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Engineering Chemistry-II (BS-104)

Water Treatment

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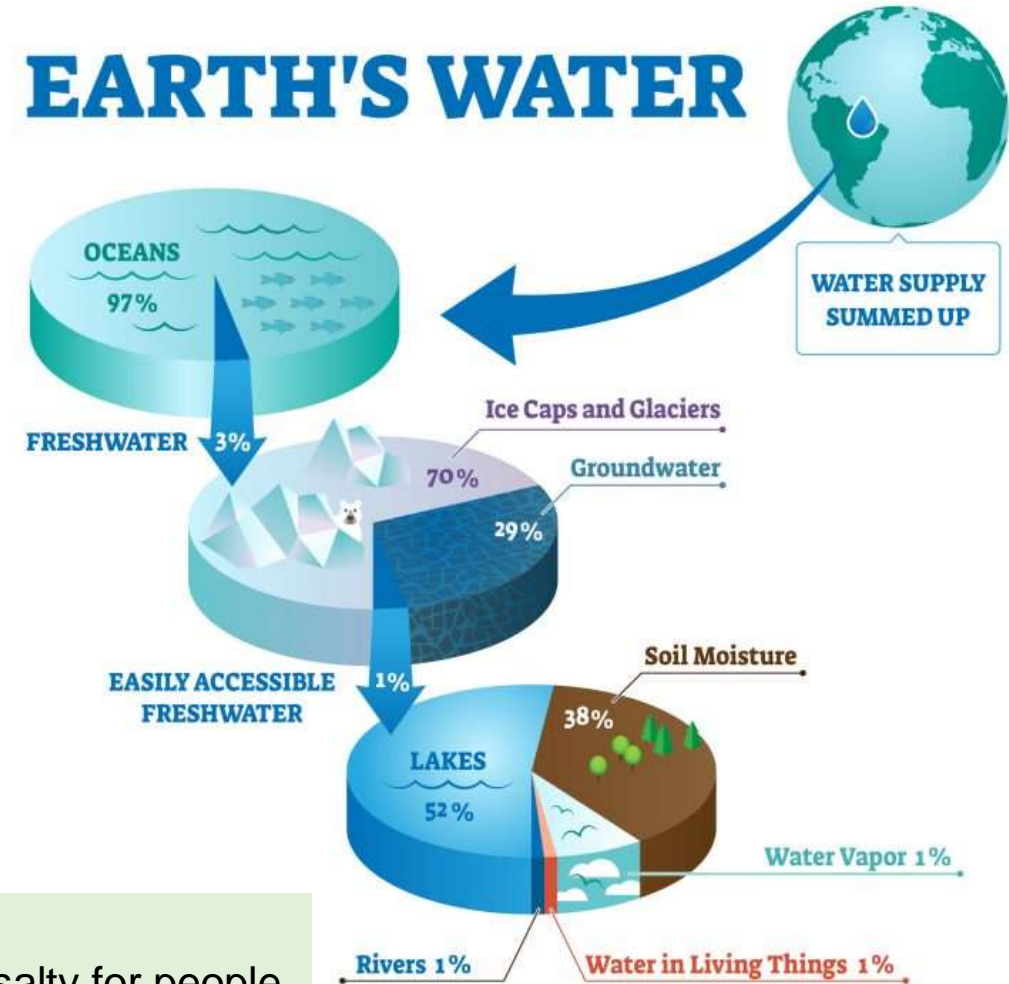


- **Water is a vital and precious natural resource**
- It is an essential source for the existence of life on the planet earth
- It is present in abundance. The total volume of water on Earth is estimated at 1.386 billion km³
- About 70 % of the human body is water
- Even animals and plants require water to complete their daily metabolic activities (Photosynthesis)
- On average, an individual uses 600 to 700 litres in a day
- It is widely used for various purposes such as drinking, washing, bathing, cleaning, cooking, irrigation, and other industrial and domestic uses



Water covers 75% of the earth's surface:

- 97% of this water is in oceans and is too salty for people, animals or plants to use
- 2% is frozen at the north and south poles, in glaciers and on snowy mountain ranges





Sources of Water:

A. Surface waters

(i). **Rain water:** purest form of natural water, since it is obtained as a result of evaporation from the surface water. However, it dissolves a considerable amount of industrial gases (like CO_2 , SO_2 , NO_2 , etc.) and suspended solid particles.

(ii). **River water:** Rivers are fed by rain and spring waters. Water from these sources flow over the surface of land, dissolves the soluble minerals of the soil and finally falls in rivers. It thus contains dissolved minerals of the soil such as chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron. River water also contains the organic matter, derived from the decomposition of plants, and small particles of sand and rock suspension. Thus, river water contains considerable amounts of dissolved as well as suspended impurities.

(iii). **Lake water:** has a more constant chemical composition. It, usually, contains much lesser amount of dissolved minerals than well water, but quantity of organic matter present in it is quite high.



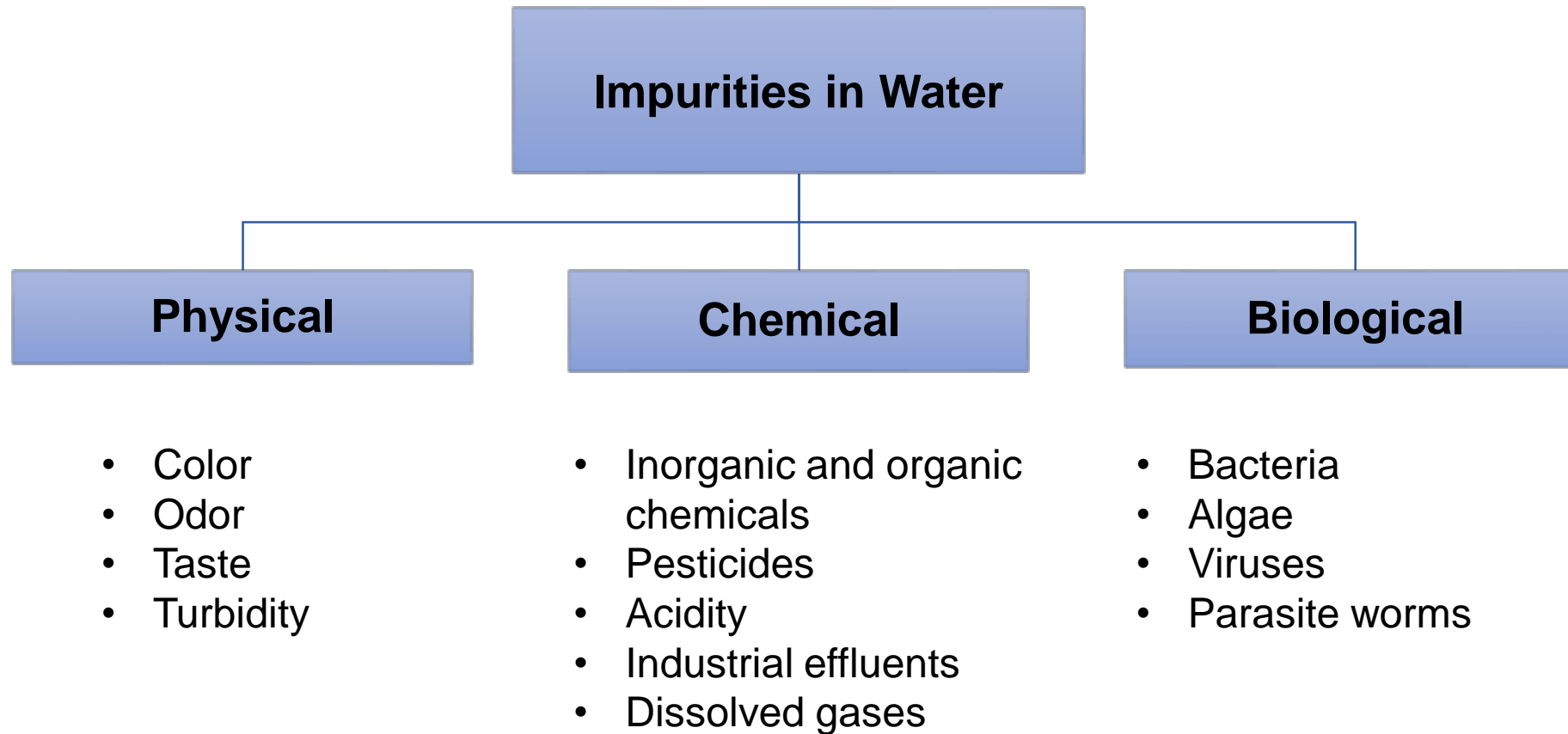


(iv). **Sea water:** is the **most impure form** of the water. Rivers join sea and throw in the impurities carried by them. Moreover, continuous evaporation of water from the surface of sea makes sea water continuously richer in dissolved impurities. Sea water contains, on an average, about 3.5% of dissolved salts, out of which about 2.6% is sodium chloride. Other salts present are sulphates of sodium; bicarbonates of potassium, magnesium and calcium; bromides of potassium and magnesium and a number of other compounds.

B. Underground waters: A part of the rain water, which reaches the surface of the earth, percolates into the earth. As this water journeys downwards, it comes in contact with a number of mineral salts present in the soil and dissolves some of them. Water continues its downwards journey, till it meet a hard rock, when it retreads upwards and it may even come out in the form of 'spring'.

C. Spring and well water (underground water): In general, it is clearer in appearance due to the filtering action of the soil, but contain more of dissolved salts. Thus, water from these sources contains more hardness. Usually, underground water is of high organic purity.

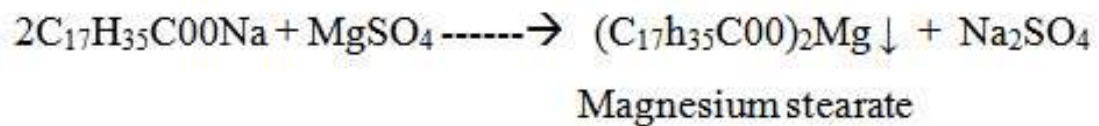
Surface water generally, contains suspended matter, which often contains the disease-producing (or pathogenic) bacteria's and hence, are not considered to be safe for human consumption.





Hardness of Water

- **Hard water:** Does not produce lather with soap solution => characteristic feature
- Salts like chlorides, bicarbonates and sulfates of Ca^{2+} , Mg^{2+} and Fe^{2+} make water hard
- On treatment with soap, which is stearic or palmitic acid salts of sodium or potassium causes the formation of white precipitate



- **Soft water:** produces lather readily with soap solution





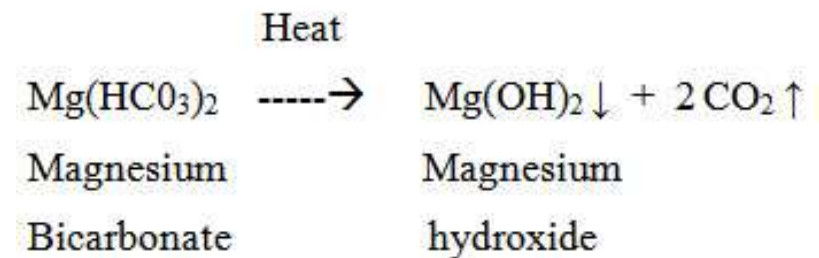
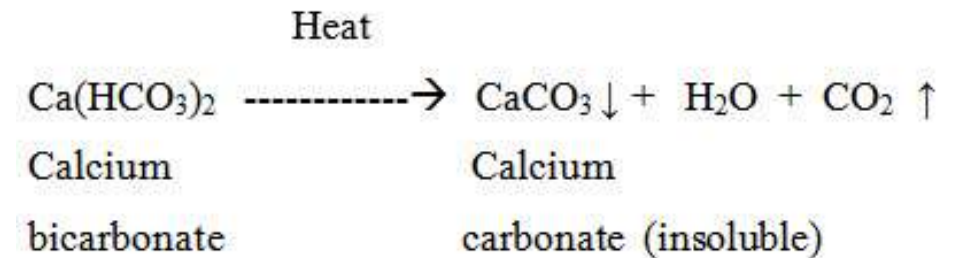
Types of hardness:

(1) **Temporary or carbonate hardness** is due to 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, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessel.

(2) **Permanent or non-carbonate hardness** is due to the presence of chlorides and sulphates of calcium, magnesium, iron and other heavy metals.

- Unlike temporary hardness, permanent hardness is not destroyed on boiling.



Removal of temporary hardness

Total hardness = temporary hardness + permanent hardness



Units of hardness:

- Both temporary and permanent hardness are expressed in **ppm as CaCO₃**

- Equivalent of CaCO₃ =

$$\begin{aligned} &= \frac{(\text{Mass of hardness producing substance}) \times (\text{Chemical equivalent of CaCO}_3)}{\text{Chemical equivalent of hardness producing substance}} \\ &= \frac{\text{Mass of hardness producing substance} \times 50}{\text{Chemical equivalent of hardness producing substance}} \end{aligned}$$

- Hardness is principally expressed in ppm units
- Milligrams per liter (mg/L) are the number of milligrams of CaCO₃ equivalent hardness present per liter of water

Other units:

$$1 \text{ Fr. degree of hardness} = \frac{1 \text{ part of hardness}}{10^5 \text{ parts of water}}$$

$$1 \text{ Clark} = \frac{1 \text{ grain of hardness}}{1 \text{ gallon or } 70,000 \text{ grains}} = \frac{1}{7 \times 10^4}$$

$$1 \text{ USA degree of hardness} = \frac{1 \text{ grain}}{1 \text{ USA gallon}} = \frac{1 \text{ grain}}{58,300 \text{ grains}} = \frac{1}{5.83 \times 10^4}$$

$$1 \text{ German degree of hardness} = \frac{1 \text{ grain}}{1 \text{ German grain}} = \frac{1 \text{ grain}}{56,000 \text{ grains}} = \frac{1}{5.6 \times 10^4}$$

Relation between various units of hardness

1 ppm	= 1 mg/l	= 0.1° Fr	= 0.07° Cl
1 mg/l	= 1 ppm	= 0.1° Fr	= 0.07° Cl
1° Cl	= 1.43° Fr	= 14.3 ppm	= 14.3 mg/l
1° Fr	= 10 ppm	= 10 mg/l	= 0.7° Cl.



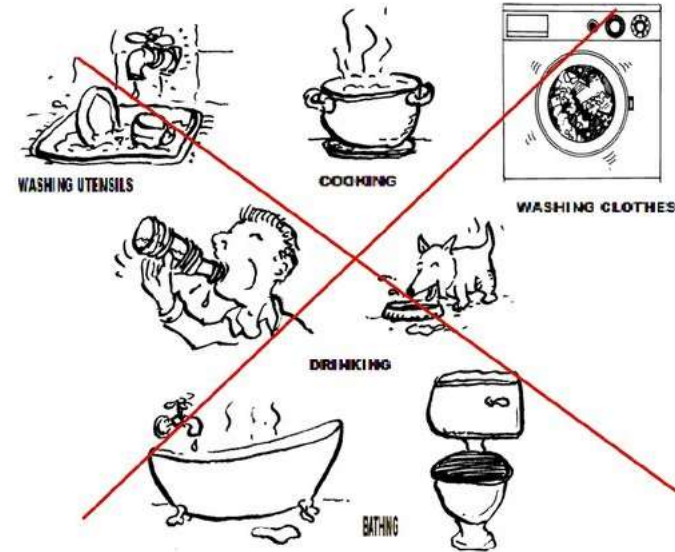
Disadvantages of Hard Water

(a) *In domestic uses.* For *washing* and *bathing*, hard water creates difficulties, since it does not form lather freely with soap. It also creates sticky precipitates that deposit on bath tub, body, clothes etc. until all the Ca/Mg salts get precipitated. Thus a lot of soap get wasted also.

For *cooking* hard water creates similar difficulties by producing scum on the bottom of the vessels. Due to the presence of hardness producing salts in hard water, boiling point gets elevated and during cooking a lot of fuel is wasted. Pulses etc. do not cook in hard water. Taste of tea, coffee becomes unpleasant. *Drinking* of hard water is also problematic since it affects the digestive system and at the same time the possibility of deposition of calcium oxalate crystals in the urinary tract is alarming.

(b) *In industrial uses.* For *textile industry* and *dyeing industry*, hard water causes the usual problem of deposition of insoluble salts that interfere with the proper dyeing and printing of the fabrics. The stains of iron salts also are undesirable on fabrics. Hard water also hampers the economy by wastage of soap as it does not form good lather.

- For *sugar industry*, the salts responsible for hardness create difficulties in sugar refining and crystallization of sugar and the sugar becomes deliquescent.
- Calcium and magnesium salts also interfere with the smooth and glossy finish of the papers in the *paper industry*. Iron salts interfere with the colour of the paper.
- In *laundry*, hard water causes wastage of costly soap and also interferes with the coloration due to the staining of iron salts.
- The hydration of cement and final hardening of cement are affected by use of hard water in *concrete making*.
- Hard water is not suitable for preparing drug solutions in *pharmaceutical industry*.
- For *steam generation in boilers*, hard water creates many problems like (i) scale formation, (ii) corrosion, (iii) priming and foaming and (iv) caustic embrittlement.

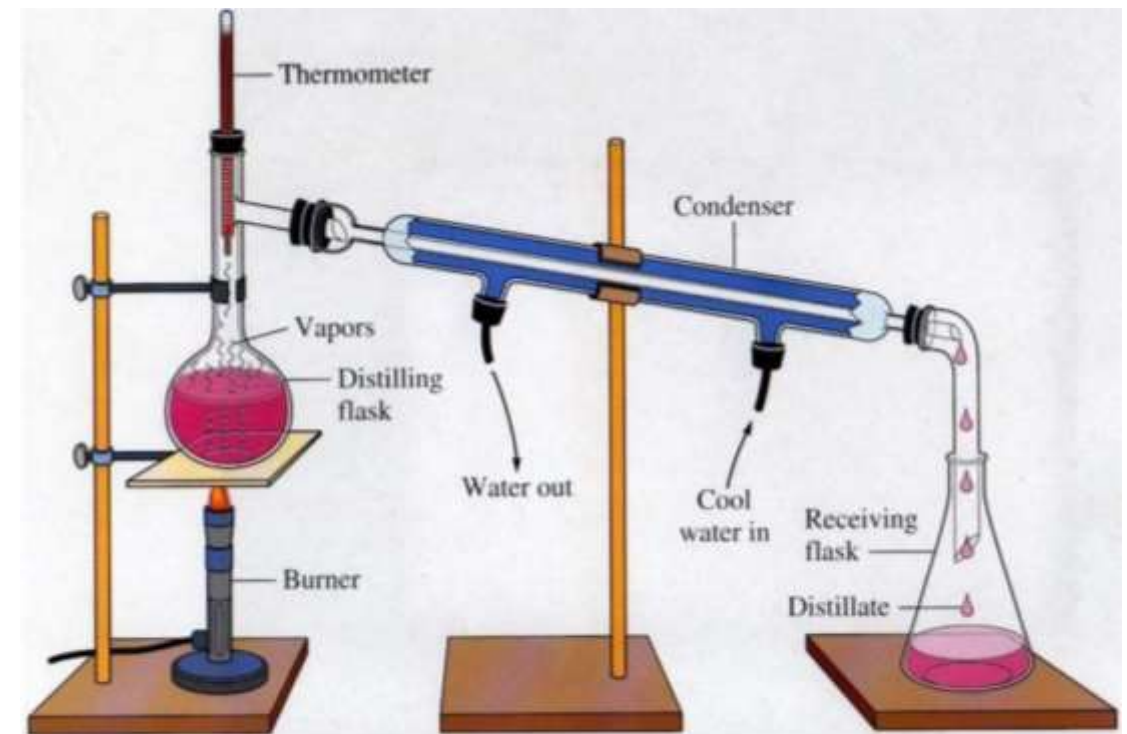


**HARD WATER IS NOT
SUITABLE FOR ALL THESE
PURPOSES**





- **Water treatment:** Any process that improves the quality of water to make it appropriate for a specific end-use
- **Softening of water:** The process of removing hardness producing salts from water i.e. removal of calcium, magnesium, iron salts and other metallic ions
- **Distillation:** widely used non-chemical method for softening of water
 - Relies on evaporation to purify water
- Three important industrial methods for softening of water:
 - I. Lime-soda process
 - II. Ion-exchange or demineralization process
 - III. Zeolite or Permutit process

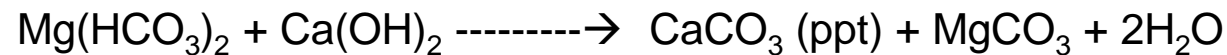
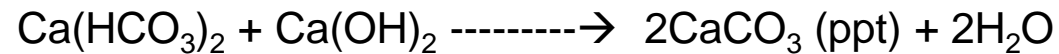


Distillation



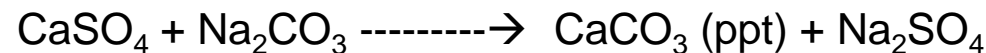
I. Lime-soda process

- In this method, the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime (Ca(OH)_2) and soda (Na_2CO_3)
- Extra addition of Ca(OH)_2 causes hardness, so calculated amounts to be added after determination of actual hardness
- Calcium carbonate (CaCO_3) and Magnesium hydroxide (Mg(OH)_2) are precipitated and are filtered off
- Both temporary and permanent hardness can be removed
- For temporary hardness,



⇒ to remove equivalent quantities of Ca and Mg hardness, the amount of lime required is in the ratio of **1:2**

- For permanent hardness,



⇒ Lime is not required for removal of permanent hardness due to Ca-salts, but is necessary for Mg-salts

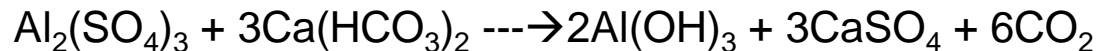


I. Lime-soda process

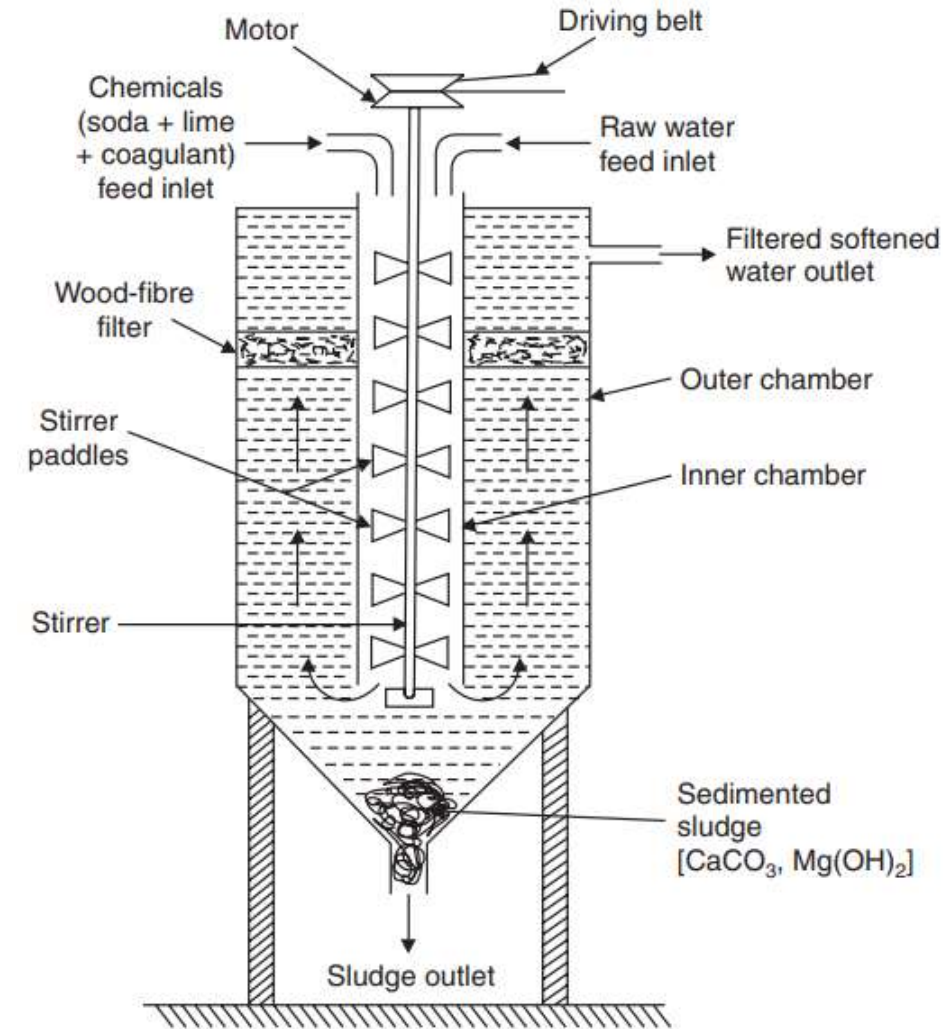
- Types of lime-soda processes:
 - Cold lime-soda process
 - Hot lime-soda process

a) Cold lime-soda process:

- Calculated quantity of chemicals (lime and soda) is mixed with water at room temperature
- Activated charcoal is acted as activator
- Small amounts of coagulants such as alums (sodium aluminates, aluminum sulfate) are added, which themselves hydrolyze to flocculants and entraps the fine precipitates



- Used for partial softening of municipal water, for softening of cooling water
- It provides water containing a residual hardness of 50 to 60 ppm, which is due to calcium hardness while magnesium hardness is brought down to almost zero

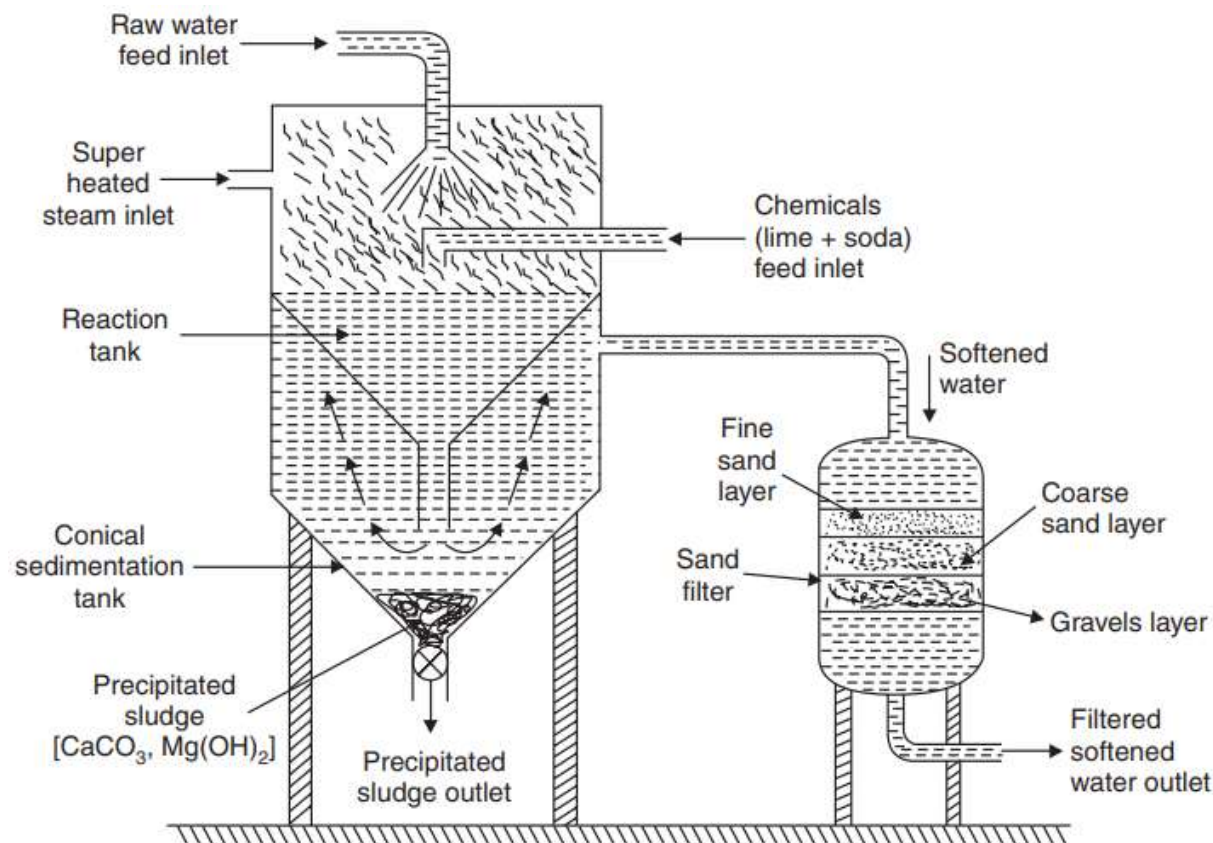


Continuous cold lime-soda softener



b) Hot lime-soda process:

- It involves the treatment of water with softening chemicals at a temperature of 80 to 150 °C maintained by exhaust steam
- Hot lime-soda process consists of three parts:
 - Reaction tank:** complete mixing of ingredients
 - Ionical sedimentation vessel:** sludge settles down
 - Sand filters:** complete removal of sludge
- Advantages:
 - the reaction proceeds faster, the precipitation reaction becomes almost complete
 - 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 (such as CO_2 and air) are removed
 - viscosity of softened water is lower, so filtration of water becomes much easier. This in-turn increases the filtering capacity of filters.
 - residual hardness is low compared to that in cold process: 15 to 30 ppm.



Continuous hot lime-soda softener

- Soft water from this process is used for feeding the boilers



- **Advantages of Lime-Soda process :**

- (i) It is very economical
- (ii) The process increases the pH value of the treated-water; thereby corrosion of the distribution pipes is reduced
- (iii) Besides the removal of hardness, the quantity of minerals in the water is reduced
- (iv) To certain extent, iron and manganese are also removed from the water
- (v) Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced

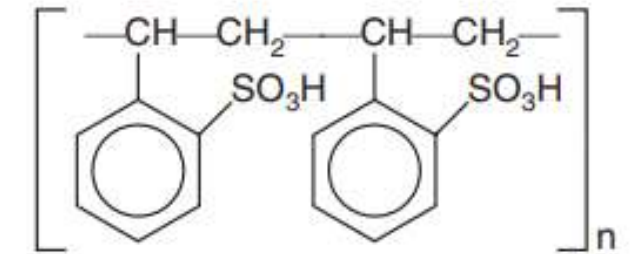
- **Disadvantage of Lime-Soda process:**

- (i) For efficient and economical softening, careful operation and skilled supervision is required
- (ii) Disposal of large amounts of sludge (insoluble precipitate) poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city
- (iii) This can remove hardness only up to 15 ppm, which is not good for high pressure boilers

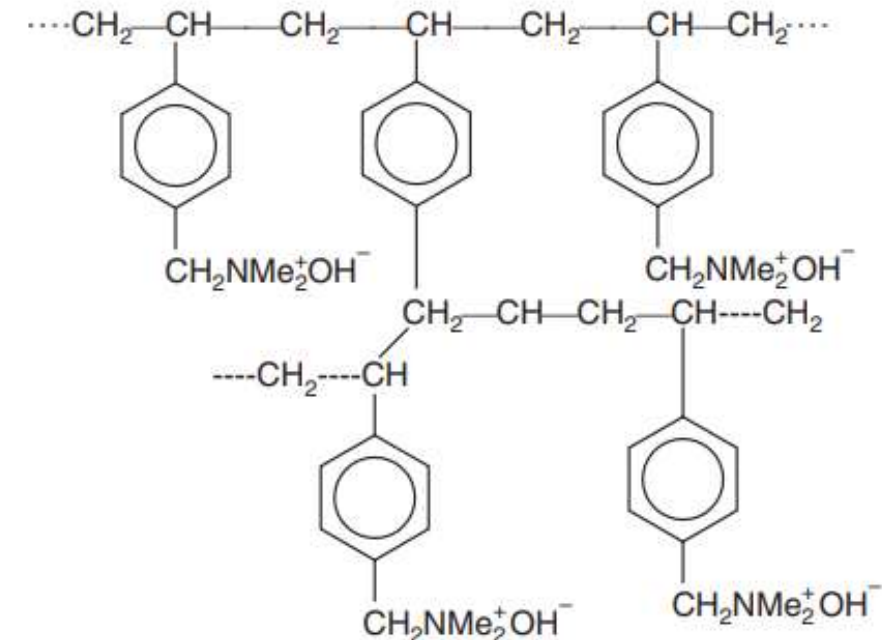


II. Ion-exchange or demineralization process

- This process removes almost all the ions present in water
- Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with a microporous structure, and the “functional groups” attached to the chains are responsible for the ion-exchanging properties
- Resins containing acidic functional groups ($-\text{COOH}$, $-\text{SO}_3\text{H}$ etc.) are capable of exchanging their H^+ ions with other cations; whereas those containing basic functional groups ($-\text{NH}_2$, $-\text{OH}$ groups) are capable of exchanging their anions with other anions.
- Classification of ion-exchange resins:
 - a) Cation exchange resins (RH^+):** mainly phenol-sulfonic acid-formaldehyde resin and styrene-divinyl benzene copolymers, which exchange their hydrogen ions with the cations in the water e.g. Ca^{2+} and Mg^{2+}
 - b) Anion exchange resins (ROH^-):** styrene-divinyl benzene or amine formaldehyde copolymers, which contain amino or quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an integral part of the resin matrix. These, after treatment with dil. NaOH solution, become capable to exchange their OH^- with anions in water e.g. Cl^- , SO_4^{2-}



cation exchange resin

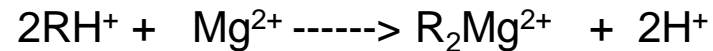
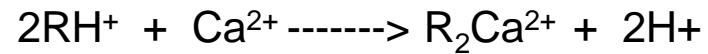


Anion exchange resin

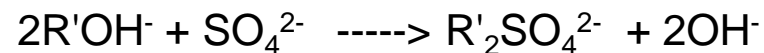
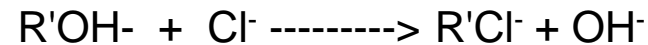


- **Process:**

- The hard water is passed first through cation exchange column, which removes all the cations like Ca^{2+} , Mg^{2+} , etc. from it, and equivalent amount of H^+ ions are released from this column to water.

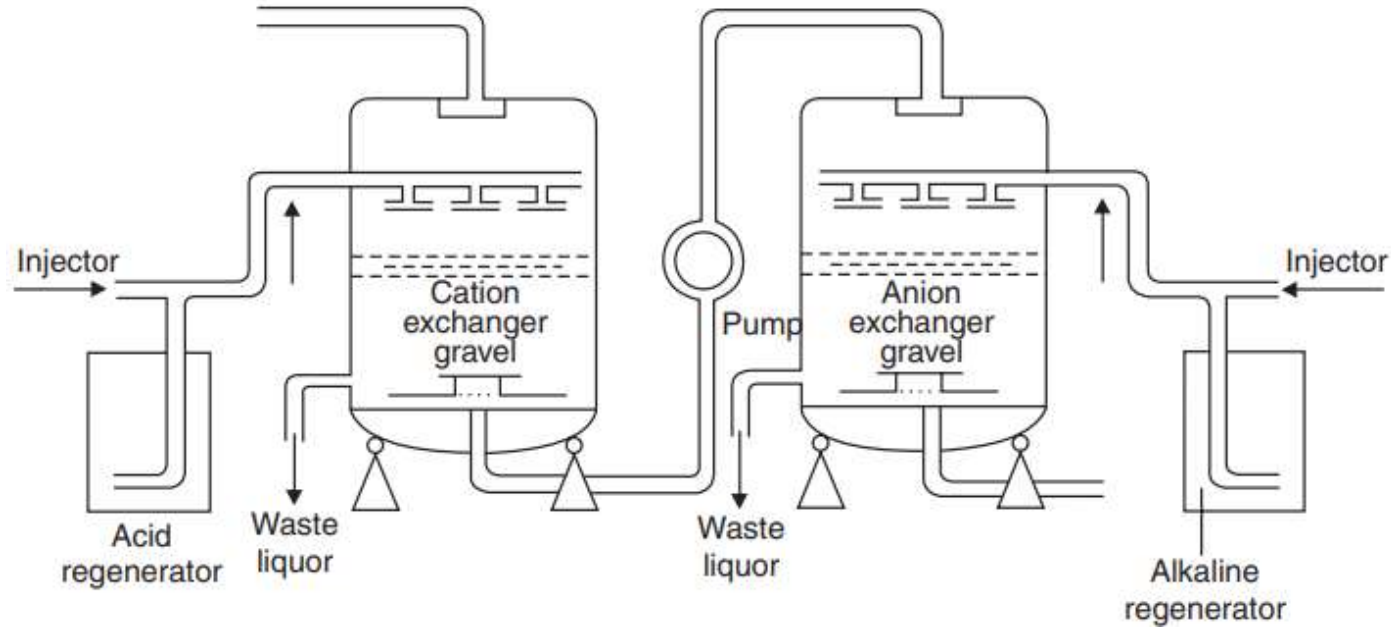


- After cation exchange column, the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- , etc. present in the water and equivalent amount of OH^- ions are released from this column to water.

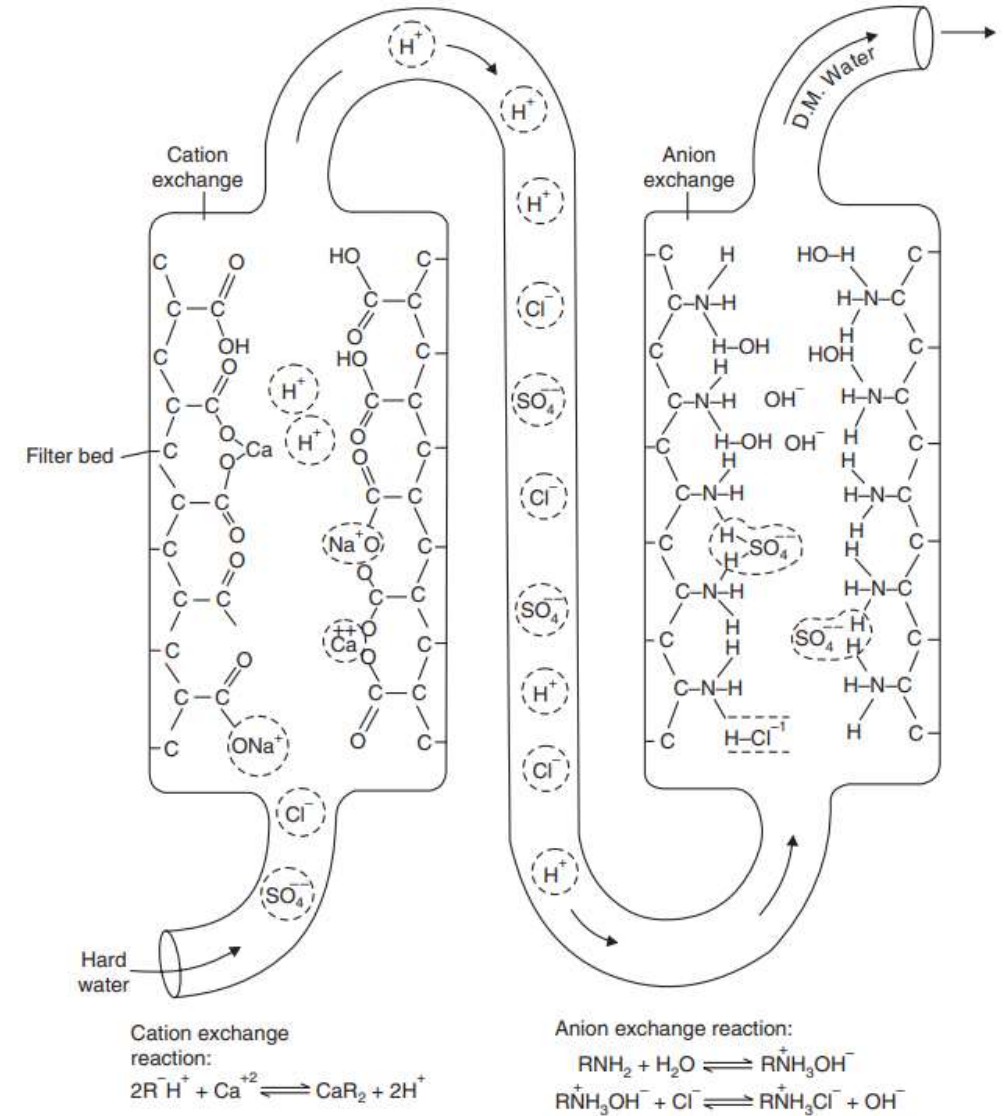


- H^+ and OH^- ions (released from cation exchange and anion exchange columns respectively) get combined to produce water molecule $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$
- Thus, the water coming out from the exchanger is free from cations as well as anions. Ion-free water, is known as deionized or demineralised water.





Demineralization of water



Demineralization of water showing ions exchange



- **Regeneration:** When capacities of cation and anion exchangers to exchange H^+ and OH^- ions respectively are lost, they are then said to be exhausted. The exhausted cation exchange column is regenerated by passing a solution of dil. HCl or dil. H_2SO_4 .



- The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH.



- The column is washed with deionised water and washing (which contains Ca^{2+} , Mg^{2+} , Na^+ and Cl^- or SO_4^{2-} ions) are discarded.
- The regenerated ion exchange resins are then used again.

- **Advantages:**

- (i) Easy regeneration
- (ii) The process can be used to soften highly acidic or alkaline waters
- (ii) It produces water of very low hardness (around 2 ppm). So it is very good for treating water for use in high-pressure boilers

- **Disadvantage of ion-exchange process:**

- (i) The equipment is costly and more expensive chemicals are needed.
- (ii) If water contains turbidity, then the output of the process is reduced. The turbidity must be below 10 ppm. If it is more, it has to be removed first by coagulation and then by filtration.



- **BOILER FEED WATER:** One of the chief uses of water in industry is the generation of steam by boilers. In order to generate steam on a constant basis, boiler should be continuously supplied with water, called as feed water.
- **Feed water:** water that undergoes purification or preheating and is then supplied to boilers for hot water and steam production. It is typically found in thermal power plants where it is stored and conditioned in tanks, known as boiler feed water.
- The different impurities in the feed water can be due to dissolved gases, dissolved solids and suspended solids. Each of these impurities affects the boiler system in a different way, and therefore it is must to treat the feed water.
- **Requirements of boiler feed water:**
 - It should have zero hardness
 - It must be free from any dissolved gases like O_2 and CO_2
 - It should be free from suspended impurities
 - It should be free from dissolved salts and alkalinity
 - It should be free from turbidity and oil
 - It should be free from hardness causing and scale forming constituents like Ca and Mg salts



Boilers

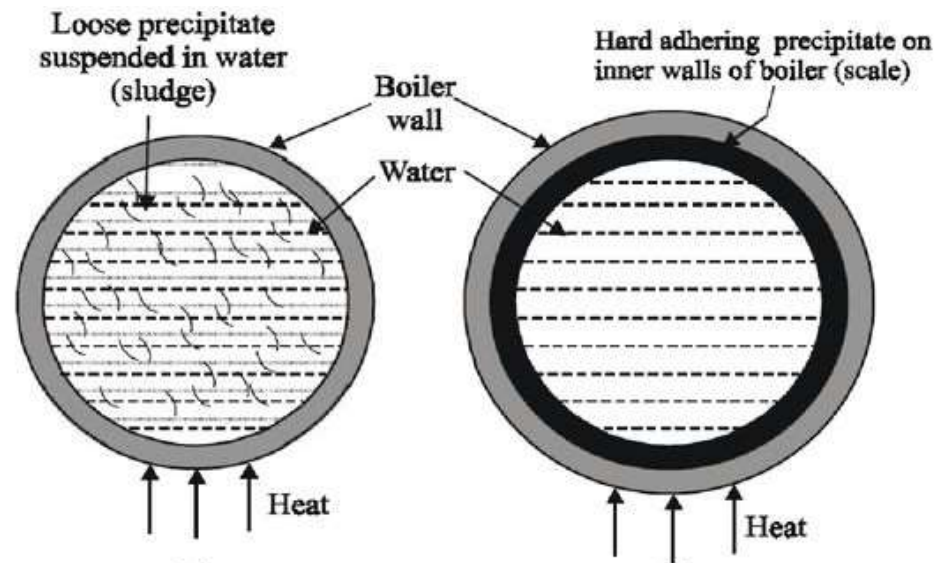


- **Disadvantages of using hard water in boilers:**

- i. Sludge and scale formation
- ii. Caustic embrittlement
- iii. Corrosion
- iv. Priming and foaming

i. **Sludge and scale formation:** On continuous evaporation of water in boilers, the concentration of soluble matter increases progressively leading to the deposition of salts

- If the precipitation takes place in the form of loose and slimy precipitate, it is called **sludge**.
- if the precipitated matter forms a hard, adhering crust/coating on the inner walls of the boiler, it is called **scale**.





- **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 can be easily removed by scrapping with brush.
- Sludge 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 formation:**
 - It is poor conductor of heat, so they tend to waste a portion of heat generated.
 - If sludge is formed along with scales, then former gets entrapped in the latter 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, gauge-glass connection, thereby causing even choking of the pipes.
- **Prevention of sludge formation:**
 - i. By using well softened water
 - ii. By frequently performing 'blow-down operation', i.e., removing the concentrated salty water from time to time so that deposition of sludge is prevented



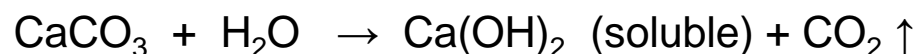


- **Scale** are hard deposits, which stick very firmly to the inner surfaces of the boiler.
 - Scales are difficult to remove, even with the help of hammer and chisel, and therefore are the main source of troubles.
 - Scale is formed by substances $\text{Ca}(\text{HCO}_3)_2$, CaSO_4 and $\text{Mg}(\text{OH})_2$
- i. Decomposition of **calcium bicarbonate**



Scale

- However, scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low-pressure boilers. But in high-pressure boilers, CaCO_3 is soluble.



- ii. The solubility of **calcium sulphate** in water decreases with rise of temperature: solubility of CaSO_4 is 3,200 ppm at 15 °C and reduces to 55 ppm at 230 °C and 27 ppm at 320 °C. In other words, CaSO_4 is soluble in cold water, but almost completely insoluble in super-heated water. Consequently, CaSO_4 gets precipitated as hard scale on the heated portions of the boiler, and is the main cause of scales in high-pressure boilers. Calcium sulphate scale is quite adherent and difficult to remove even with the help of hammer and chisel.





iii. Hydrolysis of **magnesium salts**: Dissolved magnesium salts undergo hydrolysis (at prevailing high temperature inside the boilers) forming magnesium hydroxide precipitate, which forms a soft type of scale e.g.,



iv. Presence of **silica (SiO₂)**, even present in small quantities, deposits as calcium silicate (CaSiO₃) and/ or magnesium silicate (MgSiO₃). These deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

- **Disadvantages of scale formation:**

1. **Wastage of fuel**: Scales have a low thermal conductivity, so the rate of heat transfer from boiler to inside water is greatly decreased. In order to provide a steady supply of heat to water, excessive or over heating is carried out and this causes increase in fuel consumption. The wastage depends upon the thickness and the nature of scale :

thickness of scale (mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

2. **Lowering of boiler safety**: Due to scale formation, over-heating of boiler is to be done in order to maintain a constant supply of steam. The over-heating of the boiler tube makes the boiler material softer and weaker and this causes distortion of boiler tube and makes the boiler unsafe to bear the pressure of the steam, especially in high-pressure boilers.

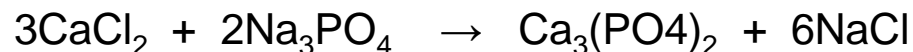


3. **Decrease in efficiency:** Scales may sometimes deposit in the valves and condensers of the boiler and choke them partially.
 4. **Danger of explosion:** When thick scales crack, due to uneven expansion, the water comes suddenly in contact with over-heated iron plates. This causes formation of a large amount of steam 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 piece of wood or wire brush, if they are loosely adhering.
 - ii. By giving thermal shocks (i.e., heating the boiler and then suddenly cooling with cold water), if they are brittle
 - iii. By dissolving them by adding them chemicals, if they are adherent and hard. Thus, calcium carbonate scales can be dissolved by using 5-10% HCl. Calcium sulphate scales can be dissolved by adding EDTA (ethylene diamine tetra acetic acid), with which they form soluble complexes.
 - iv. By frequent blow-down operation, if the scales are loosely adhering. The operation actually involves the removal of very hard water from a tap at the bottom of the boiler and replenishing the water with softened water called 'make-up water'



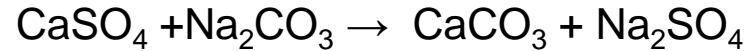
- **Prevention of scale formation:**

1. **External treatment** includes efficient 'softening of water' (i.e. removing hardness producing constituents of water).
 2. **Internal treatment:** In this process (also called sequestration), 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 boiler water either : (a) to precipitate the scale forming impurities in the form of sludges, which can be removed by blow-down operation, or (b) to convert them into compounds, which will stay in dissolved form in water and thus do not cause any harm.
- Important internal conditioning/treatment methods are:
 - i. **Colloidal conditioning:** In low-pressure boilers, scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar (a gel), etc., which get coated over the forming precipitates, thereby yielding non-sticky and loose deposits, which can easily be removed by pre-determined blow-down operations.
 - ii. **Phosphate conditioning:** In high-pressure boilers, 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 phosphates, which can be removed by blow - down operation. Main phosphates used 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).



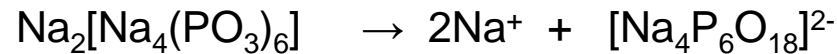


iii. **Carbonate conditioning** : In low-pressure boilers, scale-formation can be avoided by adding sodium carbonate to boiler water, where CaSO_4 is converted into calcium carbonate in equilibrium.

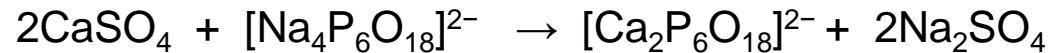


Consequently, deposition of CaSO_4 as scale does not take place and calcium is precipitated as loose sludge of CaCO_3 , which can be removed by blow-down operation.

iv. **Calgon conditioning** involves addition of calgon [sodium hexameta phosphate (NaPO_3)₆] to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with CaSO_4 .

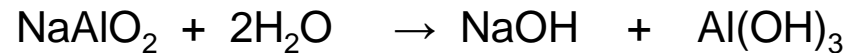


Calgon



Soluble complex ion

v. **Treatment with sodium aluminates (NaAlO_2)** : Sodium aluminates gets hydrolyzed yielding NaOH and a gelatinous precipitate of aluminium hydroxide.

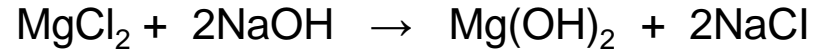


Sodium meta-aluminate

Gelatinous precipitation



The sodium hydroxide, so-formed, precipitates some of the magnesium as Mg(OH)_2 ,



The flocculent precipitate of Mg(OH)_2 and Al(OH)_3 , produced inside the boiler, entraps finely suspended and colloidal impurities, including oil drops and silica. The loose precipitate can be removed by pre-determined blow-down operation.

vi. **Electrical conditioning:** Sealed glass bulbs, containing mercury connected to a battery, are set rotating in the boiler. When water boils, mercury bulbs emit electrical discharges, which prevents scale forming particles to adhere /stick together to form scale.

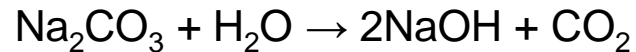
vii. **Radioactive conditioning:** Tablets containing radioactive salts are placed inside the boiler water at a few points. The energy radiations emitted by these salts prevent scale formation.

viii. Complexometric method involves addition of 1.5 % alkaline ($\text{pH} = 8.5$) solution of EDTA to feed-water. The EDTA binds to the scale-forming cations to form stable and soluble complex. As a result, the sludge and scale formation in boiler is prevented. Moreover, this treatment : (1) prevents the deposition of iron oxides in the boiler, (2) reduces the carryover of oxides with steam, and (3) protects the boiler units from corrosion by wet steam (steam containing liquid water).

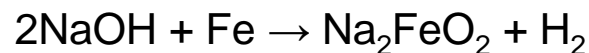


ii. Caustic embrittlement: type of boiler corrosion (electrochemical), caused by using highly alkaline water in the boiler i.e., when the concentration of NaOH is above 100 ppm

- **Embrittlement:** Boiler failure due to development of certain types of cracks resulting from excessive stress and chemical attack.
- During softening by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water, which decomposes to give sodium hydroxide and carbon dioxide at elevated temperatures in high pressure boilers thereby making water basic (caustic)



- The NaOH containing water flows into the minute hair-cracks, always present in the inner side of boiler, by capillary action, where water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate (Na_2FeO_2), which causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.), causing even failure of the boiler.



Caustic cracking



- **Prevention of caustic embrittlement:**

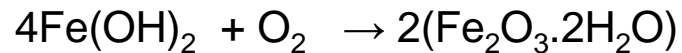
- i. by using sodium phosphate as softening agent, instead of sodium carbonate
- ii. by adding tannin or lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution in these
- iii. by adding sodium sulphate to boiler water to ensure a weight ratio of $\text{Na}_2\text{SO}_4 / \text{NaOH} > 2.5$, whereby the deposition of Na_2SO_4 prevents the penetration of NaOH into the cracks and stops caustic embrittlement in high pressure boilers
- iv. use of crack-resisting steel: certain steel containing Al added during manufacture appear to be resistant against caustic cracking
- v. By adjusting the pH of the feed water carefully between 8 and 9



iii. Corrosion: Boiler corrosion is decay of boiler material by a chemical or electro-chemical attack by its environment.

- **Main reasons** for boiler corrosion are:

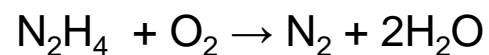
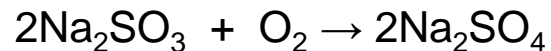
(1) Dissolved oxygen: Water usually contains about 8 mL/L of dissolved oxygen at room temperature. Dissolved oxygen in water, in presence of prevailing high temperature, attacks boiler material:



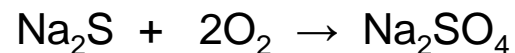
Ferrous hydroxide Rust

- **Removal of dissolved oxygen :**

a) By adding calculated quantity of sodium sulphite or hydrazine or sodium sulphide.



Hydrazine



Boiler corrosion



b) By **mechanical de-aeration**, i.e., water spraying in a perforated plate-fitted tower, heated from sides and connected to vacuum pump. High temperature, low pressure and large exposed surface (provided by perforated plates) reduces the dissolved oxygen in water.

(2) Dissolved carbon dioxide: CO_2 is carbonic acid, which has a slow corrosive effect on the boiler material

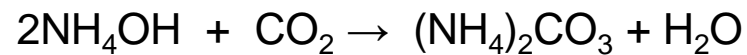


Carbon dioxide is also released inside the boiler, if water used for steam generation it contains bicarbonate, e.g.,



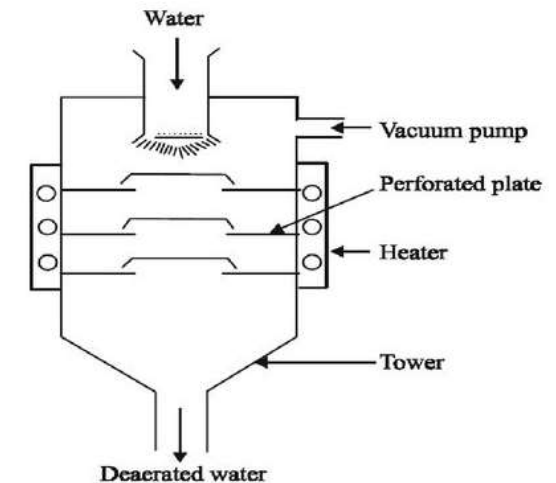
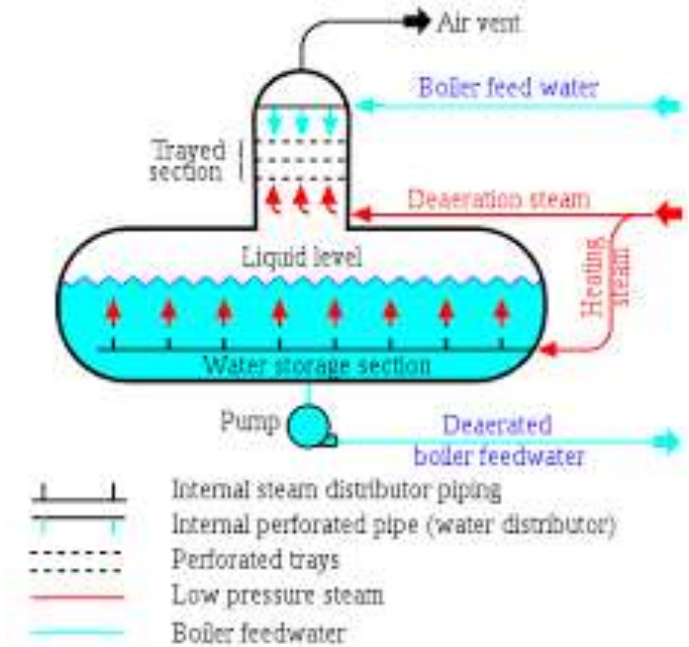
- **Removal of CO_2 :**

a) By adding calculated quantity of ammonia



b) By mechanical de-aeration process

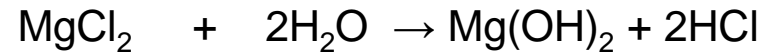
c) By heating



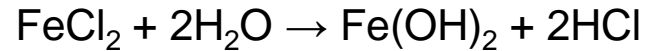
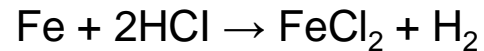
Mechanical de-aeration



(3) Acids from dissolved salts: Water containing dissolved magnesium salts liberate acids on hydrolysis, e.g.,



The liberated acid reacts with iron (of the boiler) in chain like reactions producing HCl again and again. Thus

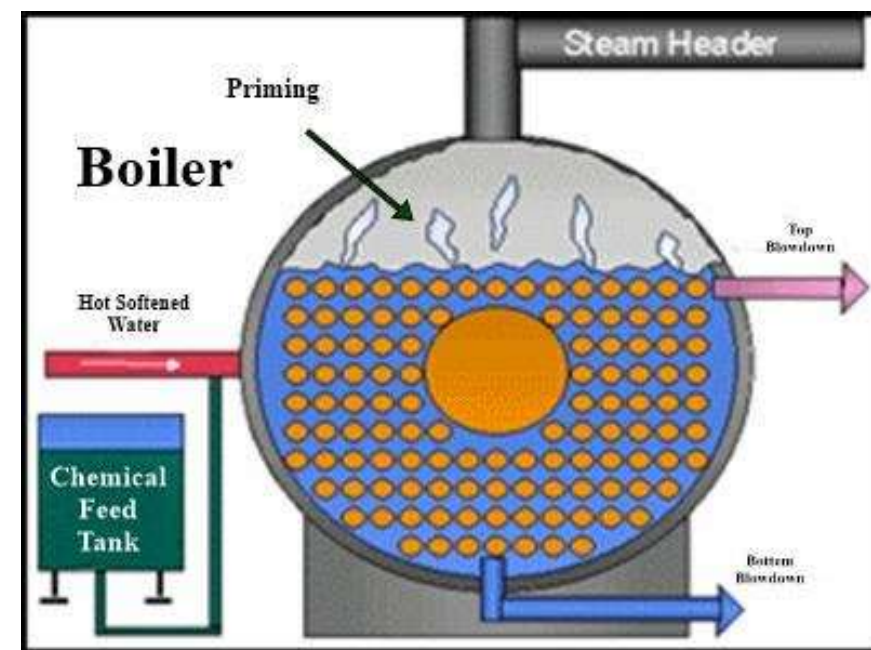


Consequently, presence of even a small amount of MgCl_2 will cause corrosion of iron to a large extent.



iv. Priming and Foaming:

- When a boiler is steaming (i.e., producing steam) rapidly, some particles of the liquid water are carried along-with the steam. This process of 'wet steam' formation is called **priming**.
- **Reasons for priming:**
 - i. the presence of a large amount of dissolved solids
 - ii. high steam velocities
 - iii. sudden boiling
 - iv. improper boiler design
 - v. sudden increase in steam-production rate
- **Priming can be prevented by:**
 - i. fitting mechanical steam purifiers
 - ii. avoiding rapid changing steaming rate
 - iii. maintaining low water levels in boilers
 - iv. efficient softening and filtration of the boiler-feed water.
- Priming can be minimized by placing a series of baffle plates or spiral baffles near the steam outlet to facilitate the condensation of water droplets carried over by the steam.



Priming



- **Foaming** is the production of persistent foam or bubbles in boilers, which do not break easily.
- Foaming is due to presence of substances like oils, grease, organic matter or finely divided solids (which greatly reduce the surface tension of water).
- **Foaming can be prevented by:**
 - i. adding anti-foaming chemicals like castor oil
 - ii. removing oil from boiler water by adding compounds like sodium aluminates.
- Priming and foaming, usually, occur together.
- **They are objectionable because:**
 - (i) 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.
 - (ii) dissolved salts may enter the parts of other machinery, where steam is being used, thereby decreasing the life of the machinery
 - (iii) actual height of the water column cannot be judged properly, thereby making the maintenance of the boiler pressure becomes difficult.



Foaming