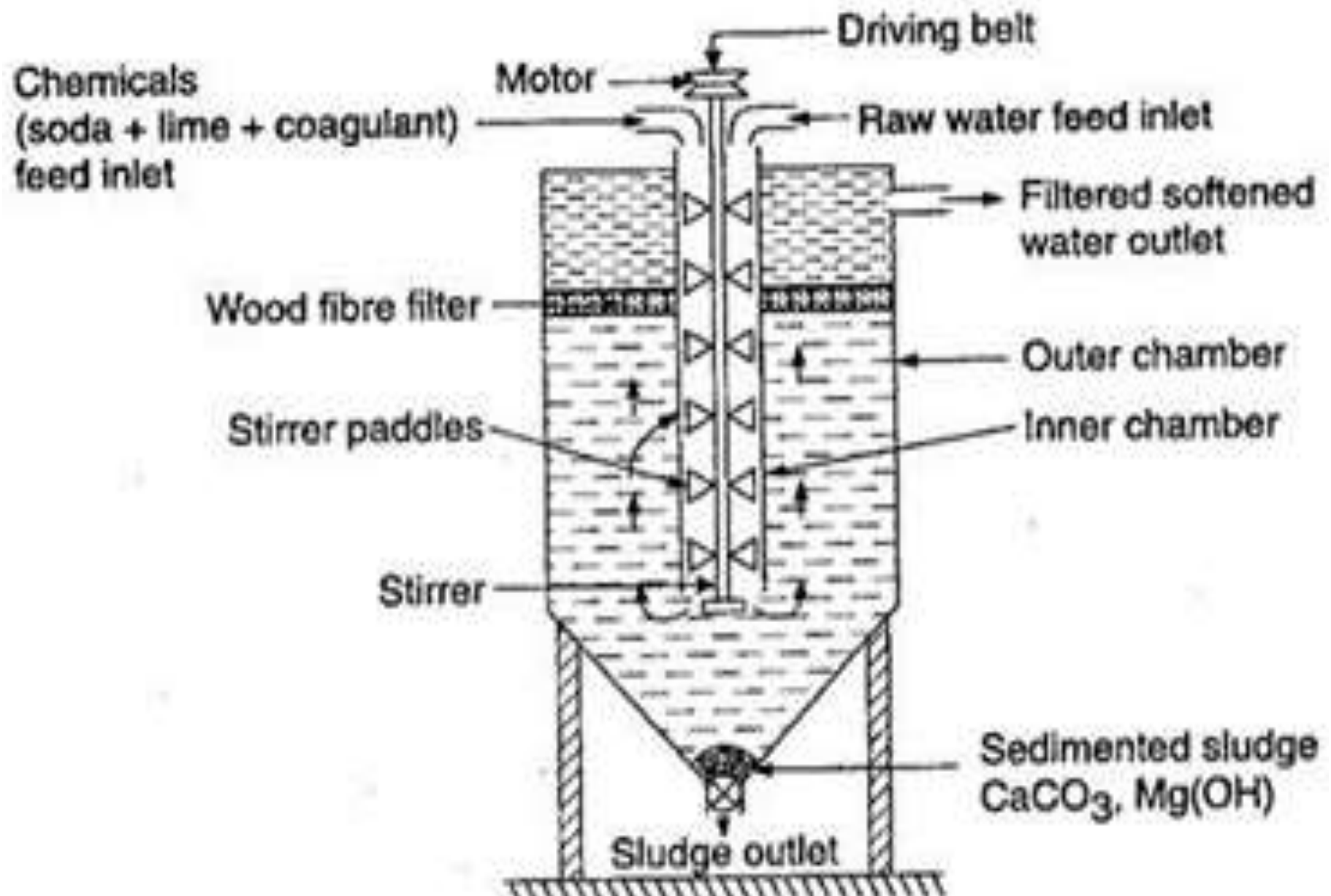
- Raw water and calculated quantities of chemicals (lime + soda + coagulant) are fed from the top into the inner vertical circular chamber, fitted with a vertical rotating shaft carrying a number of paddles.

- As the raw water and chemicals flow down, there is a vigorous stirring and continuous mixing, whereby softening of water takes place.

- As the softened water comes into the outer coaxial chamber, it rises upwards.

- The heavy sludge settles down in the outer chamber by the time the softened water reaches up. This water then passes through a filtering media to ensure complete removal of sludge.

- Filtered soft water finally flows out continuously through the outlet at the top. Sludge settling at the bottom of the outer chamber is drawn off occasionally.
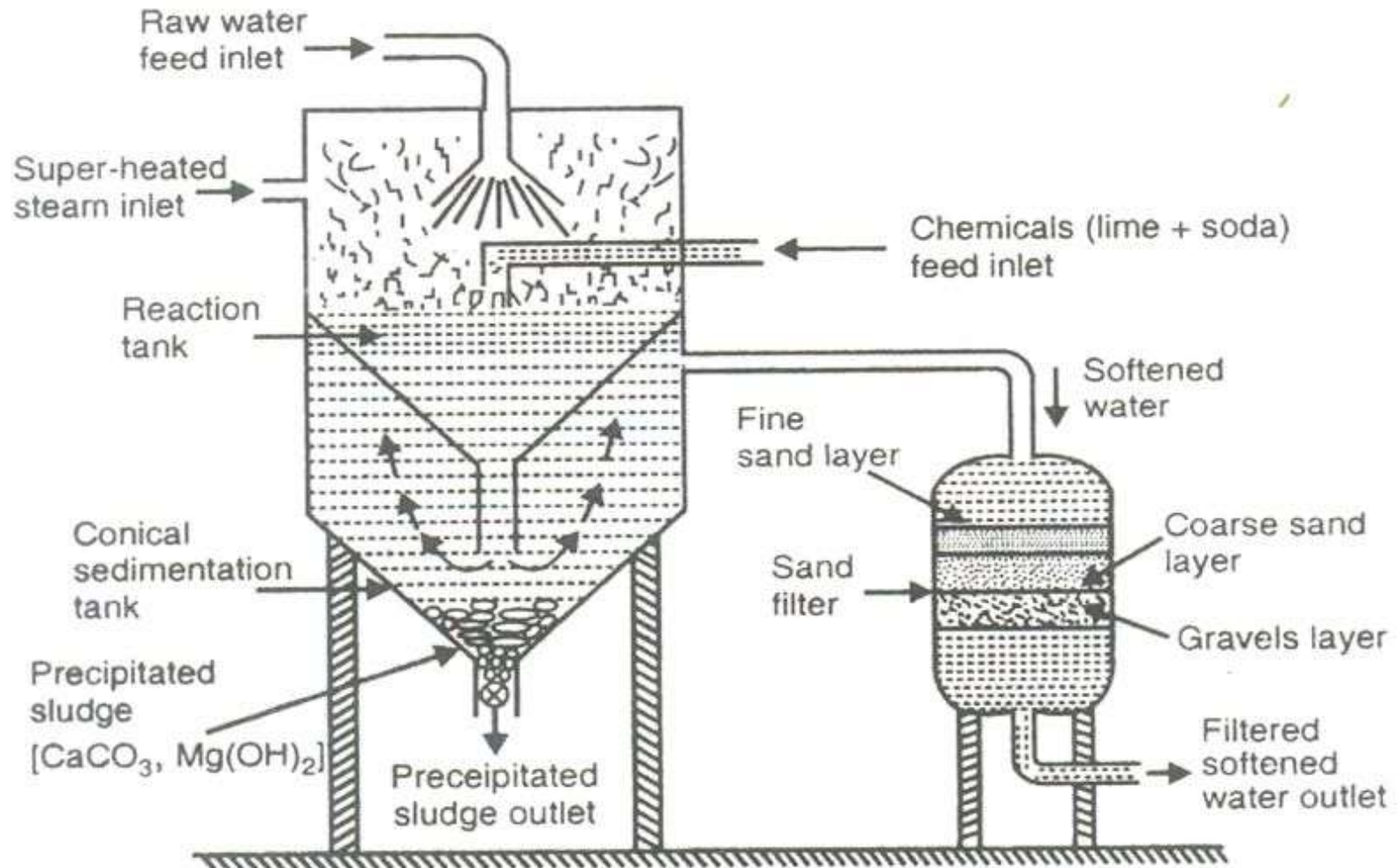
Hot Lime-Soda Process:

- Involves treating water with softening chemicals at a temperature of 80 ^{0}C.

- Since hot process is operated at a temperature close to the boiling point of the solution, so:

→ the reaction proceeds faster,

→ the softening capacity of hot process is increased to many fold,

→ the precipitate and sludge formed settle down rapidly and hence, no coagulants are needed,

→ much of the dissolved gases are driven out of the water,

→ viscosity of the softened water is lower, so filtration of water becomes much easier.

Hot lime-soda plant essentially 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.

Continuous Hot Lime Soda Process

Advantage of Lime Soda Process

- Very economical.

- If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.

- The process increases the pH value of the treated water, thereby corrosion of the distribution pipes is reduced.

- Besides the removal of hardness, the quantities of minerals in water are reduced.

- To certain extent, iron and manganese are also removed from the water.

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

Disadvantage of Lime Soda Process

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

- Disposal of large amounts of sludge poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city.

- This can remove hardness only up to 50 ppm.

Equivalents of Calcium Carbonate

- Concentration of hardness as well as non-hardness causing ions expressed in terms of equivalent amount of $CaCO_3$

- Since this mode permits the addition and subtraction of concentrations, when required.

- The choice of $CaCO_3$ in particular is due to its molecular weight is 100 (equivalent weight = 50).

- Moreover, it is the most insoluble salt that can be precipitated in water treatment.

- The equivalents of $CaCO_3$ may be defined as:

$$= \frac{\text{Mass of hardness producing substance} \times \text{Chemical equivalent of } CaCO_3}{\text{Chemical equivalent of hardness–producing substance}}$$

$$= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness–producing substance}}$$

$$= \frac{\text{Mass of hardness producing substance} \times 100}{\text{Molecular Weight of hardness–producing substance}}$$
(if substance is bivalent)

= Mass of hardness producing substance $\times$ Multiplication Factor

Multiplication Factor = $\dfrac{50}{E}$

or

Multiplication Factor = $\dfrac{100}{M}$ (for bivalent)

Multiplication Factors for Various Substances

Substance	Molecular Weight	Equivalent Weight	Multiplication Factor		
$Ca(HCO_3)_2$	162	81	100/162	or	50/81
$Mg(HCO_3)_2$	146	73	100/146	or	50/73
$CaCl_2$	111	55.5	100/111	or	50/55.5
$CaSO_4$	136	68	100/136	or	50/68
$MgCl_2$	95	47.5	100/95	or	50/47.5
$MgSO_4$	120	60	100/120	or	50/60
$CaCO_3$	100	50	100/100	or	50/50
$MgCO_3$	84	42	100/84	or	50/42
CO_2	44	22	100/44	or	50/22
H_2SO_4	98	49	100/98	or	50/49
HCl	36.5	36.5	50/36.5		
$NaAlO_2$	82	82	50/82		
$FeSO_4.7H_2O$	278	139	100/278	or	50/139

A sample of water on analysis was found to contain following impurities in mg/liter: $Ca(HCO_3)_2$ = 10.0; $Mg(HCO_3)_2$ = 8.5; $CaSO_4$ = 12.0; $MgSO_4$ = 14.0

Calculate the temporary, permanent and total hardness of water. (At.wts Ca = 40; Mg = 24; C = 12; S = 32; O = 16; H = 1)

Constituent	Amount	Multiplication Factor	$CaCO_3$ equivalent
$Ca(HCO_3)_2$	10.0	100/162	6.17 mg/l
$Mg(HCO_3)_2$	8.5	100/146	4.45 mg/l
$CaSO_4$	12.0	100/136	8.82 mg/l
$MgSO_4$	14.0	100/120	11.67 mg/l

Temporary hardness = 6.17 + 4.45 = 10.62 mg/l $CaCO_3$ eq.

Permanent hardness = 8.82 + 11.67 = 20.49 mg/l $CaCO_3$ eq.

Total hardness = 31.11 mg/l in terms of $CaCO_3$ eq.

100 parts by mass of $CaCO_3$ are equivalents to 74 parts by mass of $Ca(OH)_2$, and 106 parts by mass of Na_2CO_3

Lime Requirement for softening

= (74/100) [Temp. Ca^{2+} + 2 × Temp. Mg^{2+} + Perm. Mg^{2+} + CO_2 + HCl + H_2SO_4 + HCO_3^- + Perm. (Al^{3+} + Fe^{2+}) − $NaAlO_2$ all in terms of $CaCO_3$ equivalents]

Soda Requirement for softening

= (106/100) [Perm. Ca^{2+} + Perm. Mg^{2+} + HCl + H_2SO_4 + (Al^{3+} + Fe^{2+}) − HCO_3^- − $NaAlO_2$ all in terms of $CaCO_3$ equivalents]

- Reaction with Calcium Temporary Hardness   **L**

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

- Reaction with Calcium permanent Hardness   **S**

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

- Reaction with Magnesium Temporary Hardness   **2L**

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

- Reaction with Magnesium Permanent Hardness   **L+S**

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + \mathbf{CaCl_2}$$
$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + \mathbf{CaSO_4}$$

- Reaction with Carbon Dioxide   **L**

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

- Reaction with Free Acid Present   **L+S**

$$2HCl + Ca(OH)_2 \longrightarrow \mathbf{CaCl_2} + 2H_2O$$
$$H_2SO_4 + Ca(OH)_2 \longrightarrow \mathbf{CaSO_4} + 2H_2O$$

- Reaction with Iron and Aluminum salts   **L+S**

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3\downarrow + \mathbf{3CaSO_4}$$
$$FeSO_4 + Ca(OH)_2 \longrightarrow Fe(OH)_2\downarrow + \mathbf{CaSO_4}$$
$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3\downarrow$$

- Reaction with Bicarbonate Ions(like $NaHCO_3$, $KHCO_3$, etc.)   **L-S**

$$2NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + 2H_2O + \mathbf{Na_2CO_3}$$

Calculate the quantity of lime and soda required to soften 1,00,000 liters of water containing following salts in mg/liter: $Ca(HCO_3)_2 = 8.1$, $Mg(HCO_3)_2 = 7.3$, $CaSO_4 = 13.6$, $MgSO_4 = 12$ and $NaCl = 4.6$

Constituent	Amount	Multiplication Factor	$CaCO_3$ equivalent
$Ca(HCO_3)_2$	8.1	100/162	5 mg/l
$Mg(HCO_3)_2$	7.3	100/146	5 mg/l
$CaSO_4$	13.6	100/136	10 mg/l
$MgSO_4$	12.0	100/120	10 mg/l

Lime Requirement = $(74/100)$ [Temp. Ca^{2+} + 2 × Temp. Mg^{2+} + Perm. Mg^{2+} all in terms of $CaCO_3$ equivalents]
$= (74/100) (5 + (2 × 5) + 10) = (74/100) × 25$ mg/liter (For 1 liter)

Lime Req., 1,00,000 liter water $= (74/100) × 25 × 1,00,000$ mg
$= 1850 × 1000$ mg $= 1.850 × 1000 × 1000$ mg = **1.850 kg**

Soda Requirement = $(106/100)$ [Perm. Ca^{2+} + Perm. Mg^{2+} all in terms of $CaCO_3$ equivalents]

$= (106/100) \times (10 + 10)$

$= (106/100) \times 20$ mg/liter (For 1 Liter)

Soda Reqired for 1,00,000 liter of water

$= (106/100) \times 20 \times 1,00,000$ mg

$= 2120 \times 1000$ mg

$= 2.120 \times 1000 \times 1000$ mg

$= $ **2.120 kg**

Lime Requirement to Treat 1,00,000 liter water:**1.850 kg**

Soda Requirement to Treat 1,00,000 liter water:**2.120 kg**

Water containing following salts in mg/liter is to be treated: $Ca(HCO_3)_2$ = 324, $Mg(HCO_3)_2$ = 146, $CaSO_4$ = 68, $MgCl_2$ = 47.5, NaCl 1.0.
Calculate: **i. Temporary, permanent and total hardness of the water**
ii. Quantity of lime and soda required per 10,000 liter of water, if the lime is 90% and soda is 100% pure. 10% of chemicals are to be used in excess in order to complete the process quickly.

Constituent	Amount	Multiplication Factor	$CaCO_3$ equivalent
$Ca(HCO_3)_2$	324	100/162	200 mg/l
$Mg(HCO_3)_2$	146	100/146	100 mg/l
$CaSO_4$	68	100/136	50 mg/l
$MgCl_2$	47.5	100/95	50 mg/l

Temporary Hardness = 200 + 100 = **300 mg/liter**
Permanent hardness = 50 + 50 = **100 mg/liter**
Total Hardness = 300 + 100 = **400 mg/liter**

Lime Requirement = $(74/100)$ [Temp. Ca^{2+} + 2 × Temp. Mg^{2+} + Perm. Mg^{2+} all in terms of $CaCO_3$ equivalents]

$= (74/100) (200 + (2 × 100) + 50)$

$= (74/100) × 450$ mg/liter (For 1 liter)

Lime Required for 10,000 liter water

$= (74/100) × 450 × 10,000$ mg

$= 3330 × 1000$ mg

$= 3.330 × 1000 × 1000$ mg $= 3.330$ kg

Lime 90% purity Required $= 3.330×(100/90)$ mg

10% Excess Lime Required

$= 3.330 × (100/90) × (110/100)$ mg **= 4.070 kg**

Soda Requirement = $(106/100)$ [Perm. Ca^{2+} + Perm. Mg^{2+} all in terms of $CaCO_3$ equivalents]

$\qquad = (106/100) (50 + 50)$

$\qquad = (106/100) \times 100$ mg/liter (For 1 liter)

Soda Required for 10,000 L water

$= 106 \times 10,000$ mg

$= 1.06 \times 1000 \times 1000$ mg $= 1.06$ kg

Soda of 100% purity Required $= 1.06$ kg

10% Excess Lime Required $= 1.06 \times (110/100)$ mg

$$= 1.166 \text{ kg}$$